July 12, 1932. F. E. GARBUTT ET AL 1,866,701

METHOD AND APPARATUS FOR RECOVERING SILVER FROM FIXING SOLUTIONS

Filed March 13, 1929

Fig. 1

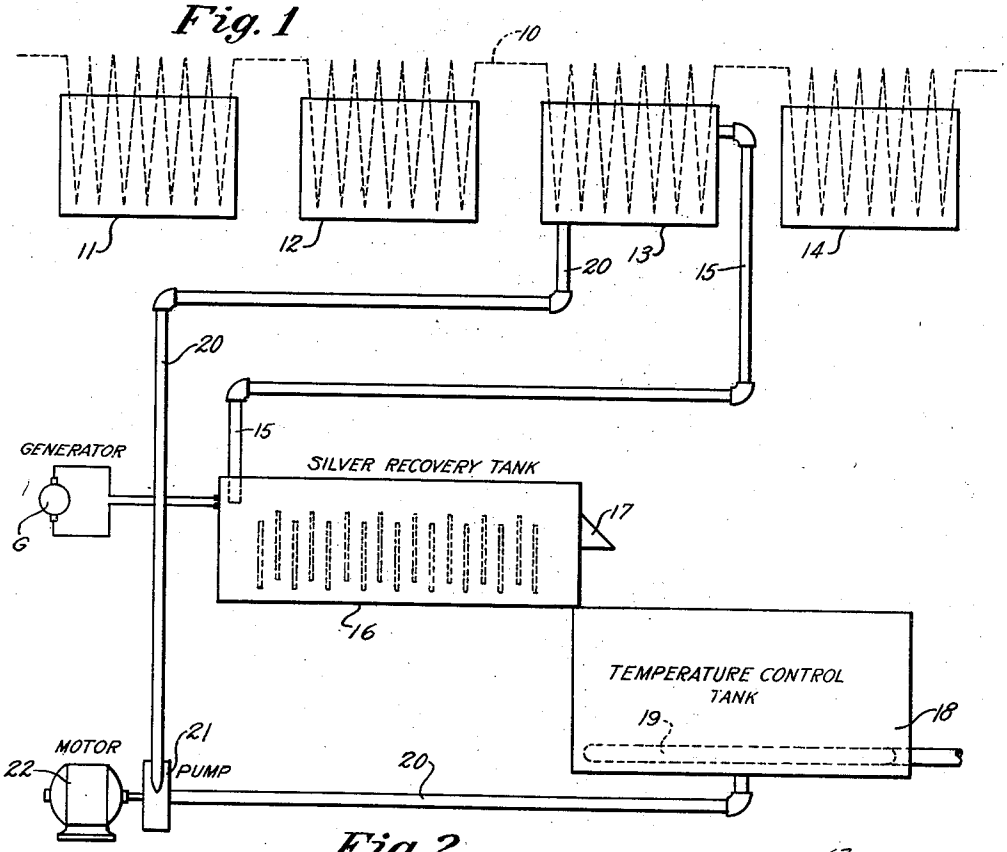


Fig. 2

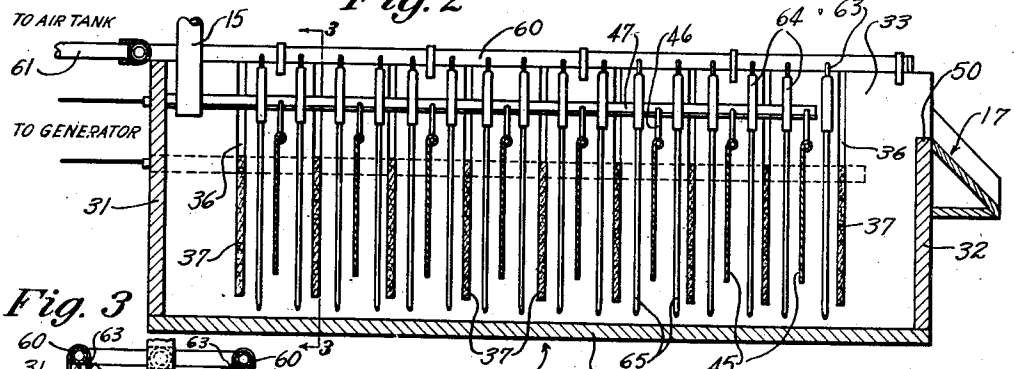


Fig. 3

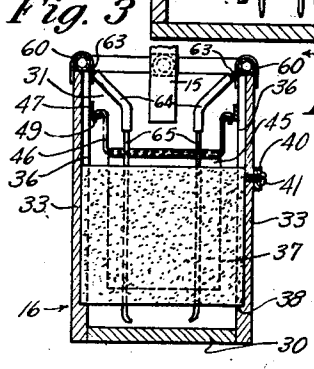
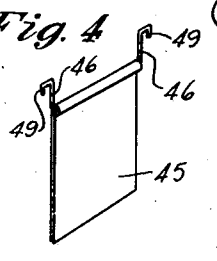


Fig. 4



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UNITED STATES PATENT OFFICE

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METHOD AND APPARATUS FOR RECOVERING SILVER FROM FIXING SOLUTIONS

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This invention is concerned with the recovery of silver from hypo solutions used in the fixing treatment in photography. The present method has particular utility when practiced in connection with the well known mechanical methods of developing and fixing motion picture films, and will therefore be described particularly with that application in view, but without necessary limitation thereto.

The common practice of manipulating hypo solution in the past has been to run film through a batch of hypo until the hypo becomes saturated with silver, or nearly so, and then to remove the silver saturated hypo solution and replace it with a fresh batch. Silver is later recovered from the saturated solution by precipitation.

This practice has several disadvantages, which will briefly be indicated. The silver saturation point of a hypo solution of usual concentration has been found to be approximately 3 oz. of silver per gallon of solution. A bath of hypo solution has commonly been used until a concentration of say 1.6 oz. of silver is reached, when the solution is replaced by a fresh batch. It has been found not practicable to approach the point of silver saturation more closely for the reason that the effectiveness of the hypo is continuously decreased as this saturation point is approached, and the silver salts may not be completely removed in the time the film is allowed in the bath. The effectiveness of the hypo thus varies continuously in accordance with the use of the solution, and the solution must be replaced before silver salts begin to be left undissolved in the film.

It has been ascertained that about one gallon of hypo is carried over and lost from the fixing solution by approximately three thousand feet of film. Assuming that the silver concentration of the hypo is normally allowed to rise to 1.6 oz. per gallon before replacement, the average concentration is .8 oz. per gallon. This means that .8 oz. of silver is lost upon the film for every three thousand feet of film run through the bath.

The two major disabilities of these methods which may be gathered from the above discussion are, first, a continuous variation in the effectiveness of the hypo on the silver salts of the film, and second, a relatively large quantity of silver lost by carrying over relatively saturated hypo on the film.

According to the present invention the hypo is maintained constantly at a low silver concentration, the silver being continuously recovered from the hypo solution at substantially the same rate that the hypo dissolves silver from the film. The effectiveness of the hypo solution on the silver salts of the film is thus maintained constant, and as the silver concentration of the solution is maintained at a relatively low value, a relatively small quantity of silver is lost by carrying over on the film. According to the present invention, this result may be accomplished, for instance, by continuously circulating the hypo solution of the fixing tank through a recovery tank within which the silver is electrically deposited upon metal cathode plates, which are periodically removed from the tank, dried, and scaled to remove the metallic silver.

Silver is not readily recoverable from hypo solutions by electro-deposition, however, and to reduce the silver concentration by this method to the low value desired we have had recourse to special methods for promoting the action. We have found, for instance, that the deposition of silver is greatly increased if the hypo solution is thoroughly agitated as by passing streams of air through it during the electrical treatment. By this means the concentration may easily be maintained at a value as low as say .2 oz. per gallon, at which the hypo is at practically full strength for the fixing treatment, and at which only a relatively small quantity of silver is lost upon the film.

The agitation produced by these air streams also prevents the precipitation of silver sulfide, which otherwise forms in large quantities.

The chemistry relating to the electrolysis of hypo solutions is very complex and need not be comprehensively set forth for a complete understanding of our invention. It is sufficient to note that the deposit on the cath-

ode of silver from the hypo solution is a secondary reaction. The liberation of sodium cations at the cathode is a primary reaction of the electrolysis and the liberated sodium ions are so reactive that they decompose any ions in the vicinity. If there are sufficient $A_gS_2O_3$ anions in the electrolyzed hypo solution adjacent the cathode, they are decomposed by the sodium ions to deposit silver on the cathode. Otherwise the sodium ions reduce water to hydrogen, or hypo to a series of compounds, most of them fatal to good silver plating.

Therefore, vigorous agitation of the silver laden hypo solution will promote the plating of metallic silver and prevent the formation of undesirable compounds such as silver sulfide. Although the whole electrolyte is agitated it will be apparent that the circulation of the hypo or fixing solution across the surface of the cathode is the most important factor in the procurement of a good metallic silver deposit on the cathode.

The invention will best be understood from the following detailed description of a present illustrative embodiment, reference for this purpose being had to the accompanying drawing, in which:

Figure 1 illustrates diagrammatically the system of the invention as a whole;

Fig. 2 is a vertical longitudinal section of the silver-recovery tank;

Fig. 3 is a vertical transverse section, taken on line 3—3 of Fig. 2; and

Fig. 4 is a perspective view of one of the removable cathode plates upon which the silver is deposited.

We have chosen to illustrate an embodiment of the invention adapted for use in connection with a mechanical system of developing and fixing motion picture film. This embodiment will be understood, however, to illustrate the invention by indicating merely one of its fields of use, and one of its practical embodiments therein.

Referring now to the drawing, and particularly to Fig. 1, the film 10 is shown passing continuously through developing tank 11, wash tank 12, fixing or hypo tank 13 and final wash tank 14. Pipe line 15 leads from one end of fixing tank 13, and discharges hypo into the end of silver-recovery tank 16, which contains a number of anode and cathode plates across which an electrical potential is maintained, as by means of D. C. generator G. Fixing tank 13 may conveniently be located above recovery tank 16 so that hypo will flow to the recovery tank without the necessity for a pump in pipe line 15. The hypo flows from pipe 15 continuously through tank 16, giving up its silver upon the cathode plates by the action of the electric current, and is discharged from the other end of the tank by way of chute 17 into a tank 18.

The electrical treatment received in trough 16 tends to warm the hypo; and for the purpose of thereafter reducing its temperature to a proper value, cooling coils 19 for circulation of a cooling medium such as brine may be provided in tank 18.

A pipe line 20 containing a pump 21 driven by motor 22 conducts the cooled hypo from tank 18 back up to fixing tank 13.

Referring now to Figs. 2 and 3, tank 16 comprises, for instance, a wooden or other insulating trough having a bottom 30, ends 31 and 32, and side walls 33. End 32 is provided with the discharge chute 17, hereinbefore mentioned.

Side walls 33 are grooved as at 36 to receive a number of carbon anode plates 37 evenly spaced longitudinally in the trough. Grooves 36 terminate a short distance, say an inch or so, above bottom 30, thereby providing shoulders 38 upon which plates 37 may rest at a suitable clearance from the bottom that the hypo may circulate under the plates. For the purpose of setting out proportions which may be suitable, but without intention of limiting the invention thereto, these anode plates may be about 15 inches square, there being any number of plates necessary to accommodate the quantity of hypo to be treated. The anode plates are preferably of carbon, as before stated, though some other material may be found suitable. The anode plates are all electrically connected together by means of a metal conducting strip 40 screwed to one side wall 33, and contact screws 41 threaded in strips 40 and passing through the side wall to make electrical contact with the edges of the plates, as shown in Fig. 3.

Evenly spaced between the carbon anode plates are removably suspended cathode plates 45, upon which the silver is to be deposited. These plates are of some suitable metal upon which the silver will readily deposit and which will not be attacked by the hypo solution. I have found that cathode plates made of Monel, a commercial alloy, meet these requirements very satisfactorily. The cathode plates are carried by wire stirrups 46, preferably of the same metal, which are removably supported from metal angle members 47 fastened to the inner faces of side walls 33, and having vertical drill holes evenly spaced between the anode plate grooves 36 to take the hooked ends 49 of the stirrups. The cathode plates are thus electrically connected together by these metal angle members 47, and the current is supplied to the plates by connecting a generator across one such angle member 47 and the anode connecting strip 40. The spacing between anode and cathode plates may preferably, though not necessarily, be about three-quarters of an inch. With such spacing, and the other proportions indicated, an applied

potential across the plates of .7 volt has been found to provide efficient conditions.

The discharge end 32 of the trough has an overflow edge 50 leading to discharge chute 17, which edge is located slightly above the upper edges of the electrode plates so that the hypo may flow both above and below the plates on its way through the trough.

Secured to the upper edges of side walls 33 are air pipes 60 supplied with air from a common supply pipe 61, pipes 60 being provided with short outlet tubes 63 connected, as by rubber connecting tubes 64, with glass discharge tubes 65 extending well down between the plates. The discharge tubes 65 are made of glass rather than of metal for the reason that metal tubes would be attacked by the hypo solution. There are preferably at least one outlet tube from each of the two side pipes 61 discharging between each pair of plates, and sufficient air is passed upwardly to agitate the hypo thoroughly, a copious foam appearing on the surface of the hypo when the action is proceeding properly.

This agitation is found to be very necessary to permit the concentration to be reduced to as low as .2 oz. per gallon, as the silver does not readily deposit from hypo to such a complete extent under ordinary plating methods, and for the further reason that without agitation the silver precipitates from the solution as silver sulfide.

It may now be seen that we have provided a system and method for manipulating the hypo solution by which the hypo is maintained at a constant and extremely low silver concentration, and that the fixing treatment is thereby rendered constant, variation of hypo strength having been eliminated, and that large losses of silver due to carrying over relatively saturated hypo on the film are greatly reduced. And it will further be seen that we have provided means for promoting the electro-deposition of silver whereby the silver concentration may be reduced to lower values than have heretofore been possible.

We claim:

1. The method of recovering silver from a silver laden photographic fixing solution which comprises impressing an electrical potential across an anode and cathode in said solution, said anode being of a substance other than silver, and agitating said solution to move the same over the surface of said cathode whereby metallic silver is deposited upon said cathode and the precipitation of silver sulfide is prevented.

2. The method of recovering silver from a silver laden photographic fixing solution which comprises impressing an electrical potential across an anode and cathode in said solution, said anode being of a substance other than silver, and bubbling a gas through said solution to move the same over the surface of said cathode whereby metallic silver is deposited upon said cathode and the precipitation of silver sulfide is prevented.

3. The method of recovering silver from a silver laden photographic fixing solution which comprises impressing an electrical potential across an anode and cathode in said solution, said anode being of a substance other than silver, and bubbling air through said solution for circulation thereof over the surface of said cathode whereby metallic silver is deposited upon said cathode and the precipitation of silver sulfide is prevented.

4. The method of recovering silver from a silver laden photographic fixing solution which comprises impressing an electrical potential across an anode plate and a cathode plate immersed in said solution and in spaced relation, said anode plate being of a substance other than silver, and passing a stream of air through the solution between said anode and cathode plates for circulation of the solution over the surface of said cathode plate.

5. The method of continuously employing a photographic fixing solution which comprises dissolving the silver halides from photographic light sensitive material in a bath of the photographic fixing solution, conducting the silver laden photographic fixing solution to an electrolytic cell, impressing an electrical potential across an anode and cathode in the solution in said cell, said anode being of a substance other than silver, agitating the silver laden fixing solution for circulation thereof over the surface of said cathode to cause the deposition of metallic silver thereon, and returning the de-silvered fixing solution to the fixing bath.

6. The method of continuously employing a photographic fixing solution which comprises dissolving the silver halides from photographic light sensitive material in a bath of the photographic fixing solution, conducting the silver laden photographic fixing solution to an electrolytic cell impressing an electrical potential across an anode and cathode in the solution in said cell, said anode being of a substance other than silver, bubbling air through the silver laden fixing solution for circulation thereof over the surface of said cathode to cause the deposition of metallic silver thereon, and returning the silver-free fixing solution to the fixing bath.

7. The method of continuously employing a photographic fixing solution which comprises dissolving the silver halides from photographic light-sensitive material in a bath of the photographic fixing solution, conducting the silver laden photographic fixing solution to an electrolytic cell, impressing an electrical potential across an anode and a cathode in the solution in said cell, said anode being of a substance other than silver, agitating the silver laden fixing solution for circulation thereof over the surface of said cath-

ode to cause the deposition of metallic silver thereon, cooling the de-silvered fixing solution to a proper temperature for fixing treatment and returning the cooled and de-silvered fixing solution to the fixing bath.

8. The method of continuously employing a photographic fixing solution which comprises dissolving the silver halides from photographic light-sensitive material in a bath of the photographic fixing solution, conducting the silver laden photographic fixing solution to an electrolytic cell, impressing an electrical potential across an anode and a cathode in the solution in said cell, said anode being of a substance other than silver, agitating the silver laden fixing solution for circulation thereof over the surface of said cathode to cause the deposition of metallic silver thereon, cooling the de-silvered fixing solution to a proper temperature for fixing treatment by indirect heat conductive contact with a cooling medium and returning the cooled and de-silvered fixing solution to the fixing bath.

9. An electrolytic unit for recovering metallic silver from used photographic fixing solutions comprising a tank adapted to contain said solution, a cathode plate and an anode plate vertically positioned in horizontal spaced relation within said tank, said anode plate being a substance other than silver and means for agitating said solution for circulation over the surface of said cathode plate.

10. An electrolytic unit for recovering metallic silver from used photographic fixing solutions comprising a tank adapted to contain said solution, a cathode plate and an anode plate vertically positioned in horizontal spaced relation within said tank, said anode plate being of a substance other than silver and agitating means for bubbling air through the solution for circulation thereof over the surface of said cathode plate.

In witness that we claim the foregoing we have hereunto subscribed our names this 21st day of February, 1929.

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