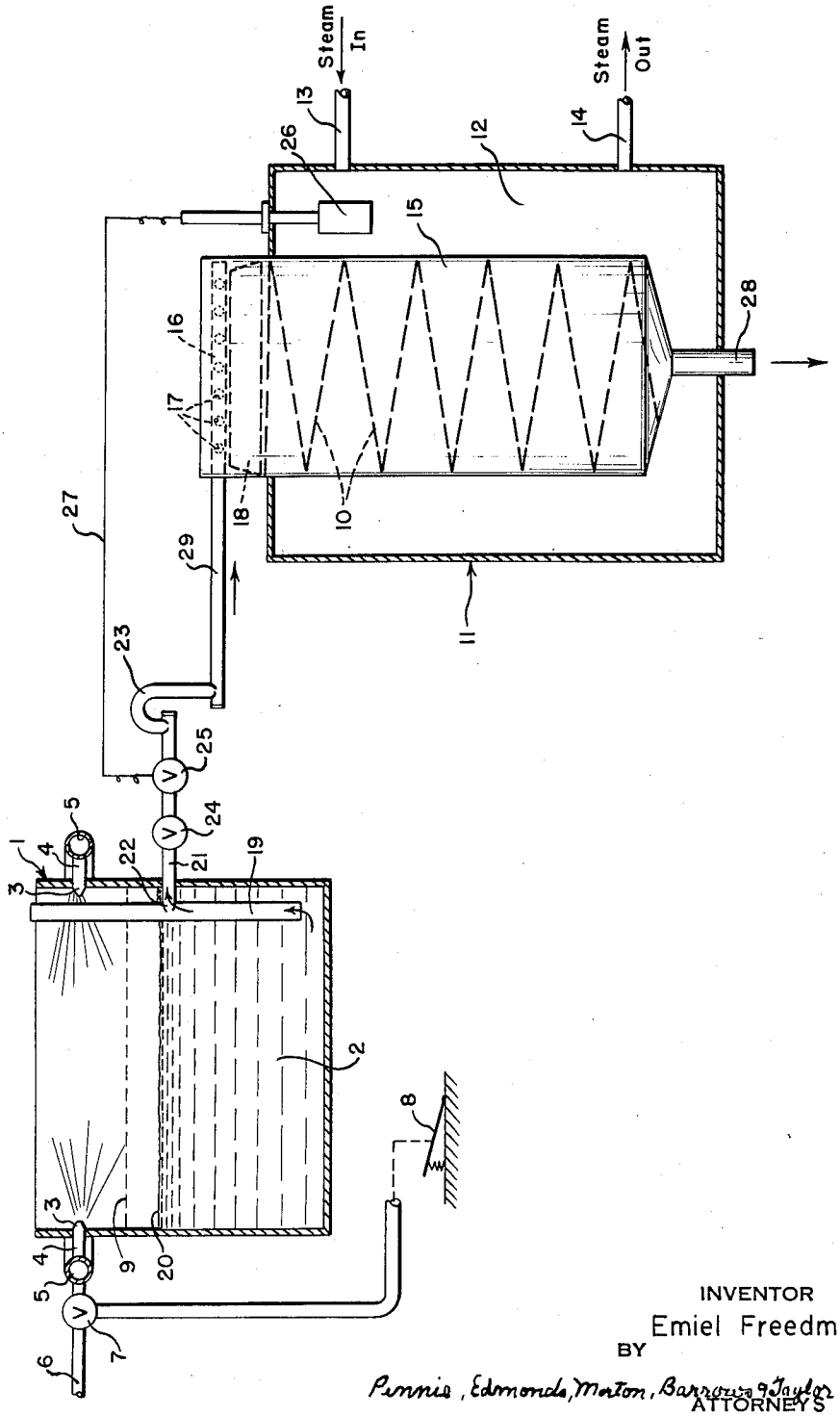
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APPARATUS FOR RECOVERING ELECTROPLATING SALTS BY EVAPORATIVE CONCENTRATION

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APPARATUS FOR RECOVERING ELECTROPLATING SALTS BY EVAPORATIVE CONCENTRATION

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This invention relates to the concentration and recovery of valuable salts, or the like, from dilute solutions thereof. It relates more particularly to the minimizing of the loss of valuable metals through the so-called "drag-out" in electroplating operations.

Though not restricted thereto, the invention is especially useful in the recovery of precious metals, or the salts thereof, normally present in the "drag-out" from the electroplating bath in the plating of jewelry or other metal parts with precious metals such as gold, platinum, palladium, rhodium, silver or the like.

In modern electroplating of jewelry, for instance, a number of parts are usually suspended from a metal rack in the plating bath or are barrel plated. Upon completion of the plating operation, the entire rack or barrel, together with the plated parts, is removed from the plating bath and washed by immersion in a tank of water. It has heretofore been recognized that considerable amounts of precious metal salts are removed from the electroplating bath by adhering to the plated parts and rack or barrel and transferred to the wash water. This is known to the art as "drag-out."

To facilitate recovery of the precious metal, it has heretofore been proposed to effect a concentration of the plating solution "drag-out" in the wash water by periodically transferring the drag-out rinses to an open boil-down tank from which water is slowly evaporated by heating. After some degree of concentration has been obtained, the heat is shut off until further dilute rinse water is added, the heating then being resumed. Decisions as to when to transfer the drag-out rinse from the wash tank to the boil-down tank, in order to avoid excessive loss by too high a concentration of the precious metal salts in the wash water, as hereinafter explained, how far to carry the concentration in the boil-down tank to avoid crystallization and precipitation of the salts therein and when to withdrawn the accumulated concentrate from the boil-down tank have depended largely on the judgment of the particular operator so that results have not been sufficiently uniform and have frequently led to undue losses. Excessive labor and supervision have also been required.

For recovery of the precious metals, it has also been proposed to periodically pump the used wash water into storage receptacles from which it is subsequently withdrawn and caused to percolate through a relatively deep bed of an ion-exchange resin adapted to retain the precious metal and from which the precious metal is periodically partially recovered by washing and finally by the burning-off of the resin.

This conventional method of recovery has been subject to various objections including the cost of handling and storing the wash water, regeneration of the ion-exchange resin and final burning-off of the resin and also the resin replacement cost as well as the requirement of considerable apparatus and the floor space occupied by the necessary equipment. Its use is also subject to many of the objections just noted with respect to the boil-down method.

The present invention provides a new and improved method of minimizing the loss of these valuable salts in the "drag-out" or wash water whereby, without interference with normal electroplating or washing operations

the salts adhering to the rack or barrel and plated parts upon removal from the plating bath are economically recovered substantially completely and automatically as an aqueous solution of uniform concentration especially suited for further processing or refining for recovery of the precious metal. The invention also provides apparatus especially adapted to the carrying out of the process.

It will be apparent that, as successive racks of plated pieces are immersed in the wash water, the concentration of the metal salts in the water increases, finally reaching a concentration at which appreciable amounts of the precious metal salts still adhere to the parts upon removal from the wash water bath. When one considers the current price of gold, for instance, and other precious metals, the price of rhodium being about four times the price of gold, it is apparent that the loss of very small quantities of these metals will aggregate a very considerable economic loss, especially in large production plants.

Frequently, in conventional practice, one wash tank is used for a plurality of plating tanks. Especially in such instances, the concentration of the salts in the wash water will build-up rather rapidly to a point where substantial loss of the precious metal will occur, due to imperfect washing caused by too great an accumulation of the precious metal salt in the wash water, thus making it necessary to replace the water in the tank with fresh water or else switch to another wash tank containing fresh water. The rate at which concentration builds-up in the wash tank will vary somewhat depending upon other operating conditions and special supervision may be required to insure against excessive wash water concentration.

A primary object of the present invention is to provide an economically practical method for eliminating or minimizing the loss of valuable metal salts through drag-out in electroplating operations. A further object is to provide a process whereby the valuable metal salts normally present in the wash water are substantially completely and continuously recovered in relatively high and uniform concentrations suitable for further refining. A still further object is to provide a compact, inexpensive apparatus adapted to carry out the process in an automatic, substantially continuous, trouble-free manner and which may be readily installed in existing plants, requiring a minimum of floor and storage space and a minimum of operating costs and supervision.

These and other advantages are obtained by the present invention, as will appear from the following description thereof with reference to the accompanying drawing of which the single figure represents conventionally and somewhat diagrammatically a side elevational view of apparatus especially adapted to the carrying out of the process.

In the drawing, an open-top, rectangular rinse or wash tank is indicated at 1 and is adapted to hold a body of rinse water 2 of a depth sufficient for complete immersion of the rack and parts to be washed. Positioned on at least two opposite sides of the tank, well above the predetermined maximum upper surface of the body of wash water, hereinafter more fully described, are a plurality of spray nozzles 3 connected to fresh water lines 4.

Advantageously the fresh water supply lines 4 are connected to a common header 5 to which fresh water is supplied from any convenient source through conduit 6 in which there is provided a control valve 7, normally closed but adapted to be opened as desired by the operator, for instance by a treadle represented at 8.

Instead of separate spray nozzles, one may use a pipe extending along opposite sides of the tank or extending entirely around the inner surface of the tank and perforated along their inner surfaces to direct a spray inwardly from at least two opposite sides of the tank.

In operation, the rack or barrel of plated parts, upon

removal from the plating bath and having a substantial amount of plating solution, i.e., "drag-out," adhering thereto, is completely immersed in the bath 2, whereby most of the adhering solution is rinsed from the rack or barrel and parts. But appreciable quantities of valuable salts present in the wash water have been found to adhere to the rack or barrel and parts upon removal from the rinse bath 2.

For recovery of these residual salts, the rack or barrel and parts are subjected to a spray rinse with fresh water by opening valve 7 and causing the sprays 3 to play upon the rack and parts from at least two opposite sides as they are being slowly removed from the wash bath.

The sides of the tank must extend to a height well above the predetermined upper surface 9 of the wash bath to insure the retaining of all of the spray rinse water in the tank. The necessary height and other dimensions of the tank will depend upon the dimensions of the particular rack or barrel to be immersed therein. The height of the rack or barrel will also determine the necessary minimum depth of the body of wash water 2. This depth may, for instance, be about 12 inches or more.

By reason of the intermittent adding of the spray rinse water to the wash bath within the tank, the volume of water within the tank tends to increase and the added spray rinse water further tends to lower somewhat the concentration of the salt in the wash baths. Each of these two factors tends further to complicate the problem of recovery of the salts in the drag-out. However, the problem is nicely met through the cooperation of the steps just described and those presently to be described.

Briefly, the concentration of the salt in the wash water is, in accordance with my invention, increased to a substantially uniform, relatively high value by an evaporation step carried out in an unusual type of evaporator represented at 11.

In ordinary evaporation methods, including that previously described, there exists the danger and tendency of the precious metal salts becoming lost by over concentration and resultant encrustation on the heating surfaces in admixture with other salts normally present in the wash water. This is avoided in accordance with my invention by the particular evaporation method employed, including a correlation and control of the rate of charge of the wash water to the evaporator, the temperature and character of the heated surfaces and the time of contact of the aqueous solution with the heating surfaces.

The evaporator shown in the drawing comprises an outer steam chamber or jacket 12 having a steam inlet 13 and an outlet 14. Coaxially positioned within the steam chamber is a cylindrical evaporator chamber 15.

The wash water to be concentrated by partial evaporation passes to the evaporator through conduit 29 and an annular distributor 16, the outer periphery of the latter being perforated as indicated at 17 so as to direct the incoming wash water toward the heated delineating side wall of the chamber 15. Just beneath the distributor 16, there is positioned a downwardly and outwardly flaring annular baffle 18 adapted to insure the uniform distribution of the entering wash water around, and in contact with, the upper end of the cylindrical side wall of the evaporator chamber. Various other arrangements may be used for uniformly distributing the wash water in contact with the chamber wall, but that just described has been found to be a particularly effective and economical construction.

I provide adjacent the chamber wall, over at least a major portion of its height, a helix, preferably, but not necessarily, of a heat-conducting metal, for instance metal wire or tubing, under sufficient spring tension to hold it in contact with the wall. This helix serves to reduce the required height of the evaporator chamber and to improve and prolong contact of the liquid with the chamber wall as well as improve heat transfer. A helix of this type is represented at 10. In the drawing, however, the pitch of the helix has been exaggerated for clarity. Normally, the flights of the helix will be spaced close together and may even touch and need not be precisely uniform.

Because of the circular section of the tube or wire, helical channels are formed along the adjacent chamber wall through which the liquid will flow. Further, it is not essential that the wire or tubing be under sufficient spring tension to avoid completely the downward passage of some of the liquid from flight to flight between the helix and the chamber wall. Indeed, most satisfactory results have been obtained where that condition has existed. By varying the number of turns and pitch of the helix, the degree of wall contact and type of material from which it is constructed, the capacity of the evaporator to effect the desired evaporation or concentration may be varied.

I have, however, found it essential to the obtaining of satisfactory results that, for any given evaporator condition, the flow of wash water to the evaporator be uniform. Nonuniform flow or dribbling of the wash water to the evaporator tends to cause either excessive concentration, with deposition of salts on the helix and on the evaporator wall, which inhibits satisfactory operation and causes loss of the metal, or results in nonuniform concentration of the metal salts.

These conditions are avoided by my present invention by establishing a predetermined maximum water level 9 and a predetermined minimum water level 20 in the wash tank 1, withdrawing wash water therefrom when the maximum level, caused by the added rinse spray, has been reached and at that point, withdrawing water and passing it to the evaporator at a constant rate until the predetermined minimum level 20 has been reached. The apparatus of my invention is so designed as to accomplish this entirely automatically.

Referring again to the drawing, I provide within the tank 1 a tube 19, open at each end and advantageously, though not necessarily, positioned vertically and close to the tank side wall. The lower end of tube 19 is positioned well below the predetermined lower surface level of the wash water, advantageously near the bottom of the tank where the wash water is apt to be less diluted by the incoming spray rinse water. The upper end of tube 19 is open to the atmosphere at a height well above the maximum liquid level 9 and preferably well above the sprays 4.

Tube 21 is connected to tube 19 at an intermediate point 22 such that the highest point of the opening through the tube coincides with the predetermined lower level 20 of the wash water. Tube 21 extends substantially horizontally outwardly through the tank wall and is connected at its outer end to the short leg of siphon 23, the long leg of which is connected to conduit 29 leading to evaporator 11.

The highest point of the opening through siphon 23 coincides with the highest predetermined level of the wash water. Consequently, when the wash water reaches the maximum level, the siphon will be filled and siphoning will begin and will continue until the wash water level has fallen to the minimum height 20, at which point air will be admitted to tube 21 and the siphoning action thereby discontinued.

From the foregoing, it will be apparent that the differential in water level will be determined by the length of the short leg of the siphon. This is subject to considerable variation, however, especially advantageous results have been obtained where this height differential was about one inch. It may with advantage range from ½ to 2 inches or more, depending upon other conditions. It is necessary that the minimum height be at all times high enough for complete immersion of the particular rack being used and that the maximum level be at all

times maintained below that at which it would interfere with the spray rinsing operation.

During the period of siphoning, the rate at which the wash water is withdrawn from tank **1** and passed to evaporator **11** may be controlled by manually-operated valve **24** positioned in line **21**. By adjustment of this valve, the extent of concentration effected by the evaporator may be regulated and controlled and coordinated with specific evaporator conditions. Usually, when optimum evaporating conditions have been established, further adjustment of valve **24** is unnecessary.

Steam temperature of the evaporator is subject to considerable variation, but should usually fall within the range of about 240° to 265° F. Steam at a gauge pressure of about 25 pounds per square inch has been found eminently satisfactory.

In order to avoid the passing of the wash water to the evaporator during temporary failure or interruption of the steam supply, I also provide in line **21** a thermostatically controlled solenoid valve **25** responsive to thermostat **26** positioned in steam chamber **12** and connected to valve **25** in conventional manner by connection **27**.

The lower end of the evaporator chamber **15** is provided with a discharge line **28** for withdrawal of the concentrated solution of the precious metal salts. Where desired, the evaporator may be surmounted by a hood for carrying off water vapors or possibly objectionable fumes, but in most instances, at least, a hood is not required.

Though not restricted thereto, I have used the present invention with particular advantage in the recovery and concentration of rhodium salts from the drag-out. In these operations, the rhodium was used in the plating bath in the form of either a sulfate or a phosphate and was present in the plating solution at concentrations equivalent to about two grams of rhodium metal per liter. The wash water accumulated in the wash tank contained the equivalent of about 0.2–0.25 gram per liter of the precious metal. Through use of the herein described method and apparatus, this concentration has been raised to the equivalent of 5 to 10 grams per liter of the metal in the concentrate.

Similarly advantageous results are obtained in the recovery of gold. In gold plating operations, the metal is usually used in the form of the cyanide or the chloride at a concentration of about 1 gram to about 10 grams of gold per liter in the plating bath. The wash water usually contains the equivalent of about 0.1 to 1 gram of gold per liter. In accordance with my present invention, this concentration may be raised to within the range of about 5 grams to about 10 grams of gold per liter in the concentrate.

The concentration of the metal salt present in the wash water, withdrawn from the wash tank for further concentration, and that of the final concentrate may be varied considerably to meet special operating conditions and requirements. Usually the concentration of the wash water will advantageously be within the range of about 5% to about 20% that of the plating bath and by my evaporating step will be increased to within the range of about 25 to 100 times that of the wash water.

To avoid corrosion and contamination of the recovered salts, all portions of the apparatus with which the salt solution comes in contact should be constructed of stainless steel or other material resistant to corrosion. For this purpose, metals or alloys known to be resistant to hot concentrated sulfuric or phosphoric acids are recommended.

I claim:

1. Apparatus of the type described comprising an open-top wash tank adapted to contain a body of water of substantial depth within a predetermined range, means for spraying fresh wash water into said tank at a height substantially above the predetermined upper surface of the body of water, an open-ended tube extending from near the bottom of said tank to a height above the spray means, a tube opening into the first said tube and extending substantially horizontally therefrom to without said tank, an upwardly-extending siphon having a short leg and a longer leg, the short leg being connected to the outer end of the last said tube, an evaporator, conduit means leading from the long leg of said siphon to the evaporator, said siphon being so constructed and arranged as to siphon water from the tank only when a maximum predetermined water level is reached and to discontinue the siphon action when a predetermined minimum water level is reached.

2. The apparatus of claim 1 in which there is positioned in the conduit leading from the tank to the evaporator a control valve adapted to regulate the rate of flow from the tank to the evaporator.

3. The apparatus of claim 1 further characterized in that the evaporator comprises a vertically-elongated, cylindrical evaporating chamber, means adapted to distribute the incoming wash water uniformly over the surface of the evaporator chamber near the upper end thereof, a helix of heat-conducting material extending along the inner wall of the evaporator chamber over a substantial portion of the height of the chamber and in loose contact with said wall, a steam chamber surrounding said evaporator chamber for a substantial portion of its height, the upper end of the evaporator chamber being open to permit escape of vapors, and conduit means for withdrawing unevaporated liquid from the bottom of said evaporator chamber.

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