June 8, 1971 S. B. FULWEILER 3,583,897

ELECTROPLATING CELL FOR RECOVERING SILVER FROM PHOTOGRAPHIC SOLUTIONS

Filed Sept. 26, 1968

Fig. 1.

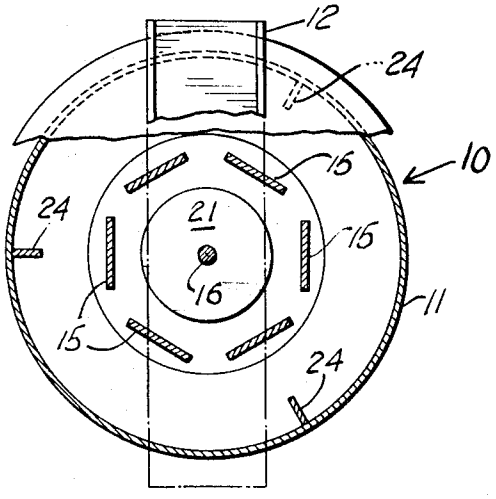


Fig. 3.

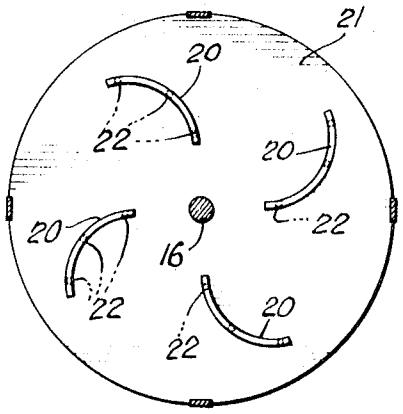
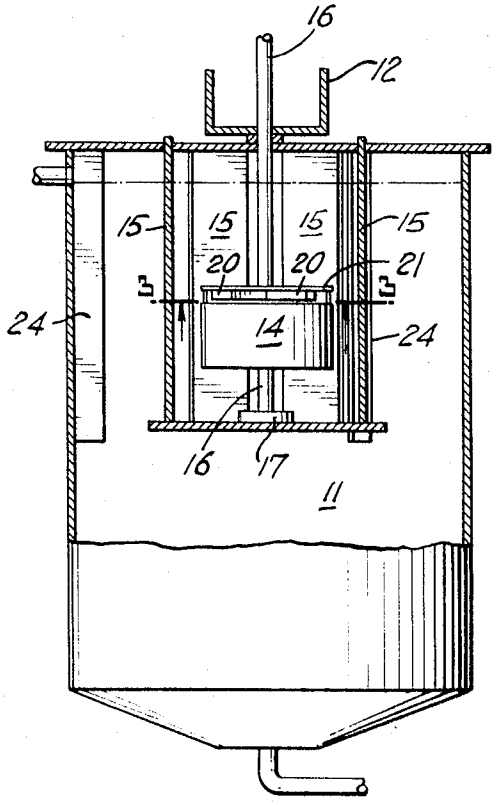


Fig. 2.



INVENTOR
SPENCER B. FULWEILER
BY Edward V. Bonnos
ATTORNEY

United States Patent Office 3,583,897
Patented June 8, 1971

3,583,897

ELECTROPLATING CELL FOR RECOVERING SILVER FROM PHOTOGRAPHIC SOLUTIONS

Spencer B. Fulweiler, New York, N.Y., assignor to Berkey Photo, Inc., New York, N.Y.

Filed Sept. 26, 1968, Ser. No. 762,731
Int. Cl. C23b *5/68;* B01k *3/00;* C22d *1/12*
U.S. Cl. 204—212 1 Claim

ABSTRACT OF THE DISCLOSURE

A schematic drawing of a tank is shown with a rotatable cylindrical cathode electrode positioned inwardly of fixed anode plates arranged in a ring around the cathode. A detail is shown of impeller blades attached to a plate for circulation of the solution past the electrodes, the plate being mounted on the same shaft and rotated with the cylindrical cathode.

The present invention relates to an electroplating cell for the plating of metals from solutions, and more particularly to a cell for the recovery of silver from solutions which are to be reused for further processing of photographic films.

Heretofore, several methods have been used for the electrolytic removal of silver from photographic solutions. Hickman Pat. No. 1,959,531 describes apparatus for this purpose in which a plurality of interleaved anode and cathode electrode plates are used with revolving paddles between the plates for mechanical agitation of the electrolyte across the electrodes. Duisenberg Pat. No. 2,791,555 describes apparatus including a plurality of rotating disc cathodes with fixed rodlike anodes. More recently Adams Pat. No. 3,342,718 described a rotating disc cathode type apparatus in which the discs are tilted so as to provide an oscillating or wobbling action as they are rotated. In another apparatus sold commercially, fixed corrugated plate cathodes, grouped together in the form of a ring, are mounted in an open octagonal plastic vessel, and positioned about movable anodes suspended from a carrier which is rotated, thus moving the anodes between the cathodes.

The present invention provides an improved electroplating cell.

In accordance with the invention an electroplating cell is provided in which a rotatable cathode of cylindrical shape is passed by plate like anodes. Preferably fluid circulation means is included to provide agitation of the fluid past the electrodes.

Objects and advantages of the invention will be apparent from the following description and from the accompanying drawing which shows, by way of example, an embodiment of the invention.

In the drawing:

FIG. 1 is a schematic top view of an electroplating cell in accordance with the invention.

FIG. 2 is a side view of the cell shown in FIG. 1.

FIG. 3 is a schematic drawing of fluid circulation means used in the cell of FIGS. 1 and 2.

Referring to the drawing there is shown an electroplating cell **10** in accordance with the invention including a tank **11** having supporting means or bridge **12** extending across the top thereof. Within the tank **11** is contained a rotatable cylindrically shaped cathode electrode **14** and a plurality of fixed anode electrodes **15**. The rotatable electrode **14** is carried by a shaft **16** journaled at its lower end in a nylon bearing **17**. The upper end of the shaft **16** is carried by the bridge **12** which is also adapted to carry a thrust bearing, a commutator,

and a motor, none of which is shown, as these items are conventional for apparatus of this type.

The anode electrodes **15** may be made of any suitable material which is electrically conducting and adapted to stand the corrosive fluids. Preferably the anodes **15** are made of carbon plates and are arranged in a generally hexagonal shape around the cylindrical cathode **14**, being spaced therefrom about three inches. The cylindrical rotating cathode **14** is preferably made of stainless steel such as No. 316, 302 or 304.

The tank may be made of stainless steel such as No. 316, or may be made of rubber, plastic or other material able to withstand the corrosive nature of the photoprocessing fluids. The cylindrical cathode **14** is made of stainless steel preferably about .06 inch (16 gauge) in thickness. The dimensions of the cylindrical cathode **14** are preferably selected so that the diameter is about twice the length of the cylindrical body.

Fluid circulation means is provided by impellers **20** carried by a plate **21** attached to the shaft **16**. Plate **21** is preferably of the same diameter as the cylinder **14** and is positioned thereabove so as to leave an open space therebetween of about one and one half inches. The impellers **20** are secured to the plate **21** by fastening means **22** which may be conventional such as screws or rivets, or by welding. Preferably the plate **21**, the impellers **20** and the fastening means **22** are all made of stainless steel. Preferably, these parts should be electrically insulated with non-conducting coatings, means being provided to conduct current to the cathode cylinder **14**. Not shown, but provided as is conventional, is a source of direct current of a capacity so that there may be a current flow of about 8 to 10 or more amperes per square foot of cathode surface.

Within the tank **11** are positioned one or more small vertical barriers **24** to retard the solution from swirling around in the tank as the cylindrical cathode is rotated.

Generally electrolytic recovery systems have a current efficiency of 3 grams of silver plated out for each ampere hours of a theoretical 4.025 grams per ampere hour. Thus a deposit of 3 grams of silver for each ampere hour would result in a current efficiency of about 75 percent. The cell in accordance with the invention operates at a current efficiency of about 3.5 grams per ampere hour, or a current efficiency of 88 percent, and under nearly ideal conditions has achieved an efficiency of 3.7 grams per ampere hour, or a current efficiency of about 92 percent.

It is a well known fact that in the electrolytic recovery of silver the electrolyte must be agitated to reduce the sulfurization of the hypo and a subsequent formation of silver sulfide sludge.

In using the electrolytic cell it has been found to be operative with the least amount of attention if it is connected to a conventional fixer recirculation system wherein a ballast tank is used to hold reserve fixer, so that at periods of high production in photoprocessing the concentration of silver will not rise to a high level, and at lower periods, the cell will not be operating on silver of very low concentration. The cell disclosed herein will perform satisfactorily on an ammonium alkaline fixer on silver concentrations as low as 0.2 gram per liter, but preferably at between 0.3 to 0.5 gram per liter.

While silver may be removed from other photographic solutions, the greatest percentage of recoverable silver is found in the fixing bath. In the processing of film, in the fixing bath the unused silver halide is converted to a soluble compound that can be removed from the film in an aqueous bath. The most commonly used fixing compounds are called "hypos" and may be sodium thiosulfate

or ammonium thiosulfate or combinations thereof. A typical fixing reaction is:

$$Ag^+ + S_2O_3^{--} \rightarrow (AgS_2O_3)^-$$

Here the usually positive silver ion is shown as part of the negative radical.

The presence of silver ions in the hypo retards the fixing reaction. This may be overcome by removing the silver from the solution or by replenishment. Obviously, it is more economical to remove the silver which has a salvage value.

During electrolysis of the hypo fixing solutions the positively charged sodium ions are attracted to the cathode. In the solution the silver is believed to be in the form of a negative radical $(AgS_2O_3)^-$. In order for the silver to be plated out this radical must go to the positively charged anode and then the silver ion must go to the negatively charged cathode where it acquires an electron and is deposited as metallic silver. If the passage of the fluid past the cathode is at a rapid rate, such as in the present case where the cathode is in the form of a cylinder rapidly rotating, the concentration of the sodium ions can be kept down to such a low limit that they will not cause decomposition of the thiosulfate and thus prevent the formation of silver sulfide which is ruinous to the fixing solution and causes loss of metallic silver.

In making comparison tests between apparatus of the prior art and the apparatus disclosed herein it was found that under similar conditions of rotational speed, decomposition of the hypo, and silver concentration, the cell in accordance with the invention would stand a current density of approximately twice as much per square foot. In tests with the apparatus in accordance with the invention it was found that at a surface speed of about 6.6 feet per second bright silver was plated out from alkaline sodium hypo solutions containing as little as 0.5 gram per liter of silver at current densities of 8 to 10 amperes per square foot. It was found that in an optimum design the cylinder is rotated so as to have a surface speed of about 10.4 feet per second when provided with a top disc separated from the cylinder and having on its under surface vanes or impellers. The purpose of the impellers is to provide a powerful recirculation of the silver bearing hypo up through the inside of the cylinder.

When the solution is electrolyzed at ambient temperature and using a 12 inch diameter cathode, the rotational speed is preferably about 230 revolutions per minute.

It has been found desirable to keep the voltage as low as possible. A cell construction of low resistance permits

the amperage to be maintained high without the use of a high voltage.

While the invention has been described and illustrated with reference to a specific embodiment thereof, it will be understood that other embodiments may be resorted to without departing from the invention. Therefore, the form of the invention set out above should be considered as illustrative and not as limiting the scope of the following claim.

I claim:

1. An electroplating cell for recovering silver from photographic solutions comprising tank means for the solution, supporting means carried by the tank, a rotatable open-ended cylindrical cathode carried by the supporting means, the diameter of the cylindrical cathode about twice its length, the cylindrical cathode positioned in the tank for immersion in a solution, a plurality of anode members positioned outwardly around the periphery of the cylindrical cathode in spaced relationship therewith, fluid circulation impellers positioned inwardly of said rotatable open-ended cylindrical cathode so as to provide fluid circulation axially of the rotatable cylindrical cathode while the rotation of the cylindrical cathode causes tangential fluid circulation, a supporting plate for said impellers positioned at one end of said cylindrical cathode spaced therefrom and rotatable therewith, said impellers each attached at one end to said plate, and coating material applied to said plate and said impellers.

References Cited

UNITED STATES PATENTS

415,024	11/1889	Coffin	204—212
2,391,039	12/1945	Schaefer	204—212
680,408	8/1901	Cowper-Coles	204—212
1,127,966	2/1915	Cowper-Coles	204—212

FOREIGN PATENTS

4,273	2/1908	Great Britain.
412,996	2/1910	France.
1,176,373	8/1964	Germany.
1,133,565	7/1962	Germany.
319,245	1934	Italy.

JOHN H. MACK, Primary Examiner

T. TUFARIELLO, Assistant Examiner

U.S. Cl. X.R.

204—109, 273