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REGENERATION OF PHOTOGRAPHIC SILVER
BLEACH SOLUTIONEugene G. Seary, Irvington, N. Y., assignor to
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corporation of DelawareNo Drawing. Application May 4, 1946,
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The general object of the present invention is to provide a novel, practical and effective method of regenerating a photographic bleaching solution containing a soluble ferricyanide as its active agent.

In processing many photographic materials, the latter are subjected to the bleaching action of a solution of the type mentioned above. Usually, the solution also contains a soluble bromide which acts as an accelerator. In the bleaching action, the ferricyanide oxidizes the metallic silver in the photographic material to silver ion, and the bromide reacts with the silver ion to form silver bromide. The reaction of the ferricyanide with the silver is an oxidizing action and results in the reduction of the ferricyanide to ferrocyanide. In consequence, ferrocyanide ion accumulates in the bleaching solution bath as the normal bleaching operation proceeds with the result of slowing down the bleaching action. If the ferricyanide in the solution is potassium ferricyanide $K_3Fe(CN)_6$, the cyanide product furnished by the conversion is potassium ferrocyanide $K_4Fe(CN)_6$. The ferricyanide constituent of the bleaching solution may well be potassium ferricyanide, the less expensive di-potassium-sodium ferricyanide, or other alkali group ferricyanide. In addition to ferricyanide, the bleaching solution may contain buffer salts such as sodium phosphates and water. The buffer salts are added for pH control. Volumetrically, water is the principal constituent of the solution. The ferricyanide is generally present in the solution in the ratio of 50 to 150 grams per liter.

The presence in the bleaching solution of a relatively small amount of ferrocyanide greatly reduces the bleaching capacity of the solution even though the unreduced ferricyanide component of the solution remains relatively high.

The purpose of the present invention is to reconvert the ferrocyanide constituent of a partially spent bleaching solution into ferricyanide. The need for a relatively inexpensive and practically feasible process of reconvert the ferrocyanide content of a partially spent bleaching solution into ferricyanide is recognized, and various methods of accomplishing the regeneration have been proposed. Thus, it has been suggested that the regeneration might be effected by electrolytic action, but that procedure is open to the practical objection that the apparatus required is expensive, requires close control, and the solution contains too much water for efficient electrolytic cell action.

It has also been proposed to precipitate and remove ferrocyanide from the solution in the form of ferric ferrocyanide, commonly called Prussian blue, but that method seems impractical because of the difficulty of filtering out the Prussian blue. Furthermore, the ferrocyanide is

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totally lost by this method and must be made up with fresh ferricyanide, which is economically undesirable.

It has also been proposed to regenerate the bleach solution by the use of bromine in some form involving appreciable dilution of the bleaching solution. In particular, it has been proposed to use sodium hypobromite in the form of an alkaline solution. The use of hypobromite as a regenerating agent is open to important practical objections. For one thing, sodium hypobromite is not a commercially available product and its preparation from bromine and sodium hydroxide is rather a dangerous process which must be conducted with extreme care. The dilution of the bleaching solution resulting from the addition of an adequate amount of sodium hypobromite is substantial and objectionable. Moreover, the addition of the hypobromite changes the pH of the bleaching solution. While the disadvantages, other than its dilution effect, attending the use of sodium hypobromite as a regenerating agent can be reduced and compensated for, more or less, by the addition of corrective chemicals, such corrective treatment requires time and close control, and is expensive.

I have found that it is practically feasible to regenerate the bleaching solution rapidly by adding bromine in gaseous, liquid or solid form, or by adding chlorine in gaseous form to the solution to be regenerated. In the form of the invention which I now consider preferable from the practical standpoint, I add liquid bromine to the solution to be regenerated while vigorously agitating the solution. The liquid bromine added preferably contains no diluent, or, at least is so concentrated that its addition to the bleaching solution has no significant diluting effect. The liquid bromine added to the partially spent, or exhausted, bleach bath, quickly oxidizes the accumulated ferrocyanide ion back to ferricyanide. The bromine also replaces the bromine ions which have passed out of the solution as silver bromide was formed. The addition of the liquid bromine in suitably concentrated form, dilutes the solution only to an infinitesimal extent, and does not change the pH of the solution. Furthermore, liquid bromine is a very much more efficient regenerative agent than sodium hypobromite.

The bleaching solution may be effectively regenerated by bromine added to the solution in gaseous or solid form, as well as in liquid form. In the use of bromine gas in regenerating a bleaching solution, the latter may be scrubbed with bromine gas in various ways, as those skilled in the art will recognize. One effective method consists in bubbling air through liquid bromine to form a gaseous mixture of air and bromine, and then bubbling said mixture through the

solution. Bromine solidifies at a temperature of minus 7° C., and solidified bromine in finely subdivided form may be added to the bleaching solution to be regenerated while the solution is being agitated as it is when being regenerated with liquid bromine. When the bromine is added to the bleaching solution in gaseous or solid form, there is no more inherent risk of objectionably diluting the solution than when the bromine is added in the form of a concentrated liquid.

When bromine is used as the regenerative agent, the regeneration of the bleaching solution takes little time and requires a minimum of control. The bromine added to the solution should not be in excess of the amount required to convert substantially all of the ferrocyanide into ferricyanide. Because of the corrosive character of bromine, free bromine in the solution would be seriously objectionable, not only because it would attack the solution containing apparatus, but also because it would injuriously attack the photographic material treated. However, I have found that it is not practically difficult to determine how much bromine should be added to a partially spent solution to obtain a suitable regeneration effect without risk of leaving free bromine in the solution. In general, approximately 0.2 gram of bromine should be added to the partially spent solution for each gram of ferrocyanide in the solution. The presence of free bromine in the solution can be readily detected by simple reaction color tests. When the regeneration of partially spent bleaching solution is affected by withdrawing solution from the bleaching chamber space for regeneration in small batches without interrupting the bleaching action the injurious consequences of a small excess of free bromine in the regenerated solution will ordinarily be confined to the regeneration apparatus. In such case, with the normal slow return to the bleaching chamber space of the regenerated solution, a small amount of free bromine therein will be immediately neutralized in said space by the ferrocyanide in the body of solution in said space.

In the successful practical use of bromine as a regenerating agent which I have made, the bleaching solution requiring regeneration has been withdrawn from the bleaching chamber space to a regeneration receptacle. Liquid bromine is added to each batch undergoing separation by allowing it to flow from a bottle through a glass tube having its discharge end immersed in the solution undergoing regeneration. That solution is vigorously agitated during the regeneration process. Such agitation of the bleaching solution may be effected in any of the ways customarily employed to continuously agitate the bleaching solution in the bleaching chamber space. In practice, I have agitated the solution undergoing regeneration by means of a propeller type mixer. It is apparent that the regeneration operation may be a continuous one, but in the considerable practical use which I have made of the invention, the process has involved successive treatment of batches of partially spent solution withdrawn from the bleaching chambers and returned to the latter after its regeneration.

My experiments have shown that for use in regenerating the above described bleaching solution, chlorine gas is substantially equivalent to bromine gas. The low boiling and solidifying temperatures of chlorine, minus 33.6° C. and minus 102.6° C., respectively, apparently preclude

the use of chlorine in liquid or solid form as a practical bleaching solution regenerating material, though it is practically feasible to pass chlorine gas into the bleaching solution through a pipe including pressure reducing means directly from a container holding liquid chlorine under pressure. In general, approximately about .0875 of a gram of chlorine should be added to the partially spent bleaching solution for each gram of ferrocyanide in the solution.

Having now described my invention, what I claim as new and desire to secure by Letters Patent, is:

1. In the process of bleaching a silver image contained in a photographic emulsion layer which also contains a dye image, said process comprising treating the silver image with a solution containing about 50 to 150 grams per liter of ferricyanide and a soluble halide whereby the silver in the silver image is oxidized to silver ions which combine with the halide ions of the solution and form a silver halide in the emulsion and a relatively small amount of the ferricyanide is reduced to ferrocyanide, and then treating the partially spent bleaching solution which contains ferricyanide, ferrocyanide and a halide with a regenerating agent, the improvement which consists in adding, as said regenerating agent, a substantially water free halogen selected from the group consisting of bromine and chlorine, to the solution in substantially the amount required to convert the ferrocyanide content of the solution into ferricyanide and to increase the soluble halide in the solution to substantially its original content without giving the regenerated solution a free halogen content.

2. In the process of bleaching a silver image contained in a photographic emulsion layer which also contains a dye image, said process comprising treating the silver image with a solution containing about 50 to 150 grams per liter of ferricyanide and a soluble halide whereby the silver in the silver image is oxidized to silver ions which combine with the halide ions of the solution and form a silver halide in the emulsion and a relatively small amount of the ferricyanide is reduced to ferrocyanide, and then treating the partially spent bleaching solution which contains ferricyanide, ferrocyanide and a halide with a regenerating agent, the improvement which consists, in adding, as said regenerating agent, bromine to the solution in substantially the amount required to convert the ferrocyanide content of the solution into ferricyanide and to increase the soluble halide in the solution to substantially its original content without giving the regenerated solution a free halogen content.

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