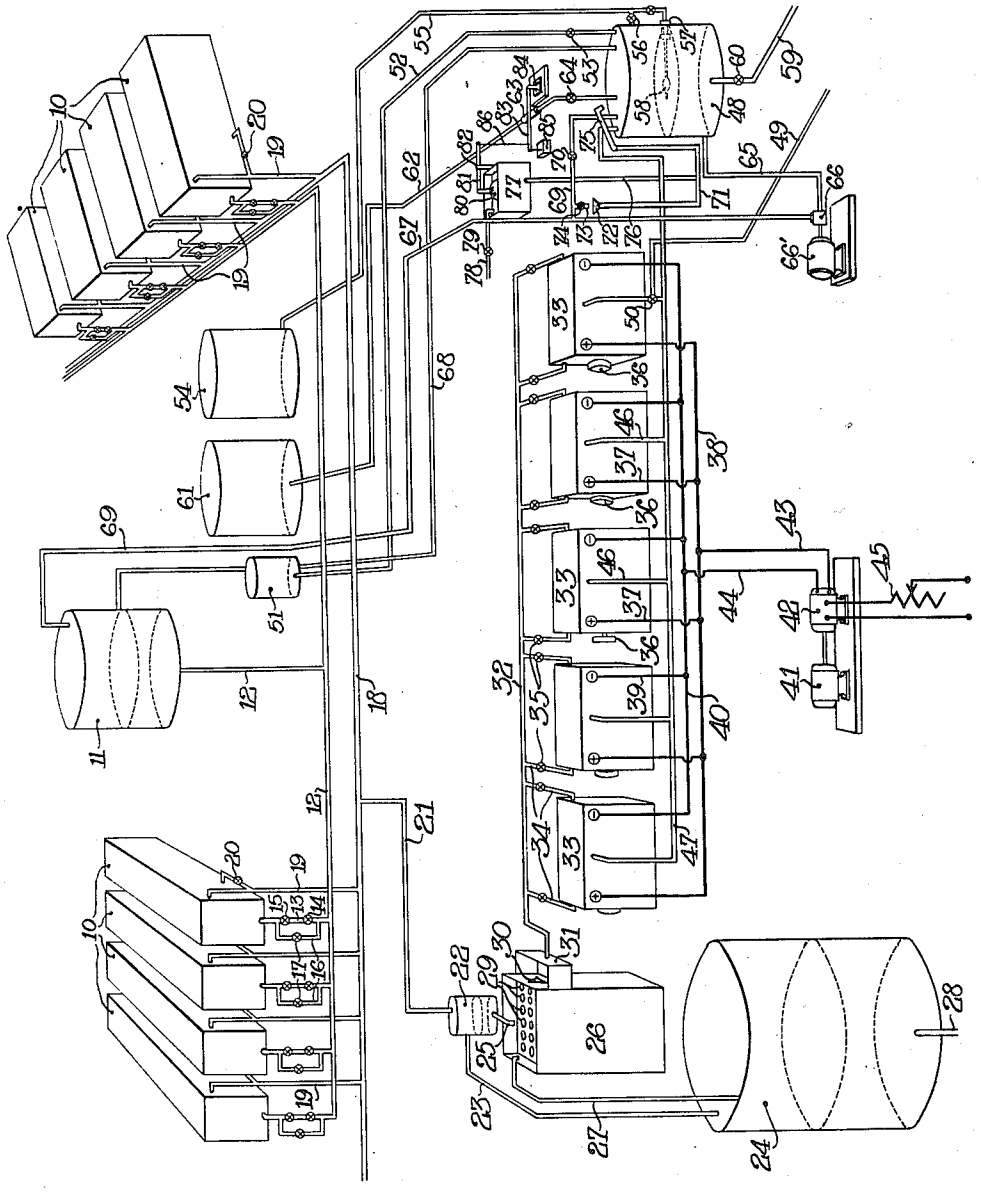
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METHOD FOR PHOTOGRAPHIC PROCESSING

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METHOD FOR PHOTOGRAPHIC PROCESSING

Application filed June 4, 1931. Serial No. 542,053.

The present invention relates to a method for photographic processing, and more particularly to a method for a continuous processing arrangement which includes the recovery of silver from the photographic fixing solution.

The primary object of the invention is the provision of a method for photographing processing which continuously circulates the fixing solution through one set of electrolytic units for high efficiency silver plating and through another set of electrolytic units for substantially complete plating of the silver from the solution.

Another object of the invention is the provision of a method for continuous processing which is adapted to automatically replenish the fixing solution so that the quantity thereof remains substantially constant.

A further object of the invention is the provision of a method for continuous photographic processing which is adapted to automatically control the concentration of the fixing solution.

Still another object of the invention is the provision of a method for electrolytically recovering silver from the fixing solution which includes grouping of the electrolytic units into working units and tailing units, the fixing solution being continuously circulated through the working units and exhausted to waste through the tailing units.

Other objects of the invention will be suggested to those skilled in the processing art as the description of my invention is developed hereinafter.

With these objects in view, the present invention consists in certain features of novelty in the method, combination and arrangement of parts by which the said objects and certain other objects are effected, all as fully described with reference to the accompanying drawing, and more particularly pointed out in the appended claims.

In the drawing like reference numerals designate similar units and Fig. 1 is a diagrammatic illustration of a processing laboratory which may be operated according to my invention and which contains the apparatus suitable for the operation of my invention.

The obvious way to utilize the electrolytic units is to fill them with silver laden fixing solution, apply a maximum plating current and gradually diminish the plating current according to the depletion of silver content. If half of the silver is removed in a unit of time, only half of the remaining silver will be plated out in the next unit of time, etc. so that it will require considerable time before all of the silver is removed from the solution. As a practical means the last traces of silver are plated from the solution more rapidly than is indicated by the exponential scale. Even so this method of operation requires periodic analyses of the solution of electrolyte so that the plating current may be properly controlled. Consequently, the intermittent method of operation is not recommended.

On the other hand with a continuous flow of silver laden fixing solution through the electrolytic units, the silver plating is effected quite efficiently when only a portion of the silver is removed from the solution. It is apparent that if N electrolytic units are required to reduce the silver content to one-half of the original, 2N electrolytic units will be necessary to reduce the silver content to one-quarter of the original, 3N electrolytic units to reduce the silver content to one-eighth of the original, etc. For removal of 99% of the silver, N units will remove approximately 50%, whereas it will require 5N electrolytic units to plate out the remaining 49% of the silver.

The electrolytic silver recovery is effected with much higher efficiency if the electrolytic units are grouped into working units and tailing units. The units comprising each of these groups may be individual plating cells or may be individual compartments within a single cell for small installations. The group of working units receives the main bulk of the fixing solution in a rapid continuous flow. Heretofore the fixing solution has been used in the processing or fixing apparatus until its silver concentration was 5–8 grams of silver per liter of fixing solution. Since the

present method greatly facilitates the removal of silver from the fixing solution and since greater efficiency of operation may be obtained with smaller silver concentration in the fixing solution, the fixing solution is used in processing only until the silver content of the solution becomes two to three grams of silver per liter of fixing solution and is then passed through the electrolytic units where the silver content is reduced to three-quarters of a gram per liter of fixing solution.

The tailing electrolytic units receive a small portion of the total fixing solution to remove substantially all the silver therefrom before allowing the solution to be discharged to waste. The flow of solution as an electrolyte through the tailing unit is somewhat smaller than through the working units so that the substantially complete recovery of silver may be effected more readily.

The economy achieved by the grouping of the electrolytic cells is well illustrated by an examination of the situation where a certain quantity of fixing solution is circulated through the units. For instance, for the purpose of the present illustration it is assumed that the fixing solution passes through the working cells three times before a portion is bled off through the tailing units to waste. The quantity of silver recovered by the working units will be

$$3N(2\tfrac{3}{4}) = 3\tfrac{3}{4} \text{ grams Ag.}$$

While that removed by the tailing units will be

$$1N = \tfrac{3}{4} \text{ grams Ag.}$$

Thus, five times as much silver will be removed at high efficiency plating as will be left at lower efficiency tailing.

In the illustrated embodiment of my invention the fixing solution is used in a processing apparatus until the silver content thereof increases to the limits previously indicated. The processing means may comprise a plurality of fixing tanks 10, for positive or negative photographic material, or both. The fixing tanks 10 may be located in different parts of the laboratory and if necessary at different levels therein.

The fixing solution contemplated throughout the disclosure of my method may be any standard solution which is suitable for the requirements at hand. As an example, only, the constituents of a photographic fixing bath are given below:

Sodium thiosulfate	300 parts
Sodium sulfite	10 parts
Acetic acid (or the equivalent)	10 parts
Chrom alum	10 parts
Water	1000 parts

The fixing solution of desired composition is supplied to a service tank 11, which is located preferably at sufficient height above the fixing tank 10 so that solution will be supplied thereto by gravity through the supply main 12. The individual fixing tanks 10 are connected to supply main 12 by pipes 13, each of which contains a regulating valve 14 and a shut-off valve 15. A by-pass 16 for the valves 14 and 15 contains a quick filling valve 17 to permit rapid flow of solution to fixing tanks 10 without altering the adjustment of regulating valve 14.

The fixing solution is discharged from the fixing tanks to a discharge main 18 connected by individual branched pipes 19 to the fixing tanks 10. One branch of pipe 19 is connected to a fixing tank 10 so as to maintain the desired level of solution within tank 10. The other branch of pipe 19 is connected through dump valve 20 to the bottom of tank 10 so that the solution therein may be rapidly discharged if necessary or desired.

The discharged fixing solution is conducted by a pipe 21 to a spill tank 22. An overflow pipe 23 is connected at an intermediate level to spill tank 22 and extends into an overflow tank 24. Spill tank 22 has a spout 25 connected to the bottom thereof and conducts the solution into a filter box 26. An air-lift 27 returns overflow solution from overflow tank 24 to filter box 26. If required, fixing solution may be discharged to waste from overflow tank 25 by a discharge pipe 28. The filter box 26 may be of any well known construction or may consist of a plurality of felt socks (not shown) suspended beneath the holes 29 in the filter box.

After filtration, the fixing solution flows through a weir 30 into a weir box 31 from whence it is conducted through an electrolytic unit supply main 32. A plurality of electrolytic units 33 are each connected to the supply main 32 by a pair of branch pipes 34. Each of the branch pipes 34 are connected at opposite ends of the electrolytic units 33 and contain valves 35 for regulating the supply of fixing solution or electrolyte to the individual electrolytic units 33. The electrolytic units are preferably constructed in accordance with the copending application of Hickman and Weyerts, Serial No. 540,621, filed May 28, 1931, for improvements in apparatus for electroplating silver from used photographic fixing solutions. The electrolytic units 33 are provided with mechanical agitating means rotated by belt drives to pulleys 36.

The plates within the electrolytic units 33 are alternately connected in a known manner by leaders 37 to an anode bus bar 38 and by leaders 39 to a cathode bus bar 40. A source of low voltage uni-directional electrical energy is provided by a low voltage direct current generator 42 driven by a motor 41, the positive side of generator 42 being connected by a wire 43 to the anode bus bar 38, while the negative side of generator 42 is connected by a wire 44 to the cathode bus bar 40. The

plating current supplied by generator 42 is controlled by regulation of a variable resistance or field rheostat 45 which is inserted in the excitation circuit for the generator. The field rheostat 45 may be manually operated to give the desired plating current or may be automatically operated to vary the plating current corresponding to the silver concentration of the fixing solution and rate of flow thereof, according to my co-pending application, Serial No. 540,620, filed May 28, 1931, for improvements in automatic silver recovery control.

The desilvered fixing solution may be conducted from the center of units 33 by outlets 46 through a discharge main 47 to a tank 48. The discharged fixing solution from one or more of units 33 may be conducted to waste by pipe 49 connected to a two-way valve 50 in outlet 46. The units 33, which have solution continuously circulating therethrough, are classed or grouped as working units, while the units 33, which are adapted to have the solution therefrom discharged to waste, are grouped as tailing units. The rate of flow of solution through the working units 33 is preferably more rapid than the rate of flow of solution through the tailing units 33, because as previously mentioned, the rate of silver plating in the working units is more rapid than in the tailing units and is not continued until the silver is substantially exhausted from the solution, as in the tailing units.

The desilvered fixing solution in tank 48 may be deficient in hardener which may be supplied from a hardener tank 51 through a pipe 52 leading into tank 48. The supply of hardener to tank 48 may be manually controlled by regulation of valve 53 in pipe 52.

Since a portion of the fixing solution is preferably discharged to waste from the tailing units 33, it will be necessary to replenish the solution in tank 48 in order to maintain a constant quantity of solution in circulation through the entire apparatus. Consequently, a tank 54 is filled with replenishing solution, which is merely a photographic fixing solution of proper composition. The tank 54 is connected by a pipe 55 through a manually controlled valve 56 to the tank 48 or alternatively through a float operated valve 57, which is automatically controlled by the position of float 58 within tank 48 to maintain a solution level, such as indicated by the dotted lines in the drawing. If desired, solution from tank 48 may be discharged to waste through pipe 59 and valve 60.

In practice the sodium thio-sulfate concentration of the solution will be diminished upon passage through the processing apparatus and desilvering in the electrolytic units 33. Therefore a tank 61 is supplied with a solution of sodium thio-sulfate which has a higher concentration than the proper or desired fixing solution. This solution of higher concentration may be conducted from tank 61 through a pipe 62 having a rubber hose 63 intermediately inserted therein and having a manually controlled valve 64.

The fixing solution is conducted from tank 48 by a pipe 65 to a pump 66 actuated by a motor 66'. The solution is discharged from pump 66 through a pipe 67 into the service tank 11. If the level of solution in service tank 11 reaches that indicated in dotted lines, the solution will overflow through pipe 68 back into tank 48.

A by-pass 69 leads from pipe 67 into tank 48. This by-pass 69 may be regulated manually by a valve 70 to control the amount of solution being returned through pipe 67 to the service tank 11. Therefore, the rate of flow of solution between tank 48 and service tank 11 will depend upon several factors, among them the capacity of pump 66, the quantity of solution being discharged from service tank 11 to fixing tanks 10 and the opening of valve 70 in the by-pass 69.

The continual use of solution for processing and subsequent desilvering thereof, will result in a decrease of sodium thio-sulfate concentration. This deficiency is automatically compensated for by automatically controlling the supply of strong sodium thio-sulfate from tank 61 to tank 48. The automatic control for the supply of strong sodium thio-sulfate comprises a balancing means which operates a valve means to control the supply of solution. The balancing means comprises in part a U-tube 71 which has a funnel-shaped end 72 under a tap 73 which leads from by-pass 69 and which may be manually controlled by a valve 74. The other end of U-tube 71 has an adjustable spout 75 which may be moved into any desired position above the tank 48. Thus, it will be seen that the level of solution in the U-tube 71 will depend directly upon the position of spout 75, while the rate of flow of solution through U-tube 71 will depend upon the adjustment of valve 74. The balancing means also includes a vertical pipe 76 connected at its lower end to the center of U-tube 71 and at its upper end to a float box 77. The float box 77 receives through a pipe 78 a supply of water which may be regulated by valve 79. The float box 77 contains a float 80. A lever 81 fulcrumed at 82 is moved by float 80 into positions corresponding to the level of water within float box 77. A lever 83 is fulcrumed to a bracket 84 at one end and has a weight 85 attached to its free end. The free end of lever 83 is connected by a rod or wire 86 to one end of lever 81. The lever 83 is located adjacent the rubber hose 63 in pipe 62, and weight 85 is heavy enough so that lever 83 will kink hose 63 to prevent the flow of strong sodium thio-sulfate from tank 61

to tank 48 but still light enough to be raised by the weight of float 80 when the liquid level in float box 77 decreases.

If solution of proper concentration is passing through U-tube 71, the head of water in pipe 76 and float box 77, which is balanced by the column of solution in one leg of U-tube 71, will be of such a level that lever 83 closes off the supply of more concentrated sodium thio-sulfate from tank 61. The quantity of solution flowing through the other leg of U-tube 71 will depend upon the adjustment of valve 74 and valve 79 for the water supply, that is, both water and solution will be discharged from spout 75. A decrease in the sodium thio-sulfate concentration of the solution being circulated between tanks 48 and 11 will decrease the weight of solution in one leg of U-tube 71. The head or column of water in float box 77 and pipe 76 will now predominate, and more water will flow through spout 75 to decrease the water level in float box 77. The float 80 will lower with the decrease in water level to raise lever 83 and allow a quantity of more concentrated solution of sodium thio-sulfate to flow into tank 48 from tank 61.

It should be noted that the spout 75 may be adjusted to alter the concentration of solution, which will be maintained by this automatic control. If spout 75 is raised, a greater column of solution will be maintained in U-tube 71 and it will require a greater head of water or higher level in float box 77 to balance the same. A larger decrease in solution concentration will be necessary before the float 80 will drop to such a level that lever 83 will be raised. Conversely, if spout 75 is lowered the decrease in water level necessary to raise lever 83 will be less. Therefore, lowering of spout 75 will increase, and raising of spout 75 will decrease the concentration of solution which is automatically maintained in tank 48.

The operation of the entire laboratory layout according to my invention will now be described:

The fixing solution may originally be supplied to service tank 11 to maintain a regulated flow through fixing tanks 10, this apparatus may properly be included in the generic term "processing means." The discharge from fixing tanks 10 is conducted to the electrolytic units 33 in the manner already particularly described. Some of the solution is circulated through the electrolytic units 33 into tank 48 from where it is returned to the service tank 11. A portion of the solution is bled off to the tailing electrolytic units from whence it is preferably discharged to waste. The tank 48, pump 66 and circulating pipes of the apparatus include a circulating means which is adapted to recirculate solution through the processing tanks and electrolytic units as well as between the tank 48 and service tank 11. The operation of the balancing means for automatically maintaining a definite fixing solution concentration has already been explained with respect to the particular description of that apparatus.

Since many modifications of my invention are possible, the present disclosure is to be construed in an illustrative and not in a limiting sense; the scope of my invention being particularly defined in the appended claims.

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

1. The method of recovering silver from a used photographic fixing solution by electrolysis in a plurality of electrolytic units, which comprises circulating the solution continuously through some of said electrolytic units, plating part of the silver from the solution in the units containing continuously circulating solution, bleeding some of the solution into the remaining electrolytic units and plating substantially all of the silver from the solution in said remaining electrolytic units.

2. The method of recovering silver from a used photographic fixing solution by electrolysis in a plurality of electrolytic units, which comprises grouping the electrolytic units into working units and tailing units, circulating the solution continuously through said working units, plating part of the silver from the solution in said working units, bleeding some of the solution into the tailing units, and plating substantially all of the silver from the solution in said tailing units.

3. The method of recovering silver from a used photographic fixing solution by electrolysis in a plurality of electrolytic units, which comprises grouping the electrolytic units into working units and tailing units, circulating the solution continuously through said working units, plating part of the silver from the solution in said working units, bleeding some of the solution into the tailing units, plating substantially all of the silver from the solution in said tailing units, discharging to waste the solution from said tailing units, and replenishing the solution from the working units.

4. The method of recovering silver from a used photographic fixing solution by electrolysis in a plurality of electrolytic units, which comprises grouping the electrolytic units into working units and tailing units, circulating the solution continuously through said working units, plating part of the silver from the solution in said working units, bleeding some of the solution into the tailing units, plating substantially all of the silver from the solution in said tailing units and conditioning the solution from the working units for further fixing with the solution

to again increase the silver concentration thereof.

5. The method of recovering silver from a photographic fixing solution by electrolysis in a plurality of electrolytic units, which comprises fixing with said solution until the silver content is 2–3 grams per liter, circulating the solution continuously through some of said electrolytic units and plating silver from the continuously circulating solution until the silver content is ½–1 grams per liter.

6. The method of recovering silver from a photographic fixing solution by electrolysis in a plurality of electrolytic units, which comprises fixing with said solution until the silver content is 2–3 grams per liter, circulating the solution rapidly and continuously through some of said electrolytic units, plating silver from the rapidly and continuously circulating solutions until the silver content is ½–1 grams per liter, bleeding some of the solution through the remaining electrolytic units and plating substantially all of the silver from solution in said remaining electrolytic units.

7. The method of recovering silver from a photographic fixing solution by electrolysis in a plurality of electrolytic units, which comprises circulating the solution continuously through the electrolytic units, plating silver from the solution in said electrolytic units, conditioning the fixing solution by the controlled addition of a solution of sodium thiosulfate of higher concentration than the fixing solution and returning the conditioned solution for further fixing.

Signed at Hollywood, California, this 1st day of June 1931.

KENNETH C. D. HICKMAN.