J. BILLITZER.

APPARATUS FOR THE ELECTROLYSIS OF ALKALI CHLORIDS.

APPLICATION FILED JUNE 17, 1908.

934,385. **Patented Sept. 14, 1909.**

Fig. 1

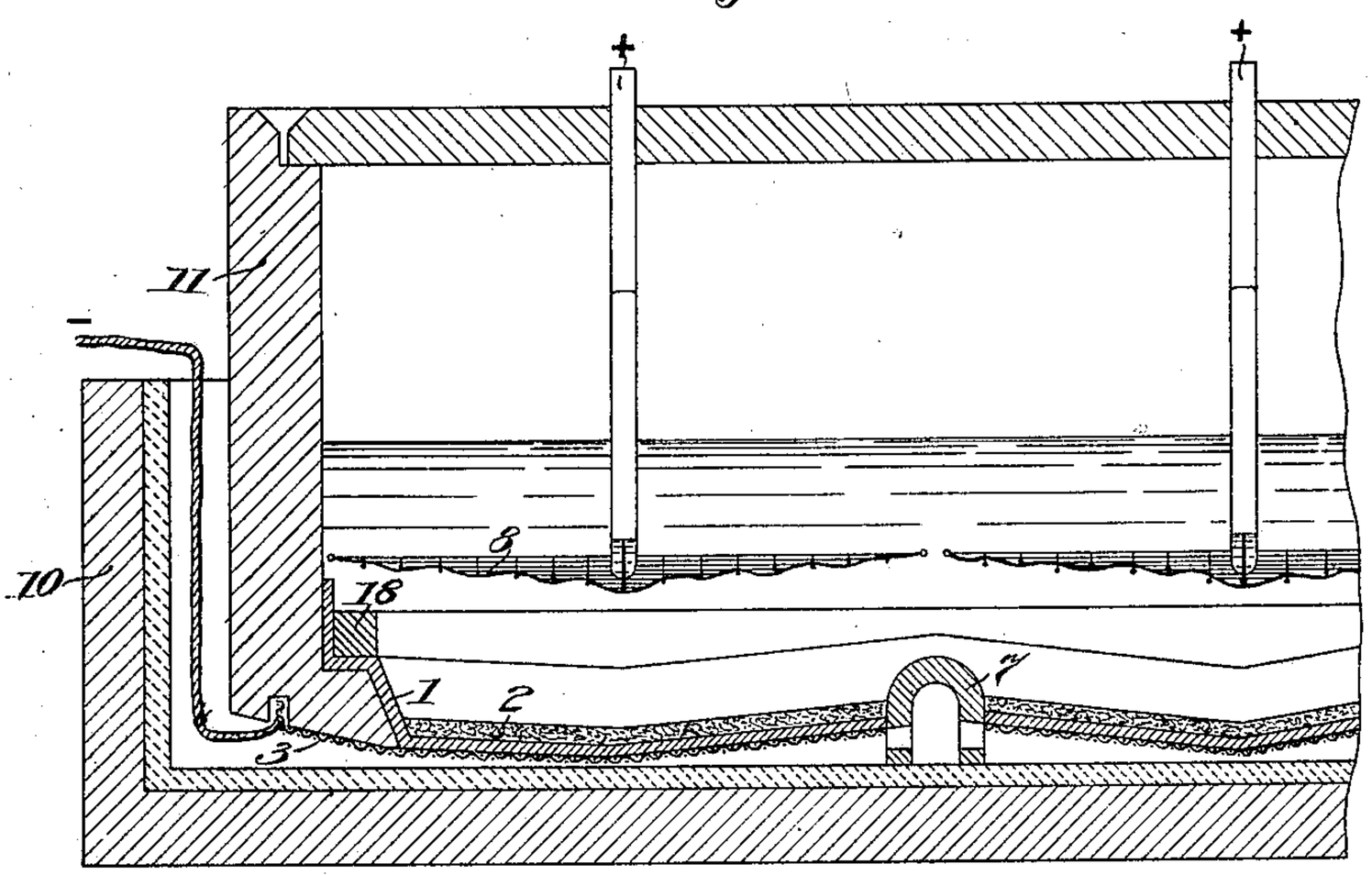


Fig. 2

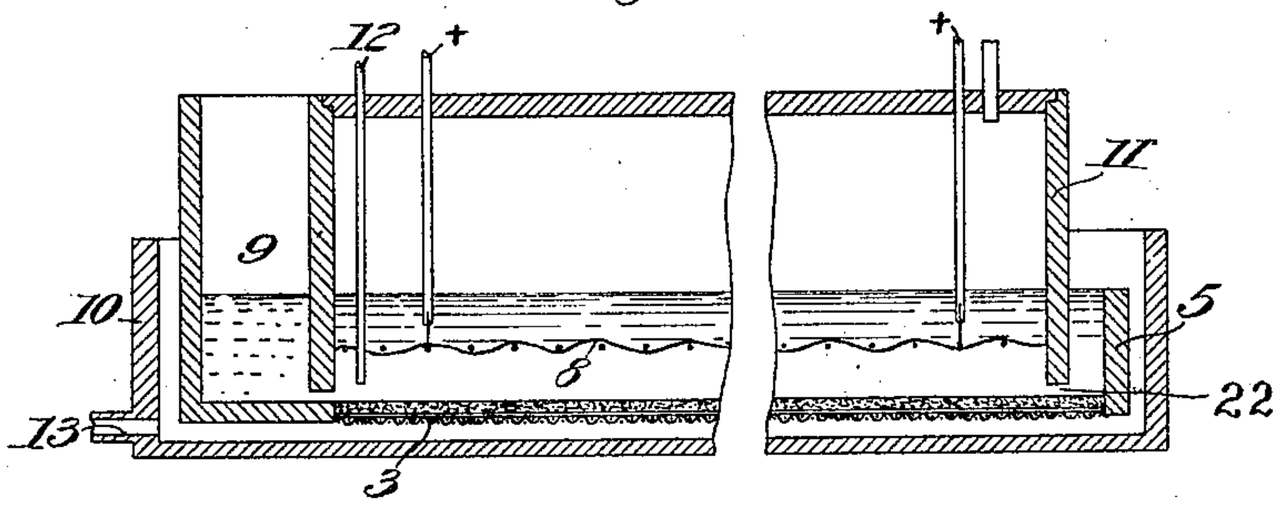
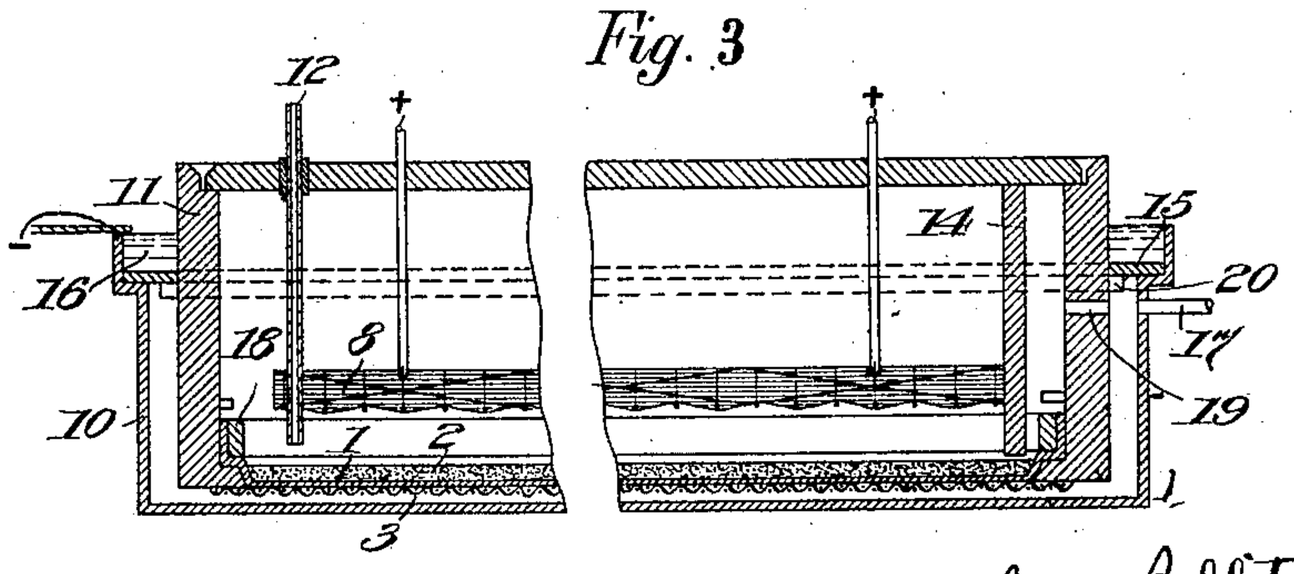


Fig. 3



Witnesses,
H. H. Knight
Ray Ernst.

Jean Billitzer,
Inventor,
by Knight Bros.
his attys

UNITED STATES PATENT OFFICE.

JEAN BILLITZER, OF VIENNA, AUSTRIA-HUNGARY.

APPARATUS FOR THE ELECTROLYSIS OF ALKALI CHLORIDS.

934,385. Specification of Letters Patent. Patented Sept. 14, 1909.

Original application filed January 22, 1907, Serial No. 353,473. Divided and this application filed June 17. 1908. Serial No. 438,981.

To all whom it may concern:

Be it known that I, JEAN BILLITZER, chemist, a subject of the Emperor of Austria-Hungary, residing at Reisnerstrasse 21, Vienna, III, Austria-Hungary, have invented certain new and useful Improvements in Apparatus for the Electrolysis of Alkali Chlorids, of which the following is a full, clear, and exact description.

It is well known that difficulty is encountered in obtaining chlorin and fairly concentrated soda lye from chlorid of sodium solutions, by means of the electric current and cheap and simple apparatus of good current efficiency. The types of mercury apparatus, though operating satisfactorily, are very expensive, complicated and require careful attention. The bell apparatus while giving a comparatively good yield, requires a high tension during the electrolysis and does not yield concentrated lyes.

In order to obtain a good yield of concentrated lye applicant has devised a new process, which forms the subject-matter of an application filed by him on January 22d, 1907, Serial No. 353,473, from which the present application has been divided. This process though principally designed for the chlorid of sodium electrolysis may be also employed without any difficulty in all cases in which through the action of the electric current upon a solution a gaseous and a liquid product is formed.

The idea involved in the apparatus, the structure of which will be described later on, is shortly as follows: In a suitably arranged apparatus having an anode disposed above a cathode both substantially horizontally with a substantially horizontal diaphragm between them near the cathode, a formation of layers is produced between the anode and said diaphragm by means of the electrolytic process, which renders the solution near the anode weaker. This will diminish the density of the anode solution, while the portion of the solution next to the cathode and immediately above the diaphragm will increase its specific weight and thus gravitate as a layer next to the diaphragm. Since layers of liquids at rest cannot be kept for any length of time from diffusing into each other, the two solutions thus produced are separated by supplying fresh salt solution from above and by compelling the lower heavier layer to flow through a slot 22, disposed near the diaphragm and extending over the whole width of the latter, and by arranging a dam behind this slot. By these means the heavier layer will be constantly removed as it is formed. In order to obtain stationary conditions the supply of fresh solution and the current intensity have to be chosen so that when the foundation of layers has once commenced as many chlorin ions go to the anode as can escape from it. In order to facilitate the formation of layers the lower layer described may be brought into contact with undissolved sodium chlorid in order to remain always saturated. In order to facilitate this formation and regeneration of layers a new and particularly suitable diaphragm is used, which has aside from its many other advantages the particular features of having an accurately regulatable permeability and of adapting itself well to the form of the cathode, so that the separation aside from being produced by the formation of layers, is further aided by the inner hydrostatic pressure. Furthermore through the rewetting of the cathode by means of the solution running off, the contact is kept permanent and the running off of the soda lye insured.

According to applicant's arrangement described above the separation by means of small quantities of liquid has been rendered possible, by having the separating layer thin, by causing the same to renew itself automatically during the process of electrolysis and by forcing it to form a distinct separating layer. Only by this arrangement it has been made possible to completely separate anode and cathode products, obtaining at the same time comparatively concentrated solutions of soda lye, that is solutions of from ten to twenty per cent.

In order to make clear the invention the apparatus will be described in detail in the following with the aid of the accompanying drawings which show diagrammatically an apparatus used for this process.

In these drawings, Figure 1 is a part of a longitudinal section of the apparatus; Fig. 2 is a transverse section of same in smaller scale; Fig. 3 is a longitudinal section of a modification of the apparatus.

The apparatus shown in Figs. 1 and 2 comprises a bell 11, which is closed at its lower end by means of a diaphragm 1, 2,

resting upon a wire net 3 of iron, nickel or other suitable material, which serves as the negative electrode. The entire bell is suitably supported and disposed within a trough 10. Within bell 11 is arranged anode 8 of platinum, carbon or other suitable material in parallel to and at a small distance from the cathode net 3.

In order to obtain a complete separation of the electrolytic products (soda lye and chlorin) the process is carried out in the following manner: The bell 11 is supplied with the electrolyte to a certain height, trough 10 being empty at the beginning of the process. The diaphragm being permeable for liquids will allow the salt solution to filter through to the cathode where soda lye is formed. The discharge opening 13 for the lye is disposed so that the liquid passing into trough 10 will attain a suitable height to just wet the cathode net. In order to facilitate the escape of the hydrogen bubbles produced on the cathode during the electrolysis the cathode may be suitably shaped for instance by arranging the net in wave form (Fig. 1) with its highest portions abutting against channel 7 formed of impermeable material, through which the gas can easily escape, or by placing the plane or corrugated cathode net altogether slightly slantingly; an incline of 1:20 would be sufficient to cause the hydrogen to wander toward the higher portion of the net. A satisfactory operation of this arrangement however is only possible by using a suitable kind of diaphragm. It is essential to use diaphragms, the permeability of which for liquids is accurately regulatable without offering great electrical resistance, and which adapt themselves well to the form of the cathode. All diaphragms which are not pliable such as carborundum, cement, sheet asbestos and the like are not suited for this purpose. Pulverized diaphragms are not suited either since they are not plastic and are not permanent.

Applicant has succeeded in designing a new diaphragm by covering the net cathode 3 with ordinary commercial asbestos cloth 1 (Fig. 1) and putting on same a pulverized diaphragm 2 of a particular kind. The pulverized diaphragms heretofore known are not suited for inclined surfaces, owing to the powder soon shifting down the incline. Besides these diaphragms have the disadvantage of cementing and thus soon becoming impermeable; for this latter reason they cannot be used for this purpose even in connection with fixed ribs, which prevent the sliding of the powder. Both of said disadvantages have been overcome by applicant by using a diaphragm body consisting of a mixture of insoluble powders, such as sulfate of barium, clay or the like, and asbestos-wool, which mixture is formed in sodium chlorid solutions into a plastic but still tough and resistive mass. Mixtures of suitable powders with asbestos-wool can be made very quickly and very easily. While for instance sulfate of barium alone requires several hours to deposit, a suspended mixture of pulverized sulfate of barium and asbestos-wool deposits in a twenty per cent. (20%) sodium chlorid solution in a few minutes. This deposit being at first tough, may be easily dried, whereby it may be formed into any shape, which it retains during its further use for a long time even in liquids. These diaphragms are extremely strong and may be used for months and years and furthermore they can be exchanged or renewed very quickly and easily, contrary to ordinary powder diaphragms. It is only necessary to renew the asbestos-wool powder layer or to exchange the whole diaphragm by lifting out the asbestos cloth with the layer. This operation requires only a few minutes. These diaphragms dry and harden in the air completely after some time, but regain their pliability and permeability when placed for a short time in water or in a solution of any suitable kind. By varying the proportion of asbestos-wool and sulfate of barium or clay powder, as well as by varying the thickness of the layer, the permeability of the diaphragm may be regulated at will. Applicant uses for producing lyes of from eight to thirteen per cent. on a diaphragm surface of one hundred square centimeters, a mixture of one hundred and ninety grams $BaSO_4$ with from three to six grams asbestos-wool; for producing thirteen to eighteen per cent. layers, two hundred and seventy-five grams $BaSO_4$ with fifteen grams asbestos-wool.

During the electrolysis in the apparatus described above soda lye is formed in trough 10 while the chlorin ions wander to the anode where they are discharged and escape as gaseous chlorin. Fresh salt solution is supplied through feeding pipe 12 (Fig. 2) which runs into the solution close to the diaphragm. Therefore the upper portion of the salt solution will be weakened in salt during the electrolysis while the lower portion will increase its density so that owing to the different densities of the two portions, a distinct layer is formed immediately above the diaphragm. In order to further facilitate the formation of the layer a chamber or pocket 9 (Fig. 2) of impermeable material may be provided in the bell, which is supplied with sodium chlorid, and which communicates near the bottom with the electrolysis chamber, so that the layer resting directly upon the diaphragm is constantly saturated with cooking salt and therefore its specific weight rendered still greater. This latter precaution is particularly advisable when the fresh solution is supplied very slowly in order to obtain very concentrated

lyes. In this case the solution would grow too weak in salt without the pocket above referred to. During the electrolysis the solution not only reaches the cathode through the diaphragm, but is also forced to run over a dam 5 (Fig. 2) in order to wet the cathode from below: Instead of using a dam, a baffle plate 14 (Fig. 3) may be provided within bell 11 having its opening near the diaphragm. The pocket thus formed by this plate communicates with the trough 10 through an outlet 19 provided at a suitable height. By this arrangement shown in the two modifications the irregularities of supply of solution or of permeability of the diaphragm are equalized on one hand, on the other hand, this being the most essential point, this arrangement had the following particular advantage.

During the passing of OH ions to the anode or owing to insufficient action of the diaphragm soda lye is apt to reach the lower layer of the liquid, which in the further course of electrolysis forms with the chlorin, hypochlorite, which latter would cause disturbances in the process and decrease the output. By compelling the solution contained in the bell to constantly flow over the dam any trace of soda lye, which may have diffused into the bell, is washed out immediately since according to the arrangement described above, just the lowermost layers next to the diaphragm are compelled to flow over the dam.

As mentioned already the liquid level is kept in the trough preferably high enough to wet the cathode net, which however is not absolutely necessary, as the liquid level may also be rather below the level of the cathode, because owing to the filtrating of the solution through the diaphragm and owing to the liquid flowing over the dam the cathode net is permanently wetted with liquid. (On account of clearness the space between dam 5 and bell 11 is shown in Fig. 2 much wider in proportion than it is in the practical apparatus where this space is chosen as narrow as possible in order to avoid diffusion.)

The apparatus has been subjected to several uninterrupted electrolysis tests, each lasting six weeks and yielding at from four to five volt tension during the time of the electrolysis an average output of twelve per cent. soda lye, being equal to ninety per cent. to ninety-five per cent. (rarely eighty-five to ninety per cent.) of the theoretical output, while at the same time substantially chemically pure chlorin of ninety-nine per cent. was obtained. No difficulty is encountered in obtaining an output of ten to fifteen per cent. and even more concentrated soda lye. An apparatus having a cathode net of one square meter surface consumes at a tension of from 4 to 4.5 volt and a temperature of 60° C., about 600 amperes.

In manufacturing the apparatus various materials may be employed. Plates of glass, wire-glass or pottery may be used, which are embedded in cement or in asphalt as shown for instance in Fig. 1, or reinforced concrete or stone plates may be utilized.

In smaller apparatus (up to 100 amperes capacity) it is more advantageous to fix the asbestos cloth to the bell. The whole bell, together with the diaphragm may then be placed upon a corrugated wire net of sufficient strength corresponding in form with the bottom of the outer trough and resting thereon. The trough 10 may be made to advantage of sheet iron, which serves in this instance also as a part of the electric circuit. For larger apparatus (consuming more than 100 amperes) the structure above referred to is not suited. In apparatus of that size it is more practical to have the cathode net fixed to the bell.

In order to facilitate the exchanging of the diaphragm without renewing the bell, the cover of the latter and the baffle plate 14 are made easily removable (Fig. 3). The asbestos cloth is not fixed to the bell but is held in place by means of a frame 18 of stone or other suitable material, running on the inside of the trough and held in place by means of wedges. For tightening the frame against leakage if necessary an insoluble powder may be used. Upon the asbestos cloth is then placed the asbestos powder mixture. For the purpose of renewing the diaphragm it is only necessary to remove the bell cover, the baffle plate and the frame, whereafter the diaphragm may be exchanged in a few minutes.

In Fig. 3 is shown an apparatus by means of which it is also possible to collect the hydrogen separately. For this purpose a tight fitting frame 15 running on the outside of bell 11 is resting upon a rim 20 provided on the bell and upon the upper rim of trough 10 which is suitably shaped for this purpose as shown in Fig. 3. The channel thus formed by the bell, the trough edge and frame 15 may be filled with a liquid 16 of suitable kind to further tighten the frame against leakage of gas. The pressure at which the hydrogen is discharged through the opening 17 may be easily regulated by regulating the liquid level at the discharge opening 13. The hydrogen may be either utilized as such or may be used with the chlorin generated during the electrolysis for directly producing chemically pure hydrochloric acid by means of a blow pipe similar to the oxyhydrogen blow pipe. In order to free the hydrogen of the atomized soda lye carried along by same while rising, it must of course pass through a long tube or over a body of large surface before it can be used in connection with chlorin as above mentioned.

While I have shown and described the apparatus as being particularly adapted for the electrolysis of alkaline salts, I do not wish to limit myself to the use of the apparatus of this particular electrolysis, as it is obvious that it may be used to the same advantage as an electrolytic cell for any electrolytical process in which layers, formed in the electrolyte, have to be removed.

I claim:

1. An apparatus of the character described, comprising a trough, a bell disposed within said trough adapted to contain the electrolyte and the anode, a cathode net of suitable material extending across the lower opening of said bell, a diaphragm resting upon said cathode net, said bell having an opening immediately above said diaphragm adapted to discharge the cathode product as it is formed and a dam suitably disposed outside of said bell within said trough adapted to cause the cathode product to flow over it before reaching said trough.

2. An apparatus of the character described, comprising a trough, a bell disposed within said trough adapted to contain the electrolyte and the anode, a cathode net of suitable material extending across the lower opening of said bell, a diaphragm resting upon said cathode net, said bell having an opening immediately above said diaphragm adapted to discharge the cathode product as it is formed, a dam suitably disposed outside of said bell within said trough adapted to cause the cathode product to flow over it before reaching said trough, and means preventing the said cathode product discharged into said trough, to assume a level higher than the line on which the underside of said cathode net is disposed.

3. An apparatus of the character described, comprising a trough, a bell disposed within said trough adapted to contain the electrolyte and the anode, a cathode net of suitable material extending across the lower opening of said bell, a flexible diaphragm resting upon said cathode net and adapted to conform with the shape of said net, said bell having an opening immediately above said diaphragm adapted to discharge the cathode product as it is formed and a dam suitably disposed outside of said bell within said trough adapted to cause the cathode product to flow over it before reaching said trough.

4. An apparatus of the character described, comprising a trough, a bell disposed within said trough adapted to contain the electrolyte and the anode, a cathode net of suitable material extending across the lower opening of said bell, a flexible diaphragm resting upon said cathode net and adapted to conform with the shape of said net, said bell having an opening immediately above said diaphragm adapted to discharge the cathode product as it is formed, a dam suitably disposed outside of said bell within said trough adapted to cause the cathode product to flow over it before reaching said trough and means preventing the cathode product discharged into said trough to assume a level higher than the line on which the underside of said cathode net is disposed.

5. In an apparatus of the character described, the combination of a trough, a bell within said trough adapted to contain the electrolyte and the anode, a cathode net suitably disposed across the lower opening of said bell and a diaphragm upon said net comprising a layer of asbestos cloth and a mixture of sulfate of barium with asbestos wool disposed upon said cloth to form a layer.

6. In an apparatus of the character described, the combination of a trough, a bell within said trough adapted to contain the electrolyte and the anode, a cathode net suitably disposed across the lower opening of said bell and a diaphragm upon said net comprising a layer of asbestos cloth and a mixture of sulfate of barium with asbestos wool disposed upon said cloth to form a layer by precipitating said mixture in a solution containing a salt in which the asbestos wool is stirred up to cause the precipitate to quickly settle and to form an even mixture.

7. In an apparatus of the character described, the combination of a trough, a bell within said trough adapted to contain the electrolyte and the anode, a cathode net fixed to said bell across its lower opening, a diaphragm resting upon said net and a frame removably fastened within said bell to tightly hold said diaphragm in place.

8. In an apparatus of the character described, the combination of a trough, a bell within said trough adapted to contain the electrolyte and the anode, a cathode net suitably disposed within said trough to extend across the lower opening of said bell, a diaphragm comprising an asbestos cloth fastened across the lower opening of said bell and adapted to receive as an independent and removable layer a mixture of asbestos wool and an insoluble powder.

9. In an apparatus of the character described, the combination with a trough, a bell within said trough adapted to contain the electrolyte and the anode, a cathode net disposed across the lower opening of said bell, a diaphragm resting upon said net, said net and said diaphragm causing the cathode product to form a layer upon the diaphragm and a chamber within said bell adapted to contain undissolved salt and communicating with said bell near the layer formed by said cathode product.

10. A diaphragm for electrolytic cells comprising a cloth and a permeable and

plastic, but insoluble outer layer, removably disposed on said cloth.

11. A diaphragm for electrolytic cells comprising a supporting layer of asbestos cloth and a second independent layer of a mixture of asbestos wool and an insoluble powder removably disposed on said cloth.

12. A diaphragm for electrolytic cells, comprising a supporting layer of asbestos cloth and a second layer of a mixture of asbestos wool and sulfate of barium suitably disposed on said cloth.

13. A diaphragm for electrolytic cells, comprising a supporting layer of asbestos cloth and a second layer of a mixture of asbestos wool and barium sulfate formed upon said cloth by precipitating said mixture in a solution containing a salt in which the asbestos wool is stirred up to cause the precipitate to quickly settle and to form an even mixture with said wool.

14. A diaphragm for electrolytic cells comprising a supporting layer of asbestos cloth and a second layer of a mixture of asbestos wool and an insoluble powder formed upon said cloth by precipitating said mixture in a solution containing a salt in which the asbestos wool is stirred up to cause the precipitate to quickly settle and to form an even mixture with said wool.

JEAN BILLITZER.

Witnesses:
AUGUST FUGGER,
ROBERT W. HEINGARTNER.