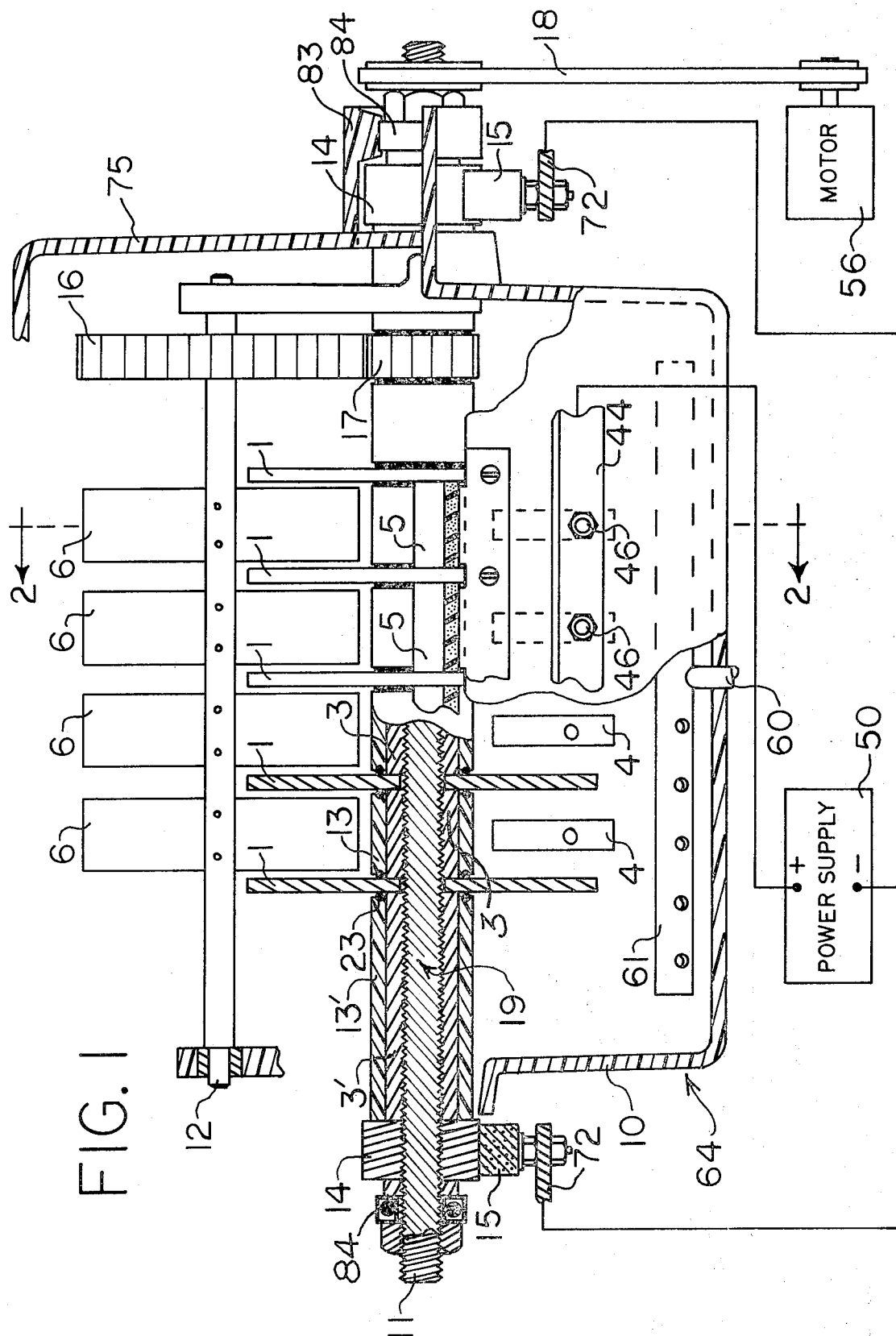


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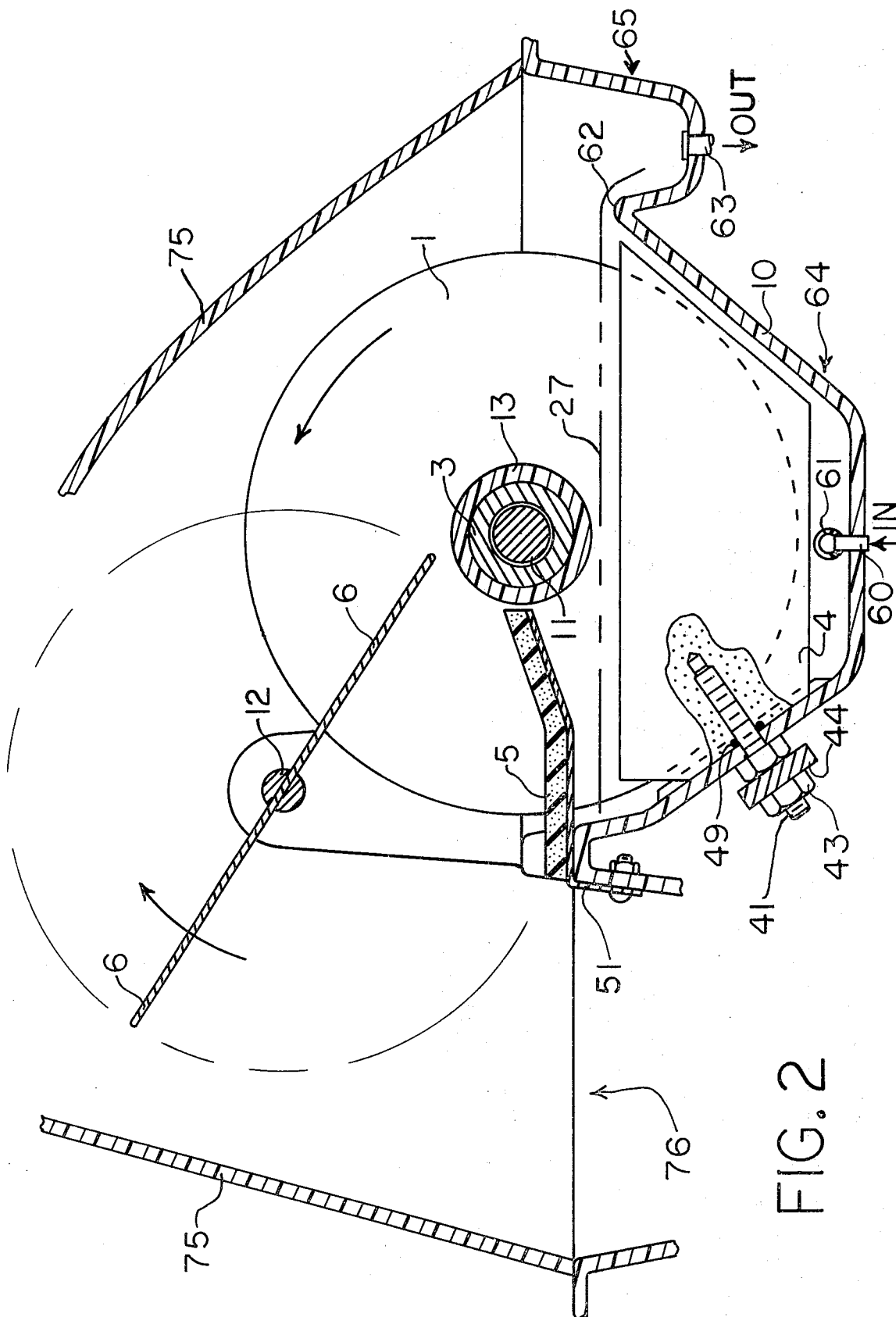
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INCLUDING SCRAPER MEANS AND ROTATING CATHODES

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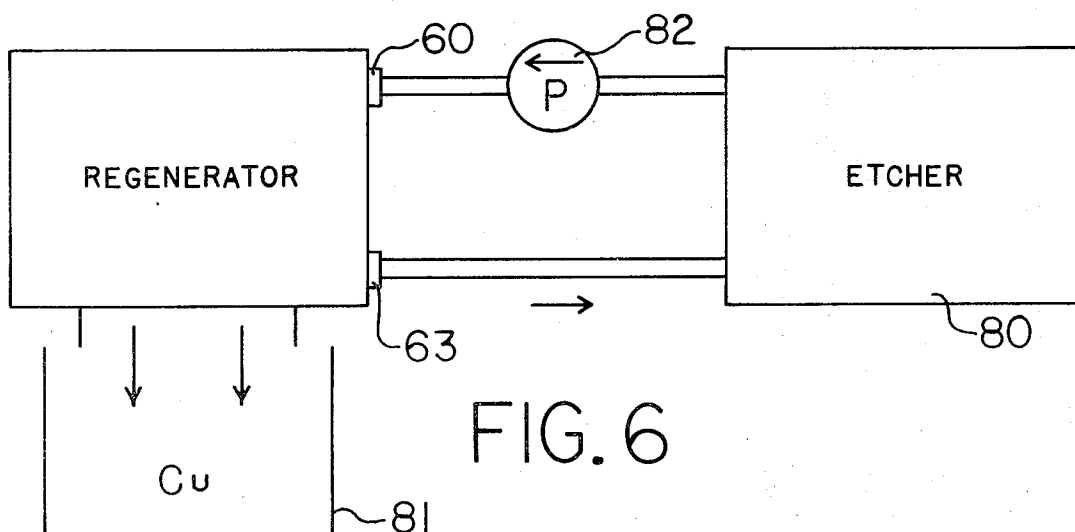
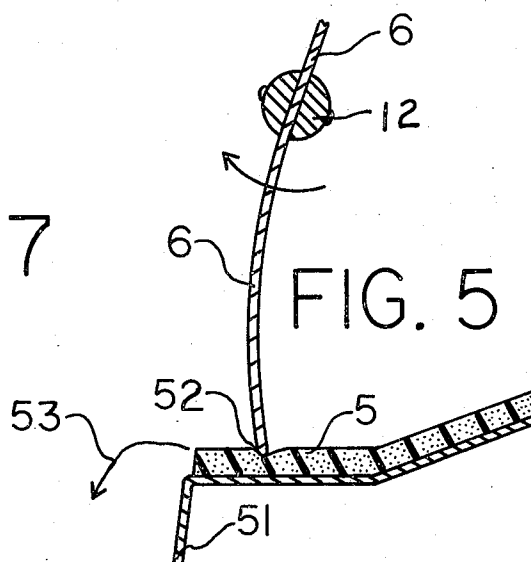
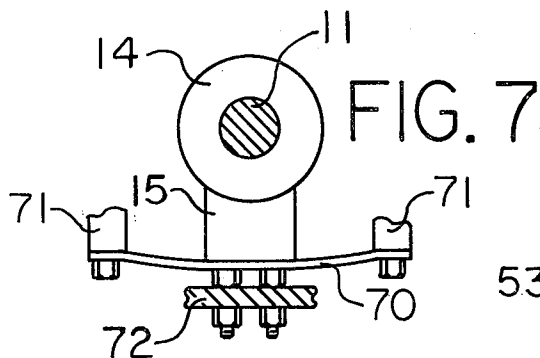
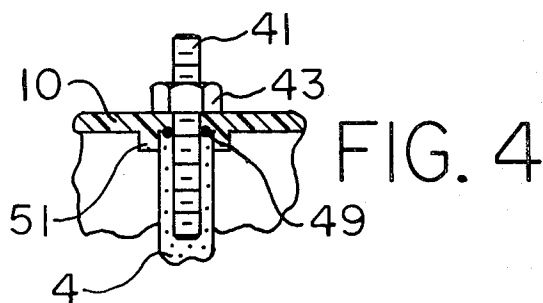
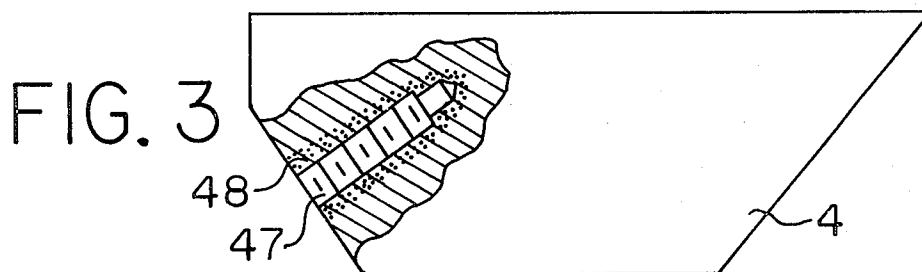
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ELECTROLYTIC REGENERATOR FOR CHEMICAL ETCHANTS INCLUDING SCRAPER MEANS AND ROTATING CATHODES

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Continuation-in-part of abandoned application Ser. No.
138,565, Apr. 29, 1971. This application Mar. 6, 1973,
Ser. No. 338,923

Int. Cl. C23b 5/68

U.S. Cl. 204—216

9 Claims

ABSTRACT OF THE DISCLOSURE

An electrolytic cell apparatus for the regeneration of chemical etchants, such as the ferric chloride solution used in the printed circuit industry. In regenerating such ferric chloride, metallic sponge copper is obtained as a by-product. The process becomes economic at high current densities, which are made practicable by novel structural features. The cathodes of the apparatus are stacked, spaced, slowly-rotating discs of, e.g., titanium. The anodes are stationary plates, preferably of a graphitic material, disposed between the disc cathodes. Mechanical wipers and collectors scrape the sponge copper from the disc cathodes and dump it into a collection bin. The regenerator apparatus is preferably installed in connection with a conventional etching apparatus, the ferric chloride or other etchant being continuously circulated from etcher to regenerator, and back again. The market value of the recovered copper approximately equals the cost of the electric energy required for regeneration.

REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of our prior application Ser. No. 138,565, filed Apr. 29, 1971 and now abandoned.

BACKGROUND OF THE INVENTION

In the electronic printed circuit industry, ferric chloride is widely used as an etchant to selectively remove portions of the copper foil cladding on circuit board stock. This etchant is highly corrosive. As it is used, in the present state of the art, it becomes laden with copper salts and ferrous chloride, and its reaction with copper slows down beyond a practical etch time, so that it must be discarded. The used or spent solution contains, however, roughly 50 percent of the original ferric chloride, and is still highly corrosive. It cannot be disposed of via a sanitary sewer system, but must be hauled away at substantial expense. The value of the combined copper is also lost.

There is hence a need for means to regenerate the spent ferric chloride solution at an economic cost, and a secondary need to reduce the copper salts to metallic copper for commercial sale. The regeneration should preferably be done at the location where the waste is produced, i.e., the etching plant itself, and on a continuous closed-loop basis.

BRIEF DESCRIPTION

This invention is an electrolytic cell for the regeneration of a chemical etchant, such as ferric chloride, used in etching copper from printed circuit boards and the like. Preferably, a regenerator according to the invention is connected by pipes to an etching apparatus. As the ferric chloride is reduced to ferrous chloride, and the etched-away copper foil is oxidized to cupric chloride, the used etchant is preferably pumped through the regenerator and then back to the etcher, in a continuous closed-loop system. The regenerator oxidizes ferrous chloride back to ferric chloride, and reduces the cupric chloride to pure metallic electrolytic copper in sponge form. The flow rate and other parameters are chosen so that the ferric content

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in the etchant is maintained at a suitable strength, e.g., 50 to 80 percent of that of fresh solution. No chemicals need be added to such a system, once it is in operation.

The regenerator comprises a series of spaced disc-shaped cathodes mounted on a common shaft. The shaft is rotated slowly by a motor, at, e.g., $\frac{1}{3}$ r.p.m. Between the cathodes are plate-like stationary anodes. The cathodes are preferably of titanium, and the anodes of a graphite composition.

Sponge copper is deposited on the slowly-rotating cathodes. It is scraped off by stationary scraper blades. The damp sponge copper accumulating on the scraper blades is then swept off by slowly-rotating collector paddles, whence it drops into a collection bin, for later sale. The blades and paddles are of novel construction.

It is known that such an electrolytic regeneration process is inefficient when operated at low or moderate current density, due to recombination effects at the electrodes. At high current density, however, of the order of 700–1000 amperes per square foot, the efficiency with respect to chemical recovery per ampere-hour, rises to above 80 percent.

The invention provides novel structural means to permit the desired high current density. The cathode support shaft is of relatively large diameter, of heavy high-conductivity metal such as copper, and threaded along its length. The disc-shaped cathodes are clamped between heavy internally-threaded metal collars, e.g., of copper, screwed individually onto the threaded shaft. The unusually low-resistance connections so obtained serve to minimize electrical power loss, and to maintain all the cathode discs at nearly the same electrical potential and so provide uniformity of action at each of the cathodes. Connections to the anodes, which are preferably of graphite composition, may be made by threaded silver or copper studs screwed into tapped holes in the anodes. Since graphite is porous, the electrolyte is kept away from the studs by local impregnation of the volume surrounding the tapped holes, with epoxy or other suitable material. This, together with an O-ring seal, prevents corrosion of the studs.

The scraper blades are preferably of sponge plastic on metal backings, and the collector paddles of thin, springy sheet titanium, long enough to indent the sponge surface and so to become slightly bent. Upon reaching the end of a blade, a paddle will straighten out with a "flipping" action, effecting clean removal of the sponge copper.

DETAILED DESCRIPTION

In the drawing:

FIG. 1 is a front view, partly cutaway and in section, of a regeneration apparatus according to the invention;

FIG. 2 is a partial sectional view taken along line 2—2 of FIG. 1;

FIG. 3 is a side view of an anode, partly in section;

FIG. 4 is a view of a detail of an anode mounting, partly in section;

FIG. 5 is a partial side view of a scraper blade and a collector paddle;

FIG. 6 is a block diagram of a continuous circulation system according to the invention, and

FIG. 7 is a semi-diagrammatic end view of a slip-ring and brush sub-assembly.

In FIG. 1, a set of disc-like cathodes 1 is shown mounted on a common shaft 11, which extends through the housing 10 and its cover 75. Shaft 11 is preferably made of copper, and may be silver-plated. It is preferably threaded all along its active length, as indicated at 19 in the cut-away sectional portion of FIG. 1. The housing or casing 10 is preferably of epoxy resin with glass fiber filler.

A practical apparatus may have about 12 cathodes. Five only are shown in FIG. 1, for simplicity of illustration.

The cathodes 1 may be made of material such as platinum, tantalum, or titanium, which will resist the corrosive action of the hot solution. For economic reasons, commercial sheet titanium is preferred. Its electrical conductivity is, however, but some 3.1 percent of that of copper. Because of this low conductivity and the high current density, the above novel means are provided to make durable low-resistance electrical connections to the electrodes. It will be seen that the collars 3, threaded onto the shaft 11, contact the shaft intimately and under high mechanical pressure over a projected area considerably larger than the area of an equivalent unthreaded shaft. Thus, the contact resistance from each collar 3 to shaft 11 is exceedingly low. Moreover, the multiple-disc structure of the invention has much less voltage drop than, e.g., an equivalent drum.

It has been found particularly important to maintain all the cathodes 1 at very nearly the same electrical potential, so that the electrolysis proceeds uniformly among all the cathodes. The present shaft and collar structure meets this purpose.

In a typical small working apparatus, the supply current is of the order of 1000 amperes.

The cathodes 1 are tightly clamped, individually, between the collars 3. Collars 3, which are preferably of copper, may be protected from the corrosive action of the FeCl_3 solution by means of non-corrosive insulating sleeves 13, FIG. 1, made for example of phenolic plastic. The sleeves may be relatively thick, e.g., $\frac{1}{4}$ inch, and sealed against entry of liquid by O-ring seals or other suitable gaskets as at 23, FIG. 1. It has been found that such seals should be resilient, in order to accommodate the effects of repeated thermal expansion and contraction of the structure between room temperature and normal operating temperature, which latter may be around 135°F .

Electric current is preferably supplied to the cathodes 1 via the shaft 11, by means of slip rings 14 and brushes 15 at either end of shaft 11, in known manner, FIGS. 1 and 7. In a typical small regenerator according to the invention, the total current may be about 1000 amperes. Each of the two brushes at the ends of shaft 11 will then carry some 500 amperes, and low-resistance connections must be maintained to each brush 15. In FIG. 7, one suitable form of mounting for the brushes is indicated. The brush 15, which may be of known carbon-copper type, is solidly connected to a flat spring 70 which is made of titanium or other non-corrosive material. Its outer ends are attached to suitable portions of the machine case or frame, as at 71. Thus, there is no likelihood of the spring 70 corroding and so relieving the pressure of brush 15 against slip ring 14. Shaft 11 may be carried in suitable bearings 84, FIG. 1, which may be held down by a suitable protruding portion 83 of cover 75.

FIGS. 1-4 show the anodes and a suitable means of mounting them and making electrical connections. In FIG. 1, a number of anodes 4 are shown between the cathodes 1. Each is mounted to a side portion of casing 10 by a threaded stud 41, which are all connected together by a bus bar or the like 44, located outside the casing 10. FIG. 2 shows a side view of an anode 4 with a sectional showing of stud 41, a nut 43, bus bar 44, and an O-ring seal 49 to seal the base portion of stud 41 from the corrosive electrolyte.

Additional sealing means are indicated in FIG. 3. Since graphite, a preferred anode material, is porous, electrolyte will soak into the anode and eventually corrode the anode mounting studs 41, unless there is additional protection. The additional protection is shown at 48 in FIG. 3, in the volume surrounding the stud hole 47. Before assembly, sealant is pumped into hole 47 under pressure. An epoxy resin is satisfactory. The sealant is held under suitable pressure long enough to permeate the volume around hole 47, indicated by the speckled area 48, as to a depth of around $\frac{1}{8}$ inch. The resin is then allowed

to set. This provides a positive sealing barrier against the corrosive intrusion of electrolyte through the porous anode to the stud.

Commercial "EDM Graphite," which is used for making the tools for electric discharge machining, has been found a satisfactory material for the anodes. Each anode may be about $\frac{3}{8}$ inch thick.

Referring to FIGS. 2 and 4, the anodes may be held in position by the studs 41 and nuts 43, and kept oriented by ribs 51 on the inside surfaces of the casing 10.

To remove the electrolytically-reduced sponge copper from the slowly-rotating cathodes 1, stationary scraper blades 5 and slowly-rotating collector paddles 6 are provided, shown best in FIGS. 2 and 5. They are also shown in front view in FIG. 1. The copper as it is deposited on the sides of the cathode discs 1 is moist and spongy and generally non-adherent. Prior apparatus in this art used jets or streams of liquid to remove it. The present invention provides dry scraping means, which yields pure sponge copper without chemical contamination.

The stationary scraper blades 5 are preferably of a plastic sponge material, glued or otherwise secured to metal backings 51, which may be of sheet titanium. The collector paddles 6, FIGS. 2 and 5, are preferably of thin sheet titanium, e.g., .025 inch thick, which will bend resiliently. The paddles 6 are made long enough to press into the sponge scrapers 5 and indent them as at 52, FIG. 5. The mechanical force required for this indentation will cause the moving paddle 6 to bend into an arc, as shown in FIG. 5. When the paddle 6 comes to the end of the scraper 5, it will straighten out and spring free. In doing so, it will "flip" the accumulated sponge copper away, so that it will fall out into a collection bin (not shown) along a path as indicated by the arrows 53, FIG. 5. This construction has been found to be effective and durable.

The collector paddles 6 may be mounted on a common shaft 12, connected by gears 16, 17 to the cathode shaft 11. Cathode shaft 11 may be rotated by an electric motor 56 and belt means 18. A suitable speed is $\frac{1}{3}$ revolution per minute. Suitable directions of rotation are indicated by arrows in FIG. 2.

Referring to FIG. 2, the casing 10 has a lower or sump portion 64, in which the anodes 4 and the lower portions of the rotating cathodes 1 are immersed. The liquid level is indicated by the dotted line 27. The used etchant pumped into the regenerator comes into the bottom of sump portion 64 through a fitting 60 and a distributor tube 61. The tube 61 has holes along its length at the bottom, and closed ends. It distributes the solution evenly along the cell.

The casing 10 also has a raised lip or weir portion 62, FIG. 2, over which the liquid may flow into a trough portion 65, then exiting through a suitable fitting 63. The normal liquid level indicated at 27 is just above the level of the weir 62.

An electrical power supply 50 is indicated in block form in FIG. 1, with its positive terminal connected to all the anodes 4 through bus 44, and its negative terminal to the cathodes via shaft 11 and brushes and slip rings 14, 15 at each end of that shaft. A typical power requirement for a small regenerator is 5 volts at 1000 amperes.

FIG. 6 indicates in block diagram form a typical closed-loop etching and regenerating system according to the invention. Inlet and outlet fittings 60, 63 of a regenerator are connected through pipes to any suitable etching apparatus 80, through a pump 82. Used etchant solution from the etcher 80 is pumped into the regenerator, and after regeneration, circulates back into the etcher. The reduced copper recovered by the regenerator is deposited in a suitable collection bin 81. After the initial filling with etchant solution, the system requires no further addition of chemicals.

It is found in practice that the market value of the recovered metallic copper is approximately equal to the

cost of the electrical energy used by the generator. A working regenerator according to the invention has the following characteristics:

Diameter of shaft 11	inch	3/4	5
Diameter of cathode discs	do	6 1/2	
Number of cathodes		12	
Number of anodes		11	
Operating current	amperes	1000	10
Power demand	kw	5	
Copper recovery	lb./hour	1-2	
FeCl ₃ regeneration to maintain 50% concentration	gallons/hour	2-4	

Referring back to FIG. 2, a suitable cover may be provided for the apparatus, as at 75. It is preferably of a plastic material and has a downward-facing opening 76 through which the sponge copper drops after it is scraped off the blades 5 by the collector paddles 6.

We claim:

1. Apparatus for the regeneration of spent chemical etchant solution, comprising:

- a casing;
- a plurality of disc-like cathodes of non-corrosive metal;
- a cathode shaft of a metal having electrical conductivity at least about that of copper;
- individual collars of metal of generally similar conductivity as said cathode shaft holding said cathodes spacedly along said shaft;
- clamp means to positively secure each said collar individually in tight intimate contact with the central portion of its adjacent cathode and with the surface of said shaft;
- a plurality of stationary plate-like anodes of non-corrosive material mounted between said cathodes;
- heavy electrical slip-ring cathode connections to the end portions of said shaft;
- means to rotate said shaft at a slow speed; and
- means to pass an electric current at a density of at least about 700 amperes per square foot between said anodes and said cathodes via said connections, said clamp means minimizing the voltage drop between those of said cathodes near the ends of said shaft and those near the middle.

2. Apparatus as in claim 1 wherein:

said clamp means comprises threads along said shaft and mating internal threads in each said collar, each said collar being individually screwed tightly against its adjacent cathode.

3. Apparatus as in claim 2 further comprising:

a non-corrosive protective sleeve covering each said collar, and gasket means at the end portions of each said sleeve.

4. Apparatus as in claim 1, further comprising:

stationary scraper blades disposed adjacent said cathodes to scrape off sponge metal deposited on said cathodes by electrolytic reduction;

a collection bin for said metal; and

slowly-rotating flexible collector paddles having end portions resiliently engaging said blades to remove

said metal therefrom and flip it into said collection bin.

5. Apparatus as in claim 4, wherein:

said scraper blades comprise an outer layer of indentable plastic sponge and the end portions of said paddles adapted to indent said sponge, said paddles thereby becoming arcuately bent,

said paddles adapted to straighten out suddenly upon leaving engagement with said blades and flip said metal into said collection bin,

whereby said blades and paddles are maintained clear of acculations of said metal and no liquid spray is required.

6. Apparatus as in claim 4, further comprising:

connections to said anodes comprising metallic studs screwed into tapped holes in edge portions of said anodes;

said casing having a sump portion and overflow means defining an electrolyte level,

said anodes being made of a graphitic material and being mounted with their upper edge portions substantially below said level; and

sealing means to seal said studs from contact with said etchant solution to prevent corrosion thereof.

7. Apparatus as in claim 6, wherein:

said sealing means comprises a gasket around each said stud and an impregnation of a sealant throughout a volume surrounding each said tapped hole,

said studs extending through said casing, and

said sealant preventing ingress of said solution into said tapped holes through the porous structure of said anodes.

8. Apparatus as in claim 1, further comprising:

a ferric chloride circuit-board etching machine, means to circulate spent etchant solution therefrom into said casing, and means to circulate regenerated solution back into said machine.

9. In an electrolytic reduction apparatus having disc-like rotating cathodes, means for removing deposits of reduced metal from said cathodes, comprising:

stationary scraper blades disposed adjacent said cathodes to scrape off said metal;

a collection bin for said metal; and

slowly-rotating flexible collector paddles having end portions resiliently engaging said blades to remove said metal therefrom and flip it into said collection bin.

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