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REGENERATION OF PHOTOGRAPHIC SILVER BLEACH SOLUTIONS

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This invention relates to the regeneration of spent photographic silver bleach solutions with water-soluble persulfates.

In the processing of color film and in many black and white photographic processes the silver which forms upon developing is converted into a hypo-soluble silver salt which is subsequently removed by fixing. A commonly employed silver bleaching solution consists essentially of an aqueous solution of an alkali ferricyanide and an alkali bromide with possibly other chemicals added. The use of these solutions for bleaching developed photographic emulsions depletes both the ferricyanide and the halide ion therein. The efficiency of the bleaching solution diminishes upon continued use and, therefore, regeneration thereof would be desirable after each use.

The prior art has suggested regeneration of bleach solutions with alkali metal bromates but the expense involved in that method makes it somewhat questionable whether or not regeneration offers anything over bleach solutions newly prepared. Electrolytic rejuvenation methods have also been disclosed but there are objections thereto such as the high capital investment necessary, high maintenance costs and the formation of sludge in bleach solutions treated in this manner.

One object of our invention is to provide a method for regenerating exhausted spent silver bleach solutions, characterized by the ease of operation and the practical nature thereof. Another object of our invention is to provide a method for regenerating spent bleach solutions in which the products incorporated in the solution as a result of the regeneration do not exhibit any effects deleterious to its value in processing photographic products. A further object of our invention is to provide a method for regenerating bleach solutions which imparts the desired effect thereto rapidly and under mild conditions. Other objects of our invention will appear herein.

We have found that spent ferricyanide type silver bleach solutions may be regenerated in a time on the order of 30 minutes at usual temperatures by the use of the water soluble persulfates over a wide pH range such as pH 3–10. We have found that the presence of persulfates, even in excess, does not impair the bleaching action of ferricyanide type bleaching solutions and is not harmful to the photographic material processed therewith. We have found that spent ferricyanide type bleach solutions may be rapidly rejuvenated in this manner, with only a build up of sulfate ion therein which, when desired, can be readily removed by the addition of calcium chloride without any undue loss in concentration of the active constituent therein, except possibly as the voluminous precipitate formed may entrap a certain amount of bleaching reagents.

Our invention involves the use as the regenerating agent of a water soluble persulfate such as of ammonium, sodium or potassium in an amount at least chemically equivalent to the ferrocyanide formed upon use of the bleaching solution. The addition of an excess of the

persulfate to the solution not only does not interfere with its bleaching effectiveness but that excess will be used up in the regenerating of the bath upon the formation of further ferrocyanide in subsequent use. However, in most processes it is desirable to avoid the addition of more persulfate than that equivalent to the ferrocyanide present particularly where pH control is important.

Because the conversion of silver to silver bromide in the bleaching operation reduces the bromide content of the bleaching solution, it is usually desirable to also add sodium bromide to the spent bleaching solution in sufficient amount to bring the bromide content thereof up to that desired. Sometimes it may be desirable to supply additional ferrocyanide to the spent bleaching bath to restore the ferricyanide content to approximately that originally present. In a typical regeneration procedure the content of potassium ferrocyanide is diminished by conversion to ferricyanide after the addition of potassium persulfate to the spent bleaching solution as illustrated in the following table:

Time after addition of 1 equivalent of $K_2S_2O_8$	Parts $K_4Fe(CN)_6$ Found
0 minute	67.1
1 minute	50.0
5 minutes	15.6
10 minutes	5.4
20 minutes	1.4
30 minutes	.9

Spent ferricyanide bleaching solution may be rapidly rejuvenated by our procedure in which a water soluble persulfate is added up to the point where the sulfate salt which results therefrom reaches its saturation equilibrium in the solution. This is not apt to be reached under actual conditions. However, if this point is reached the sulfate ion content may be removed by the addition of calcium chloride or calcium bromide thereby precipitating calcium sulfate without seriously altering the concentrations of the active constituent except as the precipitate carries down with it some of the ferrocyanide or ferricyanide which is present in the solution. We have found that potassium persulfate is probably more convenient to use as the regenerating agent primarily because of its low cost and availability. In the case of ammonium persulfate although the pH of the bleach solution is decreased the decomposition product thereof is more soluble and, therefore, ammonium persulfate is quite useful in the repeated rejuvenation of the bleach bath. The persulfate added to the spent bleach solution quantitatively oxidizes any ferrocyanide therein to ferricyanide and with the addition of further alkali metal bromide and additional ferrocyanide, if desired, the bath may be brought to a composition which is substantially as effective for bleaching purposes as the original bleaching solution.

The following example illustrates the regeneration of a spent bleaching solution in accordance with our invention:

A photographic bleach solution having the following formula: $Na_4Fe(CN)_6.10H_2O$, 1 gram; $Na_3Fe(CN)_6$, 23 grams; NaBr, 7.5 grams; water to make 1 liter, which bath had a pH of 8.3 was employed to bleach a quantity of color developed print material. The spent bleaching solution which resulted had the following composition per liter; $Na_4Fe(CN)_6.10H_2O$, 9.2 grams; $Na_3Fe(CN)_6$, 12.9 grams; NaBr, 4.75 grams. By calculation it became apparent that a minimum of the following quantities

would be needed to restore the spent bleaching solution to its original strength per liter of solution:

$Na_4Fe(CN)_6.10H_2O$

8. 9 grams; $K_2S_2O_8$, 4.84 grams; NaBr, 2.75 grams. The above-mentioned amounts of sodium ferrocyanide, potassium persulfate and sodium bromide were added to each liter of the used bleach solution and the mass was stirred until solution was complete. The mass was allowed to stand for 1 or 2 hours and where desirable, the solution was filtered. The regenerated bleach was then analyzed for ferrocyanide and ferricyanide content and if the pH value was critical that was determined also. When the ferricyanide content was below that required, amounts of ferrocyanide and persulfate were additionally added to bring the concentration to the desired point. Experience indicates that it is desirable to use a slight excess of the persulfate and the ferrocyanide to obtain the desired ferricyanide concentration because of the increase in volume upon addition of the chemicals. When the pH of the bleach is critical this value may be adjusted by the addition of an appropriate chemical such as sodium hydroxide, borax or boric acid. After the spent bleach solution had been regenerated to bring the contents of ferricyanide and sodium bromide to approximately those of the original solution, further developed print material was processed therewith. It was found that the bleaching effectiveness of the regenerated solution was substantially equivalent to that of the original bleach solution.

Our invention is also useful in preparing fresh bleach initially starting with ferrocyanide and persulfate together with the addition of alkali metal bromide thereto.

It is to be understood that we do not wish to be limited to the specific embodiment described herein except as defined by the appended claims.

We claim:

1. The processing of developed silver halide photographic emulsion layers which comprises treating said layers with a bleach solution containing an alkali metal ferricyanide and an alkali metal bromide, adding to the spent bleaching solution which results a water-soluble persulfate in an amount approximately chemically equivalent to the ferrocyanide present in the spent liquor plus sodium bromide in sufficient amount to restore the bromide content of the bleach solution and bleaching further developed silver halide photographic emulsion layers with the regenerated bleach solution thus obtained.

2. The processing of developed silver halide photographic emulsion layers which comprises treating said layers with a bleach solution containing an alkali metal ferricyanide and an alkali metal bromide, whereby a spent bleaching solution is obtained in which ferricyanide is reduced to ferrocyanide, followed by adding to the spent bleaching solution a water-soluble persulfate in an amount approximately chemically equivalent to the ferrocyanide therein and an alkali metal bromide in sufficient amount to substantially restore the original bromide content of the bleached solution.

3. The processing of developed silver halide photographic emulsion layers which comprises treating said layers with a bleach solution containing sodium ferricyanide and sodium bromide, whereby the ferricyanide of the solution is reduced to ferrocyanide, followed by adding to the spent bleaching solution potassium persulfate in an amount approximately chemically equivalent to the ferrocyanide present in the spent solution and sodium bromide in a sufficient amount to substantially restore the original bromide content of the bleached solution.

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Disclaimer

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Hereby disclaims the entire remaining portion of the term of said patent. [*Official Gazette April 29, 1975.*]