

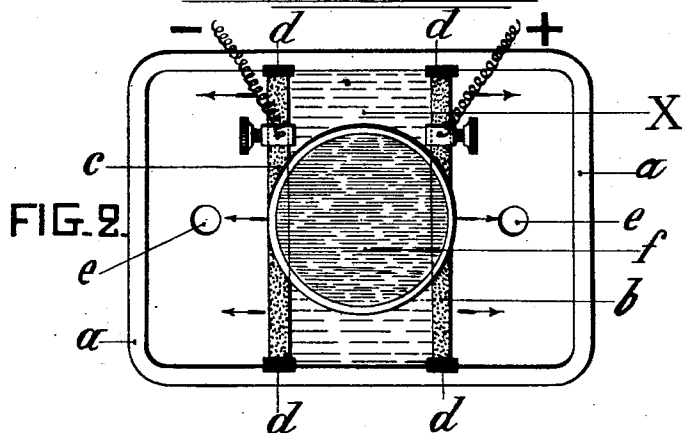
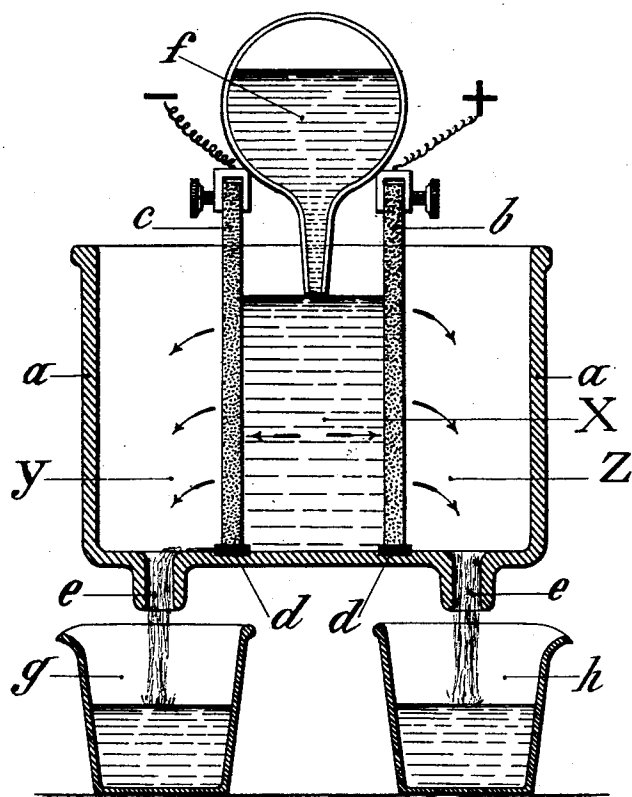
L. P. HULIN.

PROCESS OF ELECTROLYTIC DECOMPOSITION OF SOLUTIONS.

No. 586,236.

Patented July 13, 1897.

FIG. 1.



WITNESSES

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ATTORNEYS.

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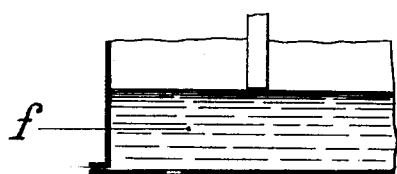


FIG. 3.

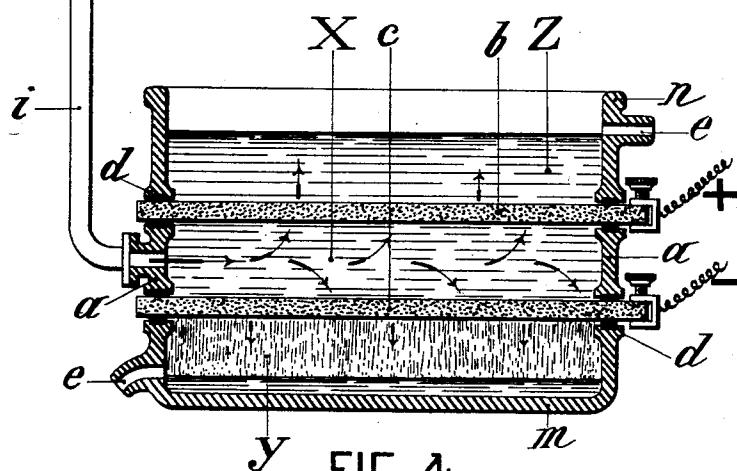
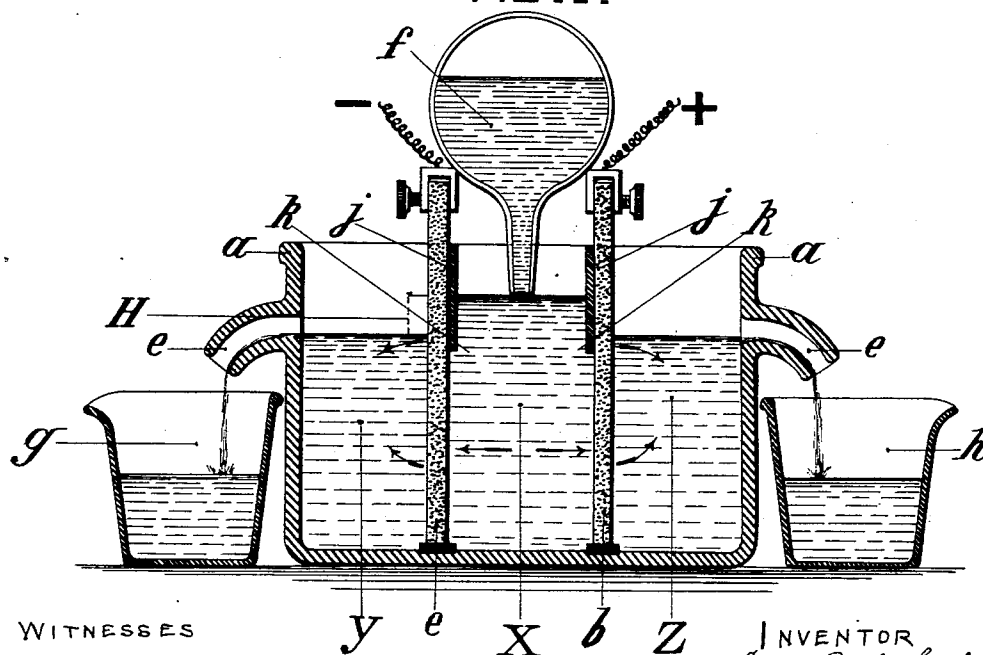


FIG. 4.



WITNESSES

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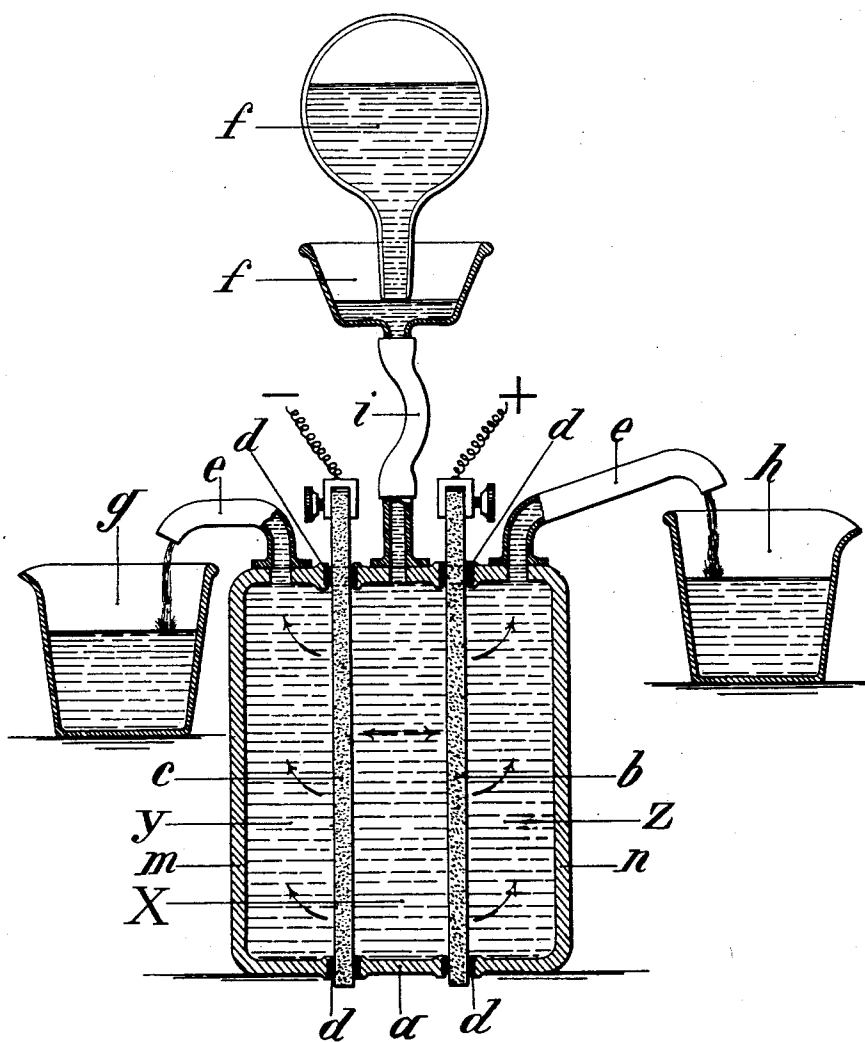
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FIG. 5.



WITNESSES

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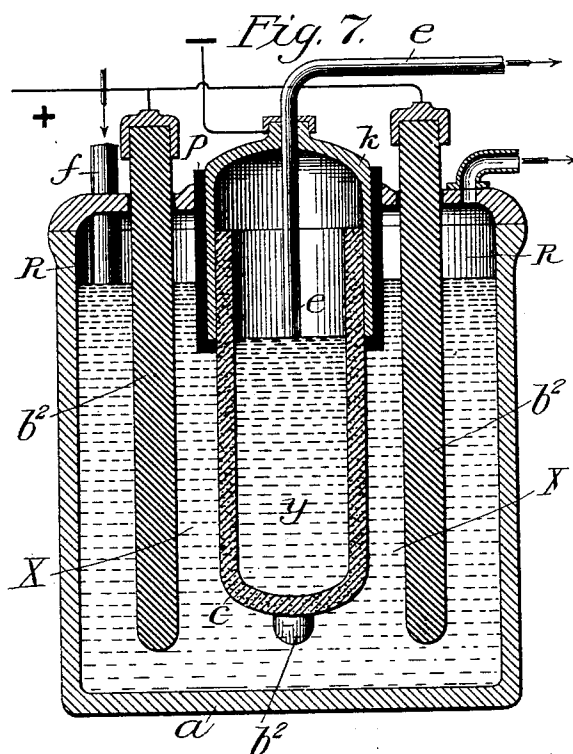
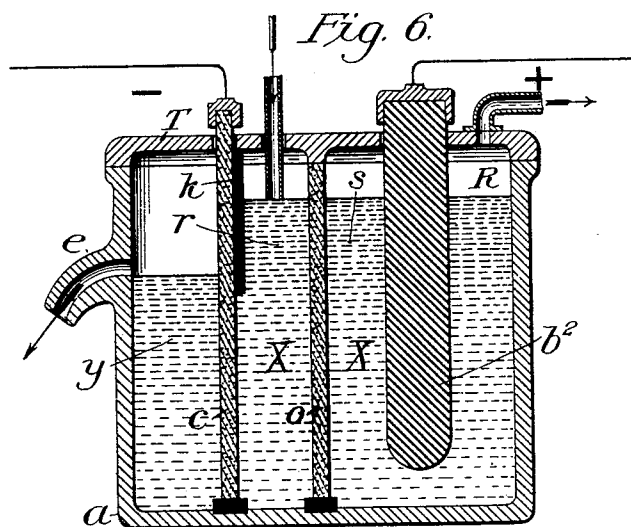
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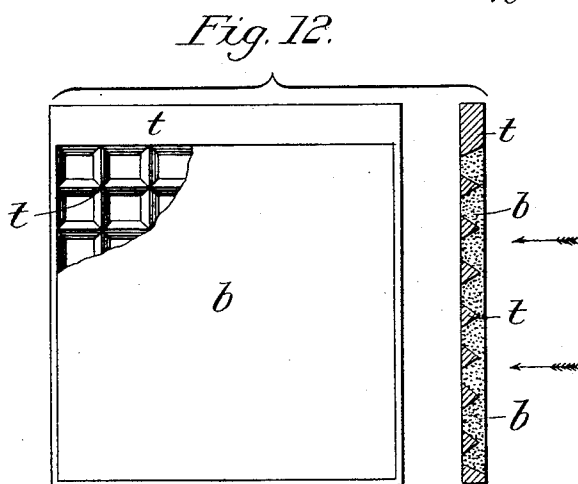
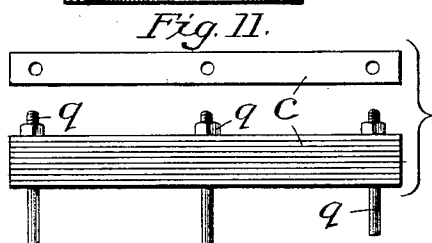
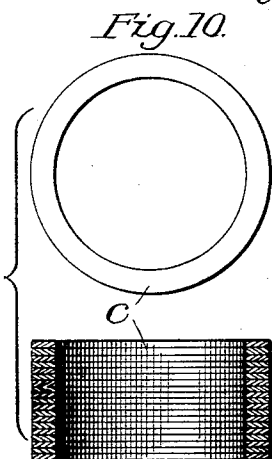
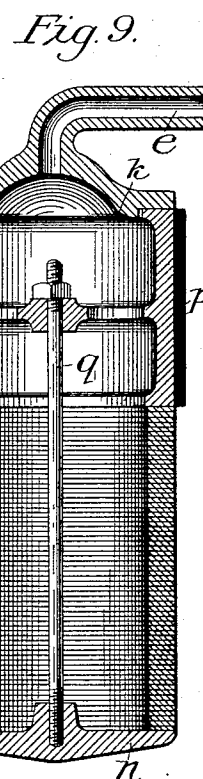
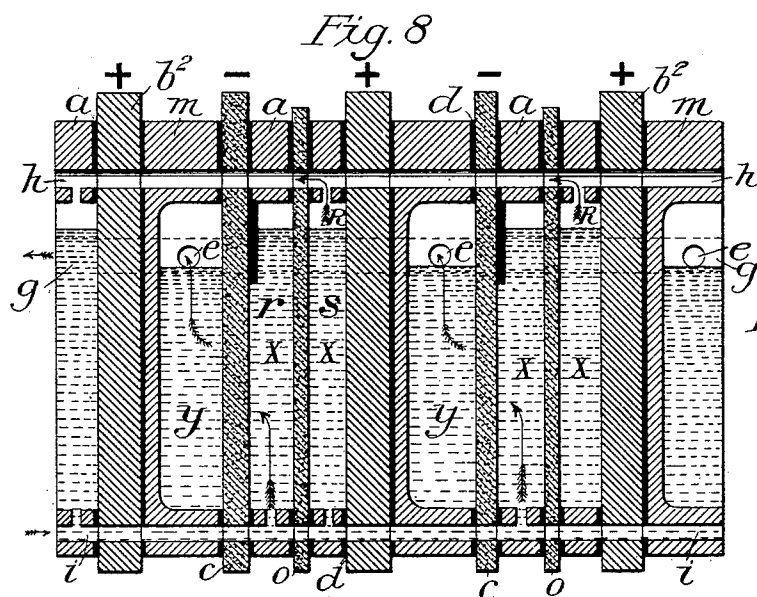
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# UNITED STATES PATENT OFFICE.

LÉON PAUL HULIN, OF MODANE, FRANCE.

## PROCESS OF ELECTROLYTIC DECOMPOSITION OF SOLUTIONS.

SPECIFICATION forming part of Letters Patent No. 586,236, dated July 13, 1897.

Application filed July 6, 1894. Serial No. 516,705. (No specimens.) Patented in France November 25, 1893, No. 234,327, and in Belgium November 27, 1893, No. 107,362.

*To all whom it may concern:*

Be it known that I, LÉON PAUL HULIN, of the city of Modane, Savoie, France, have invented improvements in the process of electrolytic decomposition of solutions and for the immediate separation therefrom of the liquid or dissolved electrolytic products, (for which I have obtained Letters Patent in France for fifteen years, dated November 25, 1893, No. 234,327, and in Belgium for fifteen years, dated November 27, 1893, No. 107,362,) of which the following is a full, clear, and exact description.

The electrolysis of saline substances gives rise to the formation at the electrodes of elementary products termed "ions," which appear either in the solid, liquid, or gaseous state, according to the kind of salt which is decomposed.

The ions may be divided into two categories—viz., first, the insoluble ions; second, the soluble or liquid ions. When these products are insoluble in the electrolyte, they separate of themselves and their extraction may be effected by simple mechanical means. Their insolubility places them outside of the electrolytic circuit and beyond the reach of secondary reactions. Under these conditions the electrolytic decomposition and the separation of the products are complete.

When the electrolytic products (ions) are soluble in the electrolyte, the progress of the electrolytic operation and the results which ensue therefrom are materially modified. The production of alkalies by the electrolysis of their salts in solution may, for instance, serve as a typical example to facilitate the comprehension of the developments herein-after set forth. These ions as soon as produced become diffused throughout the salt solution and form, with the undecomposed salt, mixed solutions, which become gradually richer in electrolytic products and proportionally poorer in the material operated on until a point is reached at which the real output of the operation is almost *nil*. The dispersion of the ions throughout the electrolyte is the primary cause of the failures experienced in electrolytic operations.

It has not heretofore been possible to lay hold of the ions without having allowed them

to accumulate in the neighborhood of the electrodes; but the total decomposition of the primary electrolyte not being practicable in the midst of the ions in excess a considerable proportion of undecomposed salt is carried off with them.

The accumulation of the ions in the electrolyte tends to cause them to recombine. A tension of reconstitution is generated, which increases with the proportion of ions present, so that the useful work is only the difference between the electrolytic output and the consumption due to the reunion of the ions.

The electrolytic action rapidly ceases to be totally efficient, for the dissolved ions themselves form one or several electrolytes either separately or by uniting with the solvent or with any other element present. The result is the production of what may be termed "lateral electrolysis," of which the importance increases as the strength in ions. Consequently a state of equilibrium between these inverse actions is inevitably reached, so that the electrolysis becomes factitious in that there is no ascertainable output notwithstanding that there still remains in the solution a considerable proportion of the salt to be decomposed. The useful effect obtained by increasing the electromotive force at the electrodes in order to obtain a more complete exhaustion is far from being proportional to this further expenditure of electrical energy, for besides the causes of loss above set forth the decomposition of the water of solution arises or increases. When the liquid ions are mixed with the electrolyte either by solution or simple dispersion, the practical results are nearly always poor or *nil*.

In order to overcome the anomalies above referred to and particularly to avoid the destruction of the products formed, recourse has been had heretofore to porous diaphragms, septa, or partitions of various kinds, dialyzers, bells, and other contrivances dividing the electrolyte into fractions or compartments respectively containing the anode and cathode. It has also been proposed to cause the ions to enter into a combination which is more stable than the electrolyte—that is to say, into a molecular group whose thermochemical value is higher than that of the compound

submitted to electrolysis. By these means the limit of useful decomposition is extended and the electrolysis of the ions attenuated as well as their recombination; but the electrical resistance is increased, the operation is complicated, and absolute constancy of the electrolytic bath is not obtained. This is due to the fact that none of these expedients solves the essential question, the fundamental condition upon which depends the avoidance of the difficulties above indicated. This radical solution of the question consists in effecting the immediate separation of the liquid ions at the precise point and instant where and when they are generated. It is this immediate separation which constitutes the very essence of my invention, and I will proceed to describe, with reference to the accompanying drawings, forming part of this specification, various examples of the means whereby it may be carried into practical effect.

The point of departure of my new method is based on the fact that the products of electrolysis (ions) are formed only on the electrodes. In examining this phenomenon in the case of the soluble or liquid ions I have ascertained that the extreme surface of the electrolyte by which the current enters the liquid—that is to say, the liquid layer without thickness which is the boundary of the bath in contact with the electrode—was exclusively composed of the product of electrolysis (ions). In order to seize hold of and separate this layer at the very moment when it is engendered by the electrolytic action, I have devised the idea of causing it to pass through the electrode itself to the rear of the electrolyzed bath by constructing the electrode in the form of a filter. By this means two simultaneous and continuous actions are established—viz., the electrolysis which produces the ions and the filtration which separates them from the electrolyte—and this by means of a single device, the filter-electrode. Such is the fundamental principle which constitutes the object of the present application for Letters Patent. These conjoint actions (electrolysis and filtration) have their values put in reciprocal harmony by means which will be hereinafter described with the apparatus.

The filter-electrode may be constituted in various ways, provided that it achieves the twofold object assigned to it. I employ by preference porous carbon in slabs, whatever may be its origin and details of manufacture, provided that it is prepared conformably with its destined use. This material is now manufactured by well-known methods. It is a good conductor of electricity, it is sufficiently unattackable under the conditions of its use, for my purpose it is readily made in the form of a homogeneous filtering medium, and it is cheap and commonly made of sizes required in practice. With two filtering-electrodes I construct my special apparatus, which consists, essentially, of a central compartment termed the “electrolytic compartment,”

which is limited on two sides by each of the active faces of the two filter-electrodes, (anode and cathode,) and of two lateral compartments termed the “evacuation-compartments,” which are contiguous to the inactive faces of the filter-electrodes.

The liquid to be electrolyzed is continuously supplied to the electrolytic compartment and penetrates the pores of the active faces of the filter-electrodes while undergoing decomposition, the ions filtering continually through and passing out at the inactive faces into the adjacent evacuation-compartments, where they are collected. This continual outflow of the ions through the electrodes is determined and regulated by a difference of pressure between the electrolytic compartment and the evacuation-compartments.

Figures 1 and 2 represent in vertical section and plan an example of the complete apparatus arranged in accordance with these essential principles, it being understood that it may be modified and supplemented in details. Fig. 3 is a vertical longitudinal section of another form of apparatus constructed in accordance with my invention. Fig. 4 is a similar section of still another form of apparatus constructed in accordance with my invention. Fig. 5 is a vertical transverse section of another form of apparatus embodying my invention. Fig. 6 is a vertical transverse section of another form of apparatus embodying my invention. Fig. 7 is a vertical transverse section of another form of apparatus embodying my invention. Fig. 8 is a vertical transverse section of another form of apparatus embodying my invention. Fig. 9 is a vertical transverse section of a modified form of filtering-electrode. Fig. 10 shows a detail of the construction shown in Fig. 9. Fig. 11 shows a plan and side view of a modified form of electrode. Fig. 12 is a side and sectional view of another form of electrode which I may employ.

In a rectangular tank *a*, of insulating material, are placed parallel to one another and at a certain distance from the ends two plates *b c*, of conductive and porous carbon, the dimensions of these plates being such as to make a tight joint *d* with the sides and bottom of the tank. The two filter-electrodes thus arranged divide the tank into the three main compartments, whereof the two outer ones are provided with outflow-apertures *e* at bottom, discharging, respectively, into receptacles *g h*. The middle electrolytic compartment is kept filled to a constant level by any suitable feed apparatus, which I have represented by the typical supply vessel *f*.

In order to enable the operation of my process and apparatus to be readily understood, I will take as an example the electrochemical decomposition of a solution of neutral sulfate of potash, it being understood that the process and apparatus are equally applicable to the electrolysis of all electrolytes which yield one or several liquid elements.

The decomposition of sulfate of potash as about to be described has for its principal object to produce a solution of caustic potash, but I also obtain as a by-product a solution of sulfuric acid.

In order to put the apparatus into active operation, the electrolytic compartment X is filled with a clarified solution of sulfate of potash and an electric current of suitable strength is passed through the electrodes *b c*, whereupon there is generated conformably with the laws of electrolysis upon every point of the active surface of the cathode a molecule of potash in a state of solution. Under the effect of hydrostatic pressure this stratum of potassic molecules penetrates the substance of the cathode and brings into contact therewith the adjacent stratum of liquid containing undecomposed salt, which is thereupon subjected to the electrolytic action and which in turn passes off into the filtering-orifices of the cathode. There is thus brought about a continual renewal of the parallel vertical strata of the liquid, which becomes electrolyzed on coming into contact with the cathode and which is absorbed by the latter and discharged at its opposite face into the evacuation-compartment *y*. At the anode a similar phenomenon occurs, it being in this case a continuous succession of liquid strata in which is generated a solution of sulfuric acid which, under the pressure of the electrolyte, passes as soon as formed into the filtering substance of the anode and runs off at the inactive face thereof into the other evacuation-compartment *z*. From the compartments *y z* the solutions of potash and sulfuric acid run off by the outlets *e* and are received in the respective vessels *g h*.

Instead of the filter-electrodes being arranged in a vertical position they may be placed horizontally the one above the other, as represented in Fig. 3, in which *a* is a frame, of insulating material, by which the electrodes are separated and against which they are clamped by the vessels *m* and *n*, secured together or to the intermediate frame *a* by any suitable appliances, means being provided for making tight joints at *d*. The solution to be decomposed is supplied continuously and at the required pressure from a reservoir *f*, placed at a higher level, through a pipe *i* to the space X between the electrodes and passes off through the filter-electrodes after having undergone electrolytic action, between which and the rate of evacuation of the ions a proper relation is maintained. With this arrangement the liquid-pressure, and consequently the filtration, are uniform over all points of the surface of the same electrode. The hydrostatic pressure which governs the output of the electrolyzed liquid is so regulated as to correspond to the electrolytic decomposition, or, in other words, the production and the evacuation of the ions is equalized either by regulating the pressure which governs the filtration or the intensity of the

current which determines the rate of production.

The respective outputs of the anode and cathode are regulated conformably with the relative values of the anion and cation either by selecting the electrodes experimentally, or by differentiating their surfaces and especially their thicknesses, or by compensating the difference by the accumulation on one of them of the filtered liquid, as at *z* in Fig. 3. Here, if as in the former case the solution supplied to X is sulfate of potash, potash is collected at *y* and sulfuric acid at *z*, these two solutions running off at the outlets *e*.

My electric process and apparatus permit in many cases of dispensing with the use of partitions and diaphragms and of thus reducing the internal resistance, and consequently of operating with a lower electromotive force. The regularity and constancy of the electrolyzed bath are also insured and the difficulties and losses due to the presence in the electrolyte of liquid ions obviated.

The evolution of gases which may take place at the filter-electrodes simultaneously with the production of the liquid ions forms no obstacle to the practical application of my process, such gaseous evolution being merely accessory to and independent of the principle of the invention. By preventing, if possible, the evolution of useless gases an advantage is gained, from an economical point of view, as well as greater regularity of working.

In the practical application of the process a sufficient number of my apparatus would be grouped together and connected up by suitable conductors or contacts, either in series or multiple arc, to a suitable source of electricity. By suitable arrangements, which will be readily imagined, a group of filter-electrodes may be grouped together in a single main tank. The electrodes, instead of being plane, may be of various forms—for instance, tubular, the external face being the active one and the interior the evacuation-compartment. Such an arrangement is shown in Figs. 7 and 9.

In the arrangement represented in Figs. 1 and 2 the filtration is not uniform over the whole height of the filter-electrodes, but in Fig. 4 I have illustrated a special arrangement of the electrodes and compartments whereby the filtering action is equalized over the whole height of a vertically-placed electrode. To accomplish this, I cover over its whole width the upper part of the active face of the electrode with a sheet of india-rubber *j*, closely applied, which descends a sufficient distance below the upper edge of the tank—say to the level of *k*, for instance. The discharge-outlets *e*, instead of being at the bottom, are situated in the sides of the compartments a little above the level *k*, so that at the back of the electrodes there is a constant head of liquid of less height than that in the electrolytic compartment X, and which has

the effect of equalizing the outflow pressure of the electrolyte at all points of its height, the effective pressure upon any given point of the electrode corresponding, in fact, to the difference of level between the liquid in the middle compartment X and that in the outflow-compartment—that is to say, to the height H.

In Fig. 4, *f* is the supply-reservoir, as before, whereby a constant level is maintained, and *y z* are the compartments where the ions are collected and whence they overflow through *e* into receptacles *g* and *h*.

Fig. 5 illustrates a modification of my apparatus whose main features are that the electrodes are vertical and have a uniform filtering action, the filtering pressures are variable at will, the elements are readily dismountable and are applicable to the decomposition of all chemical compounds producing soluble ions, this arrangement being particularly suitable for experimental work and research in laboratories and works. In this figure the same letters of reference have the same signification as in Fig. 3, *a* being the intermediate frame, between the opposite sides of which and the outer chambers *m* and *n* are clamped the filter-electrodes *b* and *c*, tight joints being made at *d*, the whole being held together by means of any suitable appliance, and *e* being the outlets by which the ions are discharged into the receptacles *g* and *h*. In order to regulate the relative outputs of the anode and the cathode, these receptacles may be placed at different heights, as shown.

*f* is the supply-reservoir, placed in communication with the middle compartment X by the tube *i*, *y z* being the compartments in which the ions are collected.

The filter-electrode may also be employed in any other form of apparatus. So, therefore, I do not limit myself to the precise construction and arrangement shown.

It will be understood that the arrangements of apparatus hereinbefore described and illustrated and the description of the particular cases in which they may be applied, as well as all the accessory details in the specification, are given by way of example only, and that the conditions under which the process may be applied are not in any way limited thereto. The basis of the invention is thus combined electrolysis and filtration, as described and claimed, considered *per se* and independently of any accessory circumstances which do not affect its essential principle.

It should thus be understood that every application of my process is inevitably characterized by the conjugation of electrolysis with filtration by means of a porous electrode and is independent of, first, the external form or composition of the filter-electrode; second, its mode of application or the apparatus in which it is employed or any accessory details with which it may be combined; third, the

nature of the electrolyte or the composition of the liquid ions to which it is applied; fourth, the intensity or electromotive force of the electric current serving for the electrolysis.

It has been before stated that the filter-electrode may be applied in any apparatus and with any other kind of electrode. I apply these apparatus having a single filter-electrode to all electrolytes yielding a liquid ion on the one hand and a non-liquid ion on the other hand, including solutions of alkaline chlorids, inasmuch as these yield alkali at the cathode (liquid cation) and chlorine at the anode (gaseous anion). An apparatus of this kind is represented in Fig. 6, in which the same letters of reference denote the same parts as in the previous figures. *c* is the filter-electrode, (cathode,) and *y* the evacuation-compartment. The supply-pipe and the exit *e* for the liquid ions are on the left, and at the center of the tank *a* is any suitable porous diaphragm *o*, dividing the electrolytic space into two compartments *r s* in the ordinary manner. *b*<sup>2</sup> is an ordinary suitable anode, generally consisting of a solid block of carbon.

Fig. 7 represents another form of apparatus characterized by the combination of a tubular filter-electrode *c* with ordinary anodes *b*<sup>2</sup> *b*<sup>2</sup>, consisting, for example, of rods circularly disposed around the electrode *c*. This tubular filter-electrode (of which mention has been made previously) is formed, like the others, of substances appropriate each case, to (such as carbon, porous metals, conductive and filterable agglomerates, thin annular disks superposed one on the other to form a tube of the kind shown in Fig. 9, &c.) said filter-electrode being closed at the bottom and inclosed at the top by a cover *k*, by which the current is introduced and through which passes a pipe *e* for the exit of the ions. The cap *k*, which is generally of metal, is protected exteriorly by an impervious insulating envelop *p*. The pipe *e* may either terminate toward the upper part of the electrode or be carried down toward the bottom. The filtration and discharge of the ions is preferably effected by establishing a vacuum in pipe *e*. This apparatus, like all the others, may be provided with a cover T or cap forming a chamber R above the electrolyte, in which may be received any gaseous ions disengaged at *b*<sup>2</sup> *b*<sup>2</sup>.

The apparatus illustrated in Fig. 5 may also be constructed by simply replacing one filter-electrode by an ordinary impervious electrode, and consequently dispensing with the evacuation-compartment Z. If necessary, the compartment X may be formed in two parts similar to the frame *a*, and between which may be placed an ordinary diaphragm. By connecting a series of elements or apparatus of this kind a group is formed which takes the external form of a filter-press, collecting-channels being provided for the introduction and

discharge of the liquids by the juxtaposition of the frames of which the elements of the electroly-filter are formed. Such an arrangement of apparatus is illustrated in Fig. 8, which represents a group of filter-electrodes *c* and of ordinary electrodes *b*<sup>2</sup>, made in the form of plates held between frames or cells of insulating material, as in the other figures.

*X* are the electrolytic compartments; *Y*, the evacuation-compartments. *o* are porous diaphragms separating the anodes and cathodes. *z* is the channel at which the electrolyte may be introduced. *I* is the outlet (indicated in dotted lines) for the liquid ions, and communicating with the evacuation-compartments by the lateral orifices *e*. To operate the filtration, a vacuum may be formed in channel *g*. The gases which disengage at the anode are discharged at one or more channels *h*—for example, at the upper part of the apparatus. A series of electrode-filter elements grouped in this manner and clamped between end plates by means of cross-bars, frames, or bolts forms a powerful apparatus for industrial uses.

The filter-electrode, and, indeed, all the apparatus, may act with highly-variable electric potentials, the intensity and electromotive force of the current employed depending solely upon the matters electrolyzed, or the products to be prepared, or the output which it is desired to obtain from each apparatus, or the greater or less economy which it is sought to realize.

The polarities of the electrodes marked in the drawings may be reversed, the poles having been merely indicated for the purpose of facilitating explanation.

Instead of employing carbon in the construction of my filter-electrodes any other material may be used—such, for example, as spongy metal when not liable to attack, or insoluble filtering conductive agglomerates mounted on a support or formed in a single piece. These electrodes may also be produced by superposing narrow thin strips of conducting material one upon the other and applying pressure to such an extent only as will allow of the liquid filtering between them, said strips being held together by means of a frame, rods, or other means of support, the space which intervenes between the strips representing the pores of the electrode. This form of filter-electrode is especially adapted for the tubular electrodes hereinbefore described. Fig. 9 represents one of these electrodes composed of a column of rings of thin sheet metal *c*, Fig. 10, which are suitably clamped between the bottom disk *n* and the cap *k* by means of a central rod *q*. In this manner a tubular filter-electrode is produced which may be employed for the purposes of the electroly-filter herein described with reference to Fig. 7.

To make flat electrodes of the same kind, I employ thin metal strips *c*, as shown in Fig. 11, which are either perforated or slitted, laid

one on the other and clamped by means of rods *q* or other suitable means, so as to form a plate whose thickness is equal to the width of the strips, as clearly shown in the figure.

I may also form my filter-electrodes of cellular conducting-frames filled with powders suitably agglomerated or of porous or spongy substances of the kind used in electrodes for secondary batteries. Such an arrangement of filter-electrode is illustrated, by way of example, in face view and transverse section in Fig. 12, in which *b* is the agglomerated active porous material, and *t* the conducting-grid forming the support for the filtering material and distributing the current throughout the mass. It will be evident that electrodes of this kind might be made tubular or of any other external form. The arrows show the direction of the filtering action.

The electrolyte may, according to circumstances and the nature of the salts treated by this system of electroly filtration, be either heated or cooled or placed in any accessory physical or mechanical condition.

The process herein described, based on the filter-electrode, forms a general method of electrolysis which may be applied to electrolytes of all kinds and conditions capable of yielding one or more filterable ions, it being especially valuable for the preparation of unstable composite products resulting from electrolytic synthesis.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, I declare that what I claim is—

1. The herein-described process of electrolysis, the same consisting in confining an electrolyte between two permeable electrodes constituting an anode and a cathode, in thereupon passing a current through the electrodes and electrolyte and causing the resulting anions to filter through the anode and the cations to filter through the cathodes, substantially as described.

2. The herein-described process of electrolysis, the same consisting in confining an electrolyte between two permeable electrodes constituting an anode and a cathode, in thereupon passing a current through the electrodes and electrolyte and carrying off the ions in solution through each electrode at the precise point where they are generated on the electrodes, substantially as specified.

3. The herein-described process of electrolysis, the same consisting in subjecting an electrolyte to the action of porous or filter electrodes having only one electrically-active surface exposed to the pressure of the electrolyte while the other electrically-inactive surface is subjected to a lesser pressure and gives passage to the ions, as specified.

4. The herein-described electrolytic apparatus, the same consisting of a tank or cell adapted to confine an electrolyte, two of whose sides are composed of porous electrodes, one

of the said sides being an anode and the other a cathode, substantially as described.

5 5. The herein-described process for the production of liquid products capable of being produced by electrolysis, the same consisting of confining a suitable electrolyte within a cell having walls composed of porous electrodes one of said electrodes being an anode and the other a cathode and in thereupon  
10 passing a current of electricity through the electrodes and regulating the current so as to maintain such a difference of potential between the electrodes that only soluble ions

are formed in the operation upon the filter-electrodes.

15 The foregoing specification of my improvements in the process of and apparatus for the electrolytic decomposition of solutions and for the immediate separation therefrom of the liquid or dissolved electrolytic products, 20 signed by me this 12th day of June, 1894.

LÉON PAUL HULIN.

Witnesses:

EDWARD P. MACLEAN,  
ALBERT MOREAU.