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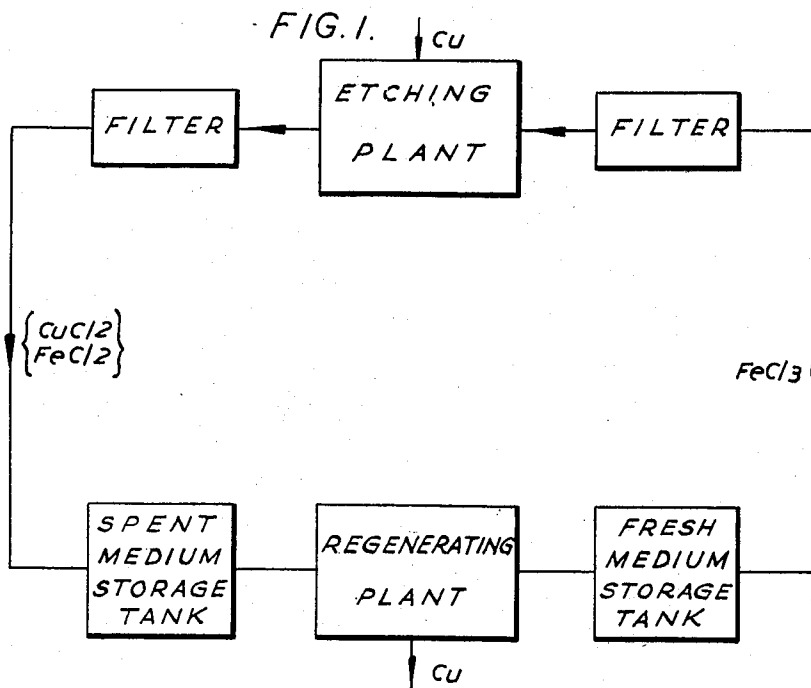
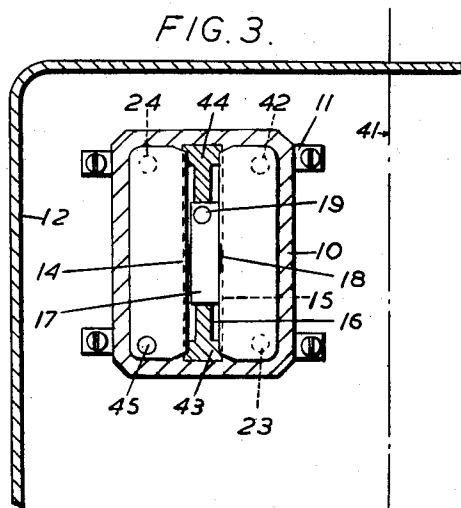
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2,748,071

APPARATUS FOR REGENERATION OF ETCHING MEDIA

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3 Sheets-Sheet 1



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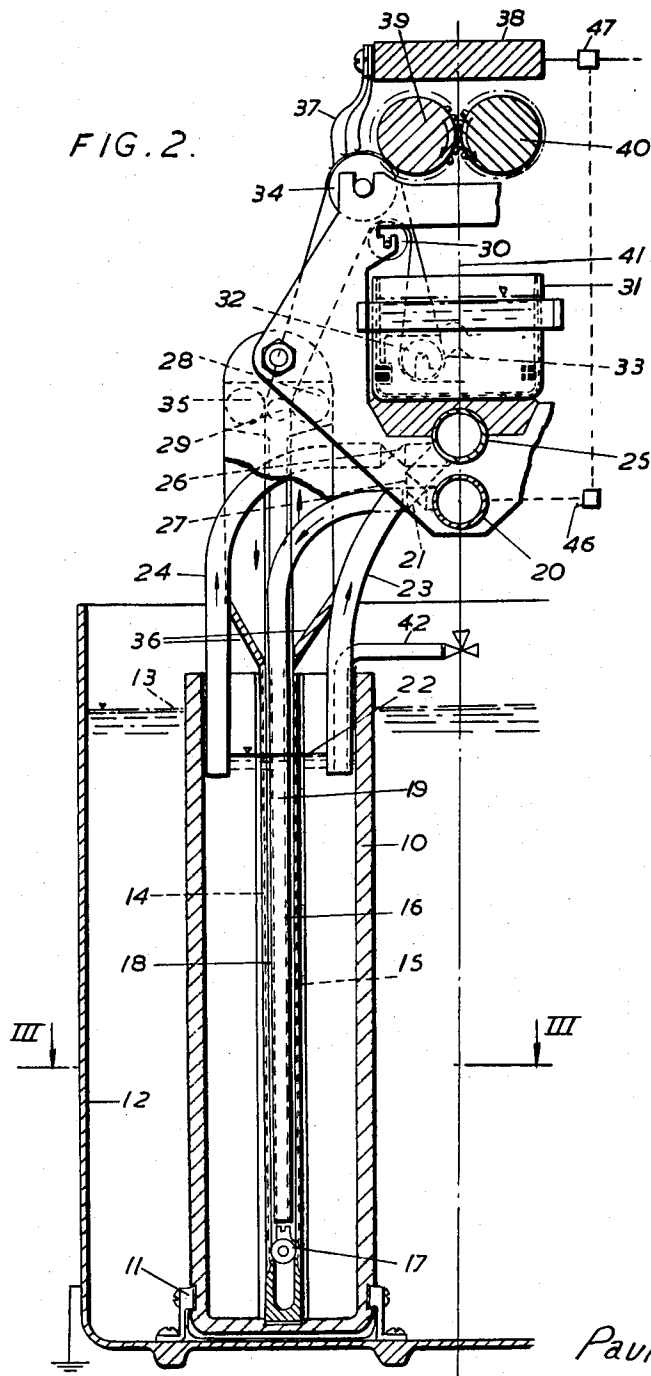
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APPARATUS FOR REGENERATION OF ETCHING MEDIA

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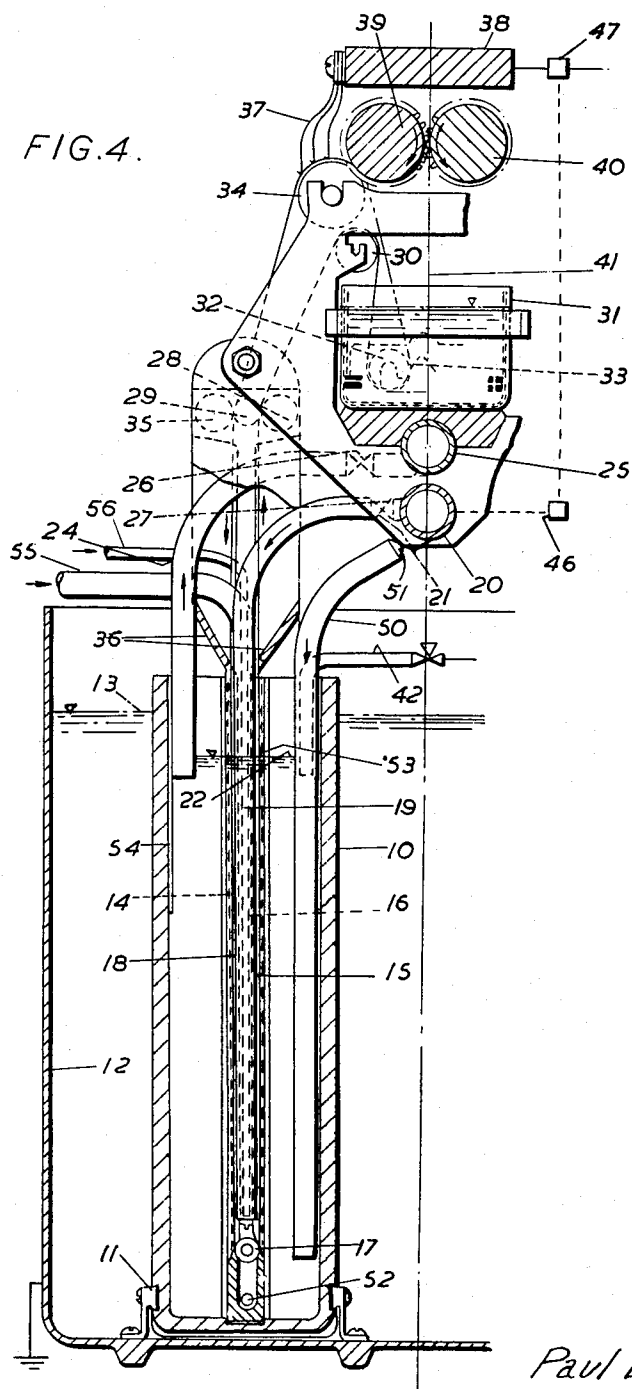
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APPARATUS FOR REGENERATION OF ETCHING MEDIA

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3 Sheets-Sheet 3



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APPARATUS FOR REGENERATION OF ETCHING MEDIA

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5 Claims. (Cl. 204—208)

This invention relates to a process and apparatus for regenerating chemical etching media.

In large scale industrial etching processes large amounts of etching media are required, and considerable quantities of metal are carried away in the spent etching media. A practical and effective system of regeneration of the spent etching medium in order to render it suitable for re-use, and to recover the metal which it contains, would therefore be highly desirable.

It is an object of the present invention to provide a process and apparatus for continuously regenerating a medium used for the chemical etching of metals, this medium before regeneration being incompletely exhausted and still retaining some of its chemical vigour.

A further object of the invention is to provide an electrolytic process and an electrolytic cell for the regeneration.

Other and further objects of the invention will become apparent from the following description.

The accompanying drawings illustrate by way of example two processes and forms of apparatus for carrying out the invention. In the drawings:

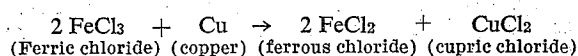
Figure 1 is a flow diagram for the etching medium,

Figure 2 is a sectional elevation of a single electrolytic cell of one form of the apparatus,

Figure 3 is a sectional plan taken on the line III—III in Figure 2, and

Figure 4 is a view similar to Figure 2 but showing another form of the apparatus.

The present invention is applicable to the regeneration of the spent medium from any etching process of the metal displacement type. In etching processes of this type the etching medium comprises a salt of a metal which is nearer to the positive end of the displacement series than is the metal to be etched away. The invention is not applicable to acid etching processes in which the etched metal displaces hydrogen or other gases. For simplicity the invention will be described particularly in relation to the etching of copper by means of an etching medium containing ferric chloride (FeCl_3) as the active ingredient, but it is to be understood that the invention is capable of extension to the etching of other metals, using any suitable metal salt as the etching medium. The particular etching process may be represented, approximately, by the following formula:



In practice the whole of the ferric chloride is not used up, and the etching medium is replaced when the con-

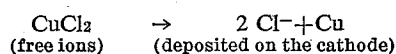
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centration of the ferric chloride has been reduced by a matter of only a few per cent. Thus the spent etching medium will actually consist of a mixture of ferric chloride, cupric chloride and ferrous chloride, and will still retain some of its chemical vigour; that is to say it will still attack any copper with which it comes into contact.

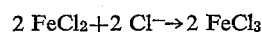
According to the invention the spent but still chemically vigorous etching medium is subjected to electrolysis in an electrolytic cell in which the cathode is contained in a porous-walled chamber, and the cathode is continuously removed from the electrolyte after a limited period of immersion, being replaced by a clean cathode.

The electrolytic reaction may be represented, approximately, by the following formulae.

At the cathode:



At the anode:



By enclosing the cathode in a porous-walled chamber the ferric chloride formed at the anode is prevented from coming into contact with and attack the copper deposited on the cathode. However, as indicated above the spent etching medium still contains a substantial proportion of ferric chloride which would attack the copper deposited on the cathode were it not for the fact that the cathode is continually being removed from the electrolyte, taking with it the deposited copper.

In one form of the invention the spent etching medium, which is relatively rich in cupric chloride, is introduced into the cell within the porous chamber. The copper ions, which are attracted to the cathode, tend to remain close to the cathode, with the result that the concentration of copper ions within the porous chamber will be higher than outside it. The presence of the porous walls tends to localise this concentration in the vicinity of the cathode and to prevent its dissipation by random currents in the electrolyte.

Introducing the spent etching medium into the porous chamber means that the liquid medium must eventually pass out through the porous walls. Hence in such a case some of the pores must be large enough to permit the passage of molecules.

In another form of the invention the spent etching medium is admitted to the cell outside the porous chamber, and in this case the pores need only be large enough to permit the passage of ions, since no liquid has to pass through the porous walls. The porous chamber must of course contain an electrolyte, and this may be a quantity of the etching medium. It is desirable to replenish this medium from time to time, since although the bulk of the ions which migrate towards the cathode through the porous walls will be copper ions, some iron ions will migrate also, with the result that the concentration of iron ions within the porous chamber will tend gradually to increase. In order to prevent the precipitation of iron or copper hydroxide and to maintain conductivity the liquid in the cathode chamber may be kept slightly acidic by the periodic addition of hydrochloric acid. The liquid which is periodically removed from the porous-walled cathode chamber may either be returned to the spent medium tank or first be run over scrap iron sheets to

precipitate any copper left in the liquid. During this treatment any ferric chloride present is reduced to ferrous chloride. This now copper-free ferrous chloride may be added to the spent medium from the etching bath or returned to the electrolytic cell outside the porous chamber.

Preferably the cathode is in the form of a continuously moving band, for example of stainless steel, which passes into the electrolyte in a clean state and leaves the electrolyte bearing a thin coating consisting of copper deposited in a finely divided and readily removable form. The band is covered with an insulating backing so that only the outside surface is active and receives the deposit. The deposit is removed from the band outside the cell and the cleaned band returns to the cell. Alternatively, by suitably controlling the conditions of deposition, the copper may be deposited as a film which can be stripped from the cathode in the form of a foil.

The cathode should have a relatively small surface area to provide a high current density, which is desirable for producing a deposition thereon which has satisfactory stripping properties.

The anode is conveniently in the form of the tank of the cell, and should be made of carbon.

The spent etching medium is denser than the regenerated medium, and so to reduce mixing and thus obtain regenerated medium which is relatively uncontaminated by spent medium, the spent medium should be introduced near to the bottom of the cell while the regenerated medium should be withdrawn from near the top.

One feature of the invention is that the process is suitable for continuous operation for 24 hours a day. The operation of the etching plant, however, will generally not be continuous. For example it might be operated for only about 8 hours a day. This is a considerable advantage since it means that the regeneration plant need be capable of handling etching medium at a rate which is only a fraction of that at which it is discharged from the etching plant. The electric current requirements of the regenerating plant will also be more favourable, being continuous and substantially uniform. As shown in Figure 1, the spent etching medium is discharged from the etching plant into a storage tank. Assuming 24 hours and 8 hours daily working times for the regenerating and etching plants respectively, the regenerating plant receives etching medium from this storage tank at approximately one third the rate at which it is discharged from the etching plant. The storage tank thus fills up when the etching plant is working and is emptied at a slower rate when the etching plant is shut down. The regenerated medium from the regenerating plant passes continuously into another storage tank, from which the etching plant draws etching medium at a greater rate while it is in operation. Filters are provided between the etching plant and the first storage tank, and between the second storage tank and the etching plant. Copper is fed into the etching plant in the form of the material to be etched, while copper is extracted from the regenerating plant in the form of a powder or foil after removal from the cathodes.

In one of its forms the regenerating plant consists of a batch of a large number of electrolytic cells of the kind shown in Figures 2 and 3, the actual number of cells depending upon the amount of medium which the regenerating plant has to handle. All the cells are connected in parallel, so that the number of cells in operation can readily be adjusted to suit requirements.

Each cell comprises a carbon tank 10 which serves as the anode and which is connected at its base by metallic connectors 11 to a large shallow metal tank 12. This tank may contain any desired number of cells, and is filled with water up to the level 13 for cooling the cells. The cooling water is continually circulated through the tank, and the warm outflow may be used in the etching plant, for example for washing the etched material. The metal tank

12 and all the anode tanks 10 are maintained at earth potential.

Extending transversely across each cell 10 are two porous parallel partitions 14 and 15 defining between them a cathode chamber 16. These partitions are conveniently made of porous polyvinyl chloride. In this example at least some of the pores must be large enough to permit molecules of electrolyte to pass through them.

Extending across the bottom of the anode tank 10 between the partitions 14 and 15 is a roller 17. Around this roller passes a relatively narrow stainless steel band 18 which is lacquered on its inner surface and polished on its outer surface. This band constitutes the cathode, and it is continually moved through the cathode chamber 16 in a manner to be described.

Extending nearly to the bottom of the cathode chamber 16 is an inlet pipe 19 leading from a conduit 20 which carries spent etching medium from the spent medium storage tank. A stop valve 21 is provided in the pipe 19 for closing the pipe when the cell is disconnected.

Extending to just below the liquid level 22 in the anode tank 10, at opposite corners thereof, are two pipes 23 and 24 both leading to a conduit 25 which passes on to the storage tank for the regenerated etching medium. Etching medium is withdrawn from the anode tanks through the pipes 23 and 24, in which are provided stop valves 26 and 27.

The upwardly moving side of the cathode band 18 (i. e. the side which is to the right in the drawings) passes upwardly out of the cell between squeegee rollers 28 and 29 and then over an idler roller 30. From the idler roller 30 the band passes downwardly into a water trough or tank 31 in which is contained a submerged roller 32. Also submerged in the water tank or trough is a doctor blade 33 which scrapes deposited copper off the stainless steel band. The copper sinks to the bottom of the tank 31 whence it can be periodically removed. The water in the tank is slightly acidified to prevent oxidation of the copper powder. From the submerged roller 32 the band passes upwardly out of the tank 31 and over a roller 34, termed herein the pressure roller. From the pressure roller the band passes between squeegee rollers 29 and 35 and thence downwardly into the cathode chamber 16.

The squeegee rollers 28 and 29 prevent etching medium from being carried by the band 18 into the water tank 31, this medium being collected in a trough 36 from which it runs back into the cathode chamber 16. The squeegee rollers 29 and 35 prevent the band from carrying water from the chamber 31 into the cell. A drain (not shown) is provided for draining water from between the rollers 29 and 35.

As the band 18 passes over the pressure roller 34 it is contacted by brushes 37 connected to a busbar 38. This busbar is maintained at the required cathode potential, for instance -6 volts.

The cathode band 18 is friction-driven by a driving roller 39, the band being urged against this roller by the pressure roller 34. The driving roller 39 may extend longitudinally over any number of cells arranged side by side and so drive the cathode bands of all these cells simultaneously. Another driving roller 40 is geared to the driving roller 39 and drives the cathode bands of a parallel bank of cells equidistant from the centre line 41.

By arranging the conduits 20, 25 and the doctor blade 33 on the centre line 41 between two symmetrical banks of cells, these parts may serve the cells in both banks.

All the cells are connected together by siphon pipes 42 which ensure that the liquid level and current density in all the cells will be identical.

It is desirable that the volume of the cathode chamber 16 should be as small as possible in relation to the area of its porous walls so that the copper ion concentration therein may be as high as possible. To this end, any spare spaces in the cathode chamber may be partially

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filled with insulating spacers such as the spacers 43 and 44 shown in Figure 3. There must of course be a clearance between these spacers and the porous walls 14 and 15 to permit the passage of etching medium through these walls over the whole area thereof.

Air may be bubbled through a pipe 45 (see Figure 3) to agitate the electrolyte gently.

Means may be provided for the automatic regulation of the plant. For instance, the current density may be regulated in dependence upon the concentration of copper in the spent etching medium. The current density may be regulated either by controlling the level of electrolyte in the cells or by controlling the cathode voltage. One form of regulating means may comprise, for instance, a meter 46 for measuring the cupric chloride concentration in the spent etching medium, and a voltage regulator 47 for regulating the cathode voltage in inverse dependence on this concentration.

The alternative form of apparatus shown in Figure 4 is in many respects very similar to the apparatus shown in Figures 2 and 3, and parts which are identical have been given the same reference numerals.

In this form of apparatus, however, the spent etching medium from the conduit 20 is fed through an inlet pipe 50 to near the bottom of the cell outside the porous partitions 14 and 15. A stop valve 51 is provided in the pipe 50 for closing the pipe when the cell is disconnected. The inlet pipe 19 leading to the cathode chamber 16 is retained, and is used for periodically replenishing the liquid in this chamber. Liquid is withdrawn from the cathode chamber through a valve-controlled aperture 52 at the bottom thereof. The withdrawn liquid may be processed separately or returned to the spent medium storage tank. An overflow aperture 53 in one or both of the porous walls determines the liquid level within the cathode chamber.

Since with this form of the apparatus no liquid is required to pass through the porous walls 14 and 15, the pores therein can be so small that they prevent the passage of molecules contained in the electrolyte. The pores must of course be large enough to permit copper ions to pass through.

In this form of the apparatus the upper portion of the carbon tank 10 is shielded by an insulating sheath 54. Hence the anode is well below the surface of the electrolyte and the anode current density will be higher than in the arrangement shown in Figures 2 and 3. Substantially complete oxidation of ferrous chloride to ferric chloride is thereby achieved, by the chlorine rising through the electrolyte towards the surface thereof. This feature of reducing the anode area may also be applied in Figures 2 and 3 if desired.

An air pipe 55 extends down to near the bottom of the cathode chamber 16 gently to agitate the liquid therein. Special agitating means are not desired for the liquid outside the porous walls.

A pipe 56 is provided for admitting periodically small amounts of hydrochloric acid into the cathode chamber 16 in order to keep the solution acid to prevent any precipitation of iron or copper hydroxide and to maintain the conductivity of the solution.

What I claim is:

1. An apparatus comprising an electrolytic cell formed of a tank, a cathode and anode, the inside walls of said tank being composed substantially of carbon constituting the anode of said cell, two partitions composed of porous polyvinyl chloride disposed vertically within said tank, said partitions constituting the walls of a cathodic chamber, a pair of rollers, one positioned within said cathodic chamber at the base thereof, the other positioned substantially above said chamber, a continuous narrow stainless steel band lacquered on its inside face and mounted upon said pair of rollers and constituting the cathode of said cell, a fluid inlet pipe extending into and terminating near the base of said cathodic chamber, a

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fluid outlet pipe extending from the anode area of said electrolyte cell near its mouth, and a water tank, the said electrolyte cell being positioned within said water tank.

2. An apparatus comprising an electrolytic cell formed of a tank, a cathode and anode, the inside walls of said tank being composed substantially of carbon constituting the anode of said cell, two partitions composed of porous polyvinyl chloride disposed vertically within said tank and constituting therebetween a cathode chamber, a pair of rollers, one positioned within said cathode chamber at the base thereof, and the second positioned substantially above said chamber, a continuous narrow stainless steel band lacquered on its inside face and mounted upon said pair of rollers and constituting the cathode of said cell, a pair of insulating spacers disposed within said cathode chamber thereby reducing the volume thereof in relation to the area of the porous walls so as to provide for high concentration of the cations, a fluid inlet pipe extending into and terminating near the base of said cathodic chamber, a fluid outlet pipe extending from the anode area of said electrolytic cell near its mouth, and a water tank, the said electrolytic cell being positioned within said water tank.

3. An apparatus comprising an electrolytic cell formed of a tank, cathode and anode, the inside walls of said tank constituting an anode, a porous cathode chamber vertically positioned within said tank, a pair of rollers, one positioned within said porous chamber at the base thereof, the second positioned substantially above said porous chamber, a trough mounted atop said porous chamber, and beneath said second roller, a continuous narrow metal band insulated electrically on its inner surface constituting the cathode, said band being partially enclosed within said porous chamber and said trough and being mounted on the said pair of rollers, means for moving said band, a pair of squeegee rollers engaging the upwardly moving side of said band, the said pair of squeegee rollers being positioned intermediate the trough and the aforementioned second roller, fluid inlet means near the base of said cell, and fluid outlet means near the mouth of said cell and extending from said cell.

4. An apparatus comprising an electrolytic cell formed of a tank, cathode and anode, the inside walls of said tank constituting an anode, a porous cathode chamber vertically positioned within said tank, a pair of rollers, one positioned within said porous chamber at the base thereof, the second positioned substantially above said porous chamber, a trough mounted atop said porous chamber, and beneath said second roller, a continuous narrow metal band insulated electrically on its inner surface constituting the cathode, said band being partially inclosed within said porous chamber and said trough and being mounted on the said pair of rollers, means for moving said band, a pair of squeegee rollers engaging the upwardly moving side of said band, the said pair of squeegee rollers being positioned intermediate the trough and the aforementioned second roller, fluid inlet means near the base of said porous chamber, and fluid outlet means near the mouth of said cell and extending from said cell.

5. An apparatus comprising an electrolytic cell formed of a tank, a cathode and anode, the inside walls of said tank being composed substantially of carbon constituting the anode of said cell, two partitions composed of porous polyvinyl chloride disposed vertically within said tank, and constituting therebetween a porous cathode chamber, a pair of rollers, one positioned within said porous cathode chamber at the base thereof, the second positioned substantially above said porous chamber, a trough mounted atop said porous chamber and beneath said second roller, a continuous narrow stainless steel band lacquered on its inside face and mounted upon said pair of rollers and constituting the cathode of said cell, means for moving said band, a pair of squeegee rollers engaging the band

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outside said porous chamber and beneath said second rollers, a pair of insulating spacers disposed within said cathode chamber thereby reducing the volume thereof in relation to the area of the porous walls thereof so as to effectuate high concentration of the cations, a fluid inlet pipe extending into and terminating near the base of said cathodic chamber, a fluid outlet pipe extending from the anode area of said electrolytic cell near its mouth, and a water tank, the said electrolytic cell being positioned within said water tank.

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