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METAL RECOVERY UNIT

This invention relates to a metal recovery unit for the recovery of metals from solution using electrolysis.

The invention is intended for use in relation to recovery of silver from photographic solutions obtained after development of photographic film, but it will be appreciated that other metals may be recovered from other solutions using this invention. However, for ease of description, the current invention will be described with reference to photographic solutions and more particularly with reference to recovery of silver from fixer solutions.

Fixer solution is used in the photographic process to remove silver salts from photographic emulsion and prevent darkening of the developed negative upon exposure to light. As a result, a fixer solution rich in silver salts is obtained as a waste product of the photographic process. Various methods for recovering silver from fixer solution are known, but the preferred method is electrowinning, a method which is clean, simple and easily modified to contend with differing silver concentrations.

Silver recovery units relying upon electrowinning are generally of three types. The first type is the batch process unit, where fixer is stored in a holding tank until a specified quantity is reached, whereupon the fixer is transferred to an electrolytic cell for treatment. Treatment takes place, after which the fixer is discharged from the unit. Treatment in batch units generally takes place with high current flow (2-8 amps) and with agitation of the fixer solution. The duration of treatment is often pre-set. The disadvantages of this type of unit include the necessity of using pumps to move the fixer solution from holding tank to electrolytic cell and to discharge the electrolytic cell. Due to the corrosive nature of the fixer, frequent malfunctions of the pumps occur, resulting in down time and even loss of fixer. Secondly, in most batch processors there is no provision for changes in silver concentration in the fixer. As a result, treatment for the usual or pre-set time may not extract as much silver as is

possible, or over-extraction may occur, leading to the precipitation of silver sulphite which apart from being odorous, also pollutes the pure silver already collected.

The second type of unit in use is a continuously stirred tank reactor ("CSTR"). As implied by the name, a CSTR relies upon constant agitation of the fixer and uses a high current flow. It differs from batch-type reactors in that fixer may be continually fed through an inlet, forcing treated fixer out of the CSTR. The CSTR shares the problem of the batch-type unit, in that agitation is achieved using an impeller, jetted liquid or air sparging, all of which require mechanical means such as pumps or motors. These mechanisms are subject to corrosion due to the nature of the fixer, and loss of function may result from excessive corrosion. In addition, the rate of flow of fixer into a CSTR will govern the residence time in the electrolytic cell so that either the fixer leaving the CSTR will still contain some silver or, if the electric current is high, all silver will be removed, at the cost of overextraction which causes silver sulphite to also precipitate, polluting the pure silver.

The third type of silver recovery unit is called a plug flow unit. These units are similar to CSTR's in that fixer may be continuously fed into the unit, but no agitation of the fixer solution is required. Instead, early plug flow units relied upon the principle that fixer solution arriving from the inlet is rich in silver and therefore denser than fixer which has had the silver partially or totally removed, to provide mass transfer within the unit. It was believed that upon arrival in an electrolytic cell, fresh fixer sank to the bottom of the cell, rising as silver was removed from the solution and it was displaced by further silver rich solution. Eventually, the solution, stripped of silver, rose to the top of the cell and was removed through an outlet.

It has now been discovered that in practice, the fixer solution is normally warmed by the developing process. As a result the warm fixer does not necessarily sink directly to the bottom of the cell, but can form a boundary layer at the

top of the cell which slowly sinks as it cools and as further warm fixer is added above it. The current invention enhances and makes use of this phenomenon to approach idealised plug flow.

5 Because no agitation is required, plug flow units use lower electrical currents and employ a large cathode/anode area. Normally, the area of the anode and cathode is kept as equal as possible to obtain uniform current distribution over the cathode and thereby obtain even plating, even at high
10 concentrations of silver. This is not an ideal situation as anodes are often made of expensive materials and it is desirable to minimise anode size.

 Ideally, plug flow units receive a continuous flow rate into the unit to ensure good mass transfer and to avoid dead
15 spots within the unit. In practice, however, a continuous flow rate is rarely obtained due to fluctuations in the amount of film being processed from moment to moment or due to total lack of input, for example overnight or on weekends. When input drops, mass transfer within the unit falls,
20 favouring formation of silver sulphite.

 It has now been found that a silver recovery unit, with no moving parts, can have improved mass transfer characteristics. A further advantage is that a small anode to cathode area ratio can be used, while still producing
25 substantially even plating of silver on cathode.

 In accordance with the invention there is provided a metal recover unit comprising a container having a base and walls and having an electrolyte inlet at an upstream end and an electrolyte outlet at a downstream end. The inlet and the
30 outlet are set above the base of the container. The container is partitioned by at least one baffle defining at least two chambers within the container, each said baffle having fluid communication means therein to allow fluid communication of an electrolyte between the upstream and
35 downstream sides of the baffle. On each baffle said fluid communication means is located at a position below the level of the electrolyte outlet, the baffle otherwise being

preferably sealed in a fluid-tight manner to the base and walls of the container. Each chamber of the unit contains at least one cathode and one anode.

Preferably each chamber is substantially rectangular and is equipped with one cathode and two anodes; said cathode being set substantially at right angles to the base of the container and set diagonally across the chamber. Most preferably it extends substantially from one vertical edge to the diagonally opposite vertical edge of the chamber. It is also preferred that each cathode is electrically connected in parallel with each other cathode, and each anode is electrically connected in parallel with each other anode. The cathodes provided in each chamber are preferably composed of a corrosion resistant metal, such as stainless steel, and are preferably in the form of solid rectangular plates of suitable dimensions to extend diagonally across the chambers in which they are placed. Each cathode may be removably connected to each other cathode in a parallel electrical circuit.

Each of the said anodes are preferably substantially smaller than the cathode and situated one on either side of the cathode. Most preferably the anodes are located adjacent the remaining vertical edges of the chamber. The anodes are preferably comprised of a grid or mesh rather than a solid plate to increase the surface area of the anode relative to its volume, and are preferably composed of a corrosion resistant material. The preferred composition is titanium coated with platinum. The anodes may be set parallel to the cathode or alternatively at an angle to the cathode.

Although it is preferred to wire the cathodes and anodes in parallel, in applications where there is a high flow of electrolyte, this may result in less than maximum recovery of silver. Under these circumstances the cathodes and anodes respectively may be wired in series to allow greater control of the current and improve silver extraction.

The container of the invention may be composed of any non-conducting, corrosion resistant material such as glass or suitable plastics. Preferably, the container walls are

at least partially transparent to allow an operator to easily ascertain the quality and quantity of silver which has collected on the cathode in each chamber. It is also preferred that the inlet and outlet be located in the upper portion of the upstream wall and downstream wall respectively. It is also desirable, that the container be fitted with a cover to reduce fumes from the unit and to prevent accidental contamination of the electrolyte solution in the container.

The baffle may be formed from any suitable non-conducting, corrosion resistance substance, such as glass or plastic, and is preferably placed to divide the container into substantially equal sized chambers. Preferably, the baffle is at least partially transparent to allow easier visual access to the cathodes. The fluid communication means may comprise a number of small apertures but is preferably a single aperture passing through the baffle, and is preferably located adjacent to the edge of the baffle which is sealed to the base of the container. Most preferably the fluid communication means is horizontally offset to one side of the baffle and the electrolyte inlet and electrolyte outlet are horizontally offset in the opposite direction. This configuration of inlet, fluid communication means and outlet, maximizes contact between the cathode and fixer solution. Where the inlet, outlet and fluid communication means are offset as described, it is preferred to arrange the anodes and cathodes in each chamber so that the anodes are placed adjacent to the vertical edges nearest to the inlet, outlet and fluid communication means.

In one embodiment of the invention, two or more containers are linked, so that the outlet of an upstream container leads to the inlet of an adjacent, downstream container. The connection from outlet to inlet may be direct, or may be via a pipe or tube. The outlet of each container should be lower than the outlet of any preceding upstream container, as this will ensure that the electrolyte surface level in each downstream container is lower than that of the outlet of the adjacent upstream container,

preventing communication of electrolyte between containers in an upstream direction.

In a particularly preferred embodiment, two containers are abutted so that they share a common wall. The upstream container outlet and downstream container inlet consists of at least one aperture in the common wall, said aperture forming a weir which allows fluid communication only from the upstream container to the downstream container. This embodiment has been found to provide for efficient extraction of silver from a fixer solution, using an overall electric current of 0.2 amps. Variations in the number of containers provided or the silver concentration would allow for variation in this current.

In use, the performance of the invention is determined by the hydrodynamic conditions within the reactor, that is, by the reactor geometry and flow rate through the reactor. Flow rate is in turn determined by the condition of the fixer which enters the unit.

Whilst it is believed that the invention is an improvement over the prior art due to its optimisation of reactor geometry and flow rate, as further set out below, the invention should not be considered as limited to any particular theory of operation. Normally, the fluid is heated by the film processor to about 38°C and the warm fixer forms a boundary layer at the surface of the fixer, spreading throughout the chamber and moving through the chamber to the fluid communication means.

The attached drawings make clear particularly preferred embodiments of the invention.

FIG. 1 shows a perspective view of a preferred embodiment of the invention having an upstream container and a downstream container, with the cathodes and anodes removed.

FIG. 2 shows an exploded perspective drawing of two chambers showing the position of the anodes and cathodes within each chamber, relative to the apertures and inlet, along with the flow path of electrolyte through the compartments.

FIG. 3 shows the flow pattern of electrolyte through a preferred embodiment of the invention.

FIG. 4 shows the boundary layer formation and the convection of the electrolyte within individual boundary layers.

Flow characteristics will now be discussed with reference to a preferred embodiment of the invention, consisting of a recovery unit comprising an upstream container 1 and a downstream container 2, each container abutting the other and being separated by a single common wall 3, having an aperture 4 therein, said aperture 4 acting as an outlet for the upstream container 1 and an inlet for the downstream container 2, each container being divided into a first chamber 5a, 5b and second chamber 6a, 6b by baffles 7a, 7b having apertures 8a, 8b therein.

When operating under normal steady state conditions, the feed temperature to the recovery unit will be approximately 38°C. When fluid enters the reactor through inlet 10 at this temperature, it does not disperse, but instead forms a boundary layer 9 upon the surface (FIG. 3a). As this layer cools, it gradually flows down through the entire cross-section of the chamber, remaining parallel to the fluid surface and travelling towards the aperture 8a between the first 5a and second 6a upstream chambers. In the second upstream chamber 6a, the boundary condition is still evident across the total cross section of that chamber, indicating very little dispersion as the layer moves upward toward aperture 4 (FIG. 3b). The greatest amount of mixing occurs upon passage through the barrier aperture between the upstream 1 and downstream 2 containers; however the boundary layer can still be clearly distinguished even in the second downstream chamber 6b (FIG. 3c).

Although the recovery unit has a relatively large surface area, resulting in rapid cooling of the fixer which reaches ambient temperature in the second upstream chamber, density differences are sufficient at this stage to prevent dispersion.

Convection currents within individual boundary layers are caused by the removal of silver at the cathode, resulting in a less dense solution. Normally, this less

dense solution would rise through the compartment, but is prevented from doing so by the layer of warmer solution above it. Consequently, it flows outwards, away from the cathode, allowing denser, silver rich solution to contact the cathode. This circulation within a single boundary layer, ensures a high degree of contact of the solution with the cathode (see FIG.4). This effect continues even after the solution has cooled to ambient temperature, due to density differences.

When the recovery unit of the invention is operating under normal steady state conditions, the unit has been found to recover up to between 96 to 99 % of silver from solution. This may be compared with observed recovery rates of 92.3% for batch-type units or 97.5% for CSTR-type units, both of which require higher operating currents and mechanical agitation of the fixer solution.

A further advantage of the invention is that little evidence of sulphite formation is observed due to the movement of the boundary layers through the chambers, providing slight, but continuous agitation to all parts of the reactor. This mass transfer is enough to inhibit the formation of silver sulphite without mechanical agitation.

Although the anodes and cathode of the invention are of unequal size, the unique geometry of the current invention allows for an even deposit by smoothing current distribution over the entire surface of the cathode. This substantially prevents the uneven accumulation of silver experienced where there is higher current density in some areas than others, which is normally experienced when using relatively small anodes compared to cathodes. Consequently, small anodes may be used with the current invention, minimising on the cost of anode construction.



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A metal recovery unit comprising a container having a base and walls, and an electrolyte inlet at an upstream end and an electrolyte outlet at a downstream end, said inlet and outlet being set above the base of the container, said container being partitioned by at least one baffle defining an upstream chamber and a downstream chamber within the container, said baffle having fluid communication means therein to allow fluid communication of an electrolyte between the upstream and downstream chambers, said fluid communication means being located at a position below the level of the electrolyte outlet, each chamber having therein at least one anode and one cathode.
2. The metal recovery unit of claim 1 wherein at least two containers are linked in series so that the electrolyte outlet of an upstream container is connected to the electrolyte inlet of a downstream container, the outlet of the upstream container being at a higher level than the outlet of the downstream container so that the level of electrolyte in the downstream container is below the outlet of the upstream container.
3. The metal recovery unit of claim 2 wherein the upstream container and the downstream container share a common wall and the outlet of the upstream container and the inlet of the downstream container comprise at least one aperture in the common wall, said aperture forming a weir which allows fluid communication only from the upstream container to the downstream container.
4. The metal recovery unit of any one of the preceding claims, wherein each chamber contains one cathode and two anodes.
5. The metal recovery unit of claim 4 wherein the cathode comprises a plate set in a plane running between two diagonally opposite vertical edges of each chamber, and the anodes are arrayed on opposite sides of the plate from each other.
6. The metal recovery unit of either one of claims 4 or 5, wherein the anodes are situated adjacent diagonally



opposite vertical edges of the chamber.

7. The metal recovery unit of any one of claims 4 to 6, wherein each anode is smaller than the associated cathode.

8. The metal recovery unit of any one of the preceding claims, wherein each cathode is electrically connected in parallel with each other cathode and each anode is electrically connected in parallel with each other anode.

9. A metal recovery unit substantially as hereinbefore particularly described with reference to any one of figures 1 to 3.

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