

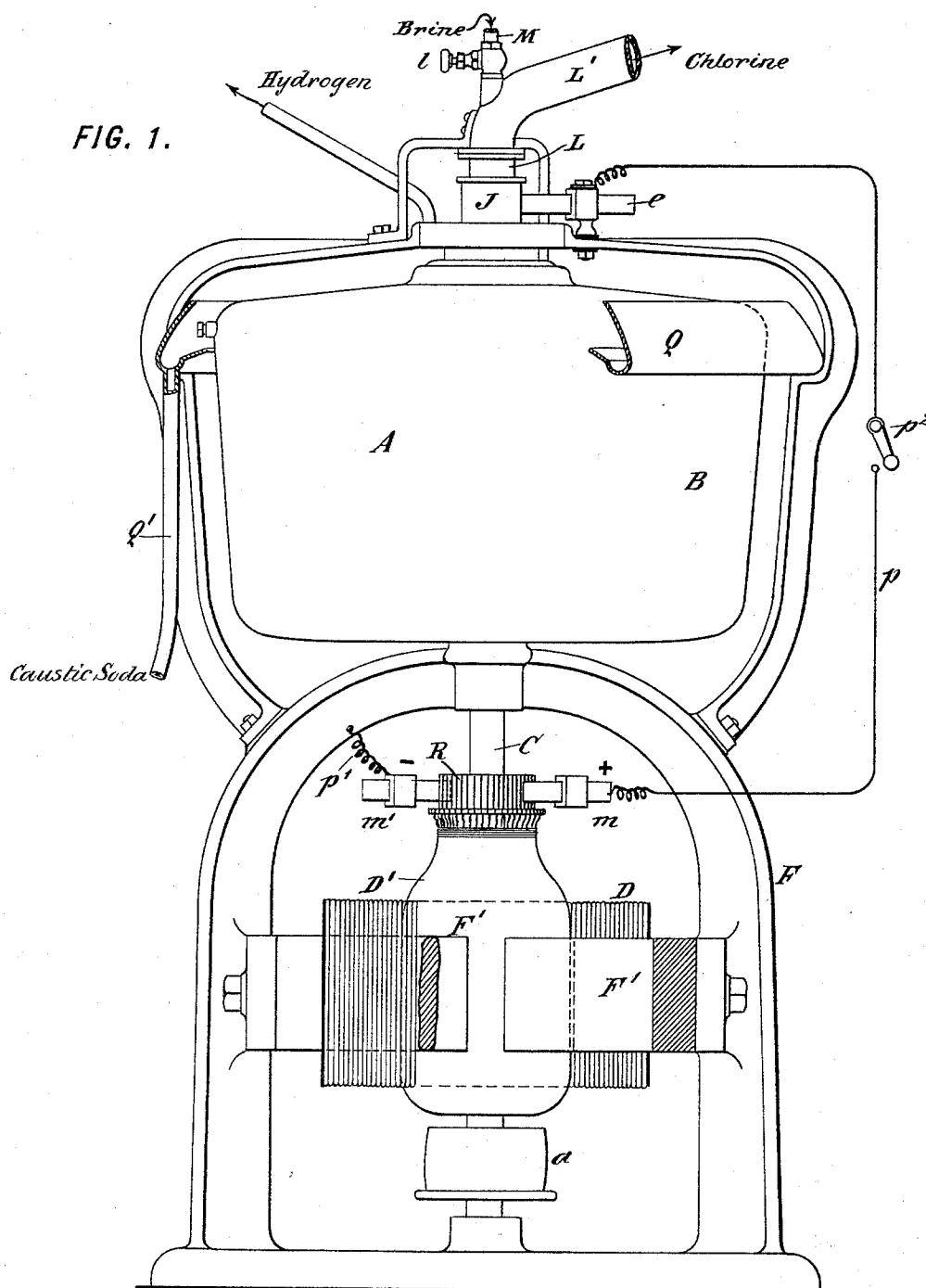
(No Model.)

3 Sheets—Sheet 1.

H. BLACKMAN.
ELECTROLYTIC PROCESS AND APPARATUS.

No. 484,990.

Patented Oct. 25, 1892.



WITNESSES:

John Becker
Fred White

INVENTOR:

Henry Blackman,

By his Attorneys,

Arthur C. Frazer & Co.

(No Model.)

3 Sheets—Sheet 2.

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FIG. 2.

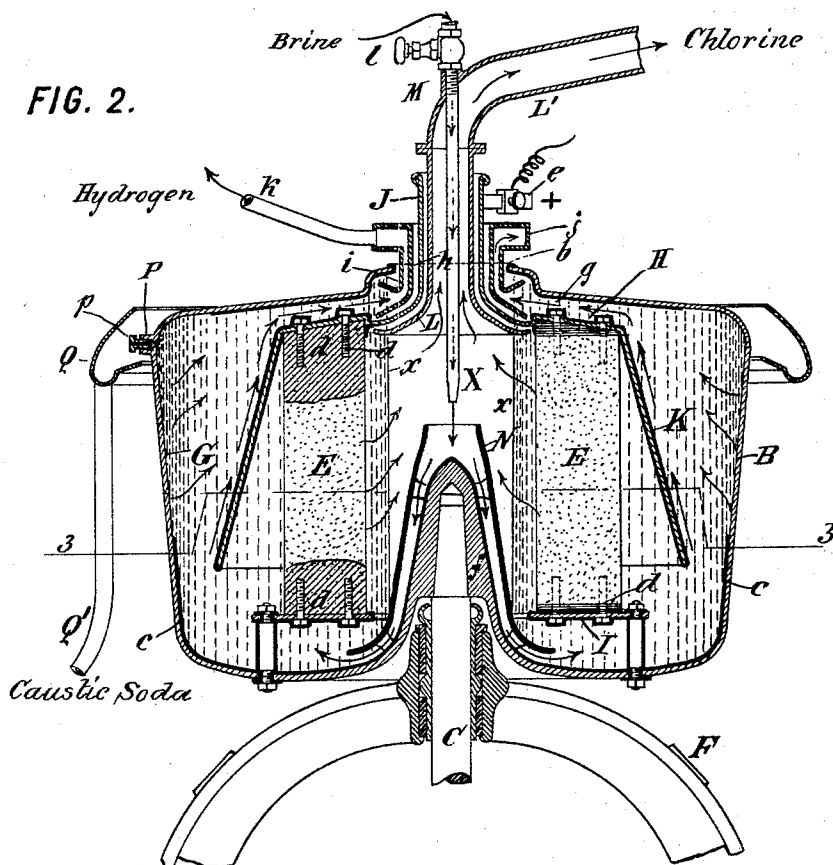
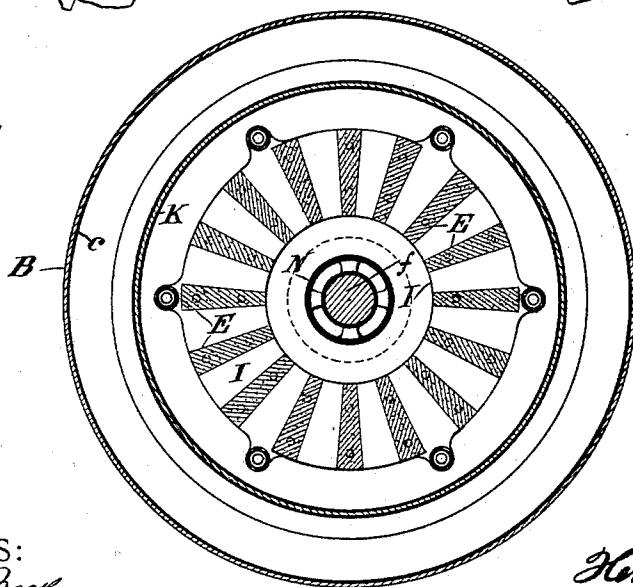


FIG. 3.



WITNESSES:

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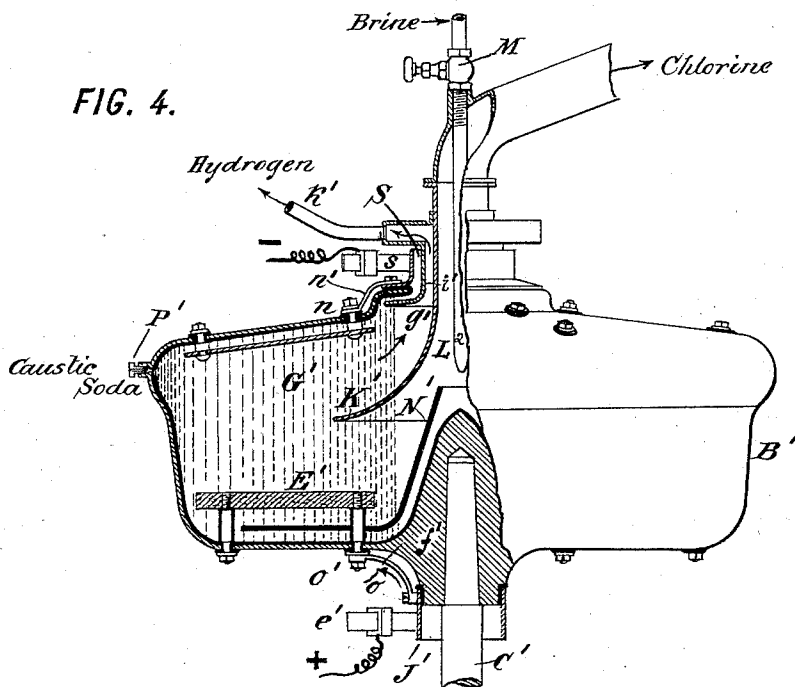
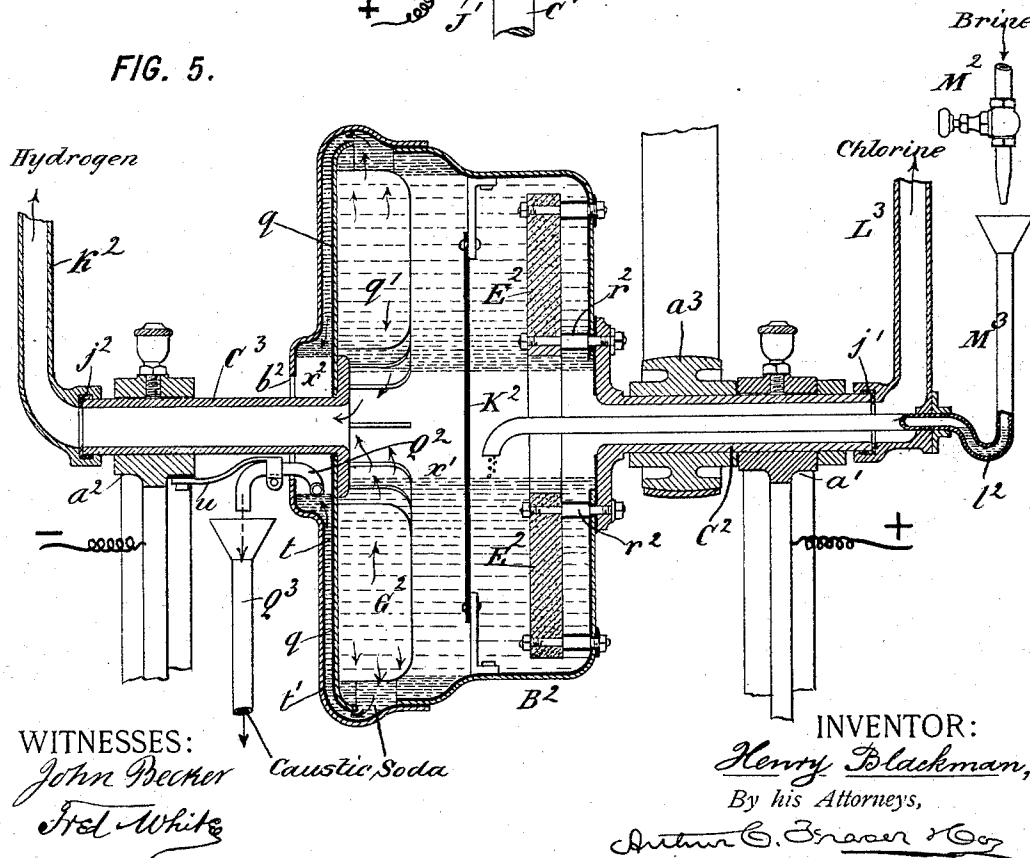
Arthur C. Fraser & Co

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**FIG. 5.**

UNITED STATES PATENT OFFICE.

HENRY BLACKMAN, OF NEW YORK, N. Y.

ELECTROLYTIC PROCESS AND APPARATUS.

SPECIFICATION forming part of Letters Patent No. 484,990, dated October 25, 1892.

Application filed January 15, 1892. Serial No. 418,090. (No model.)

To all whom it may concern:

Be it known that I, HENRY BLACKMAN, a citizen the United States, residing in the city, county, and State of New York, have invented certain new and useful Improvements in Electrolytic Processes and Apparatus, of which the following is a specification.

My invention relates to means for performing chemical decompositions by electrolysis. Such electrolytic decompositions are commonly performed in a stationary cell in which an anode and cathode are placed, separated in some instances by a porous partition, while the electrolyte or liquid to be decomposed is contained in the cell and comes in contact with the anode and cathode. In certain kinds of electrolytic decomposition difficulty is experienced by reason of the chemical affinities of the substances resulting from the decomposition, whereby these substances seek to recombine and form some other substances differing from the original electrolyte and affording less resistance to decomposition, so that these other or reconstituted substances are thereafter decomposed by the current in preference to the electrolyte, thereby giving rise to a local action in the cell, by means of which heat is generated and the electric power is wasted. Several expedients have been resorted to in order to avoid this difficulty.

My invention is particularly designed for the generation of chlorine and caustic soda by electrolysis from a solution of common salt. Such a solution or brine consists of sodium chloride (NaCl) dissolved in water, (H_2O). With the passage of an electric current the sodium chloride is decomposed, its chlorine (Cl) being liberated at the anode, and its sodium (Na) at the cathode, where the liberated sodium immediately decomposes, water uniting with one equivalent of oxygen and hydrogen, forming sodium hydrate or caustic soda, (NaHO), while the other equivalent of hydrogen escapes as a gas bubbling up from the cathode. The products of the operation are, consequently, sodium hydrate dissolved in water, chlorine in gaseous form, and hydrogen in gaseous form. It is practically essential to prevent any contact between either the chlorine and the hydrogen, which would form hydrochloric acid, or the chlorine

and the caustic soda, which would form chlorinated soda. In the former case the chlorine would be converted from a valuable into a comparatively-worthless condition, while in the latter case the chlorinated soda in solution would be decomposed by the current more readily than the brine, and after being thus decomposed would immediately and constantly recombine, thereby absorbing the electric power in useless local action and more or less suppress the electrolytic decomposition of the brine. According to my invention I overcome the difficulty of the tendency to recombination of these substances by utilizing the varying specific gravities of the electrolyte and of the products of the electrolysis to keep the latter from coming into contact with one another. A solution of caustic soda has a slightly-greater specific gravity than a saturated solution of common salt; but this difference is not sufficient under ordinary circumstances to insure the separation of the former from the latter by gravity alone. Consequently in electrolysis as heretofore practiced when the liberated chlorine, which is largely soluble in brine, impregnates the latter, in which, also, the caustic soda is largely diffused, the chlorine and caustic soda are brought into contact by reason of being both held in solution in the brine, and they are thereby permitted to recombine. According to my invention, however, I introduce the principle of centrifugal action in order to make the differences of density effective to separate the respective products and to keep them wholly out of contact with one another, whereby the possibility of their recombining is avoided. By carrying on the electrolytic decomposition in a rapidly-revolving vessel of the nature of a centrifugal machine the differences of specific gravity of the respective liquids are so augmented that they resolve themselves into distinct layers, and all mixture of the respective products of the electrolysis is avoided. At the same time I am able to render the electrolytic decomposition a continuous process, the brine being fed into the machine in a continuous stream and the chlorine and caustic soda being continually drawn off therefrom.

My invention constitutes a new discovery in the art of electrolytic decomposition,

whereby many of the difficulties heretofore considered insuperable in the practice of this process are overcome.

My invention is not limited in its application to the electrolysis of brine for the production of soda and chlorine, but is applicable to many other electrolytic decompositions.

In practicing my invention I provide a suitable circular vessel mounted on a vertical shaft adapted to be revolved at high velocities. This vessel is adapted to receive the brine or other electrolyte and to contain it while whirling at the highest speed. From the central portion of the vessel an outlet-passage leads off to conduct away the chlorine gas. Another passage is also provided for conducting away the hydrogen. An anode is provided, arranged to be submerged in the electrolyte during the whirling of the vessel and provided with means for conducting an electric current to it from the exterior. This anode consists, preferably, of a plate or plates of carbon. A cathode-surface is also provided, which may consist of the exposed surface of the vessel if the latter be made of iron or other suitable metal or of a separate plate of iron or other suitable material constructed within the vessel, means being provided for conducting the current away from the cathode while the vessel is revolving.

In operation chlorine gas is liberated in bubbles at the anode and hydrogen gas at the cathode, and both being of much less specific gravity than the electrolyte (brine) are forced rapidly toward the center. To prevent their mixing, a partition is provided which separates the chlorine-outlet from the hydrogen-outlet. Simultaneously sodium hydrate is generated against the cathode, and by reason of its greater specific gravity it instantly separates itself from the brine and forms in a distinct annular layer against the outer portion of the vessel. A minute delivery-orifice communicates with this outer portion for permitting the sodium hydrate to escape as it is generated, the escaping drops being thrown off tangentially and caught in a trough.

I will now proceed to describe my improved apparatus in detail with reference to the accompanying drawings, wherein—

Figure 1 is an elevation, partly broken away and in section, showing the entire apparatus. Fig. 2 is a vertical mid-section of the centrifugal electrolytic cell, showing it in operation. Fig. 3 is a horizontal section thereof on the line 3 3 in Fig. 2. Fig. 4 is an elevation, partly in vertical mid-section, of a modified construction. Fig. 5 is a vertical mid-section of a further modification.

Fig. 1 shows the entire machine, of which the lower portion (lettered D) is the dynamo for generating the electric currents, while the upper portion (lettered A) constitutes the centrifugal machine.

Fig. 2 shows the details of construction of the centrifugal machine. It comprises an outer vessel B, mounted on the vertical shaft

C, so as to be rapidly revolved by means of a belt on a pulley *a* or otherwise. This shaft is supported in suitable bearings in the frame F of the machine.

The centrifugal vessel or cylinder B is made of suitably-strong material, preferably wrought or cast iron or steel, and is closed at the top to within a suitable distance of the center, leaving a central opening or neck *b*. The interior surface of the vessel B should be covered with insulation, as shown at *c c*, except where the cathode-surface is located. By omitting the insulation at this portion the cathode G is constituted, consisting merely of the naked iron surface left by interrupting the insulation *c*.

The anode E consists, preferably, of refractory retort-carbon, which may be variously arranged, preferably in the form of radial plates, as best shown in cross-section, Fig. 3. These plates are fastened at top and bottom between supporting-plates H and I, which may be of iron or other metal, and to which the plates of carbon may be fastened by bolts or pins *d d* or otherwise. The plate H is preferably formed integrally with or is otherwise connected to a tubular conducting-sleeve J, which passes up through the opening *b* and projects above the top of the cylinder B, its metallic surface being bared and rubbed by a conducting-brush *e*, connected with the positive pole of the dynamo. By this means the electric current enters through the brush *e* and passes down through the conducting-tube J to the plate H, and thence into the carbons E E, constituting the anode. From these carbons it passes through the electrolyte to the cathode-surface G and thence through the conducting medium of the cylinder B to its hub *f* and out by the shaft C and its bearings to the frame F, which is connected to the negative terminal of the dynamo.

An intercepting shield or partition K is constructed within the cylinder B and between the anode and cathode in order that the bubbles of hydrogen liberated from the cathode-surface may be prevented from coming into contact with the anode. By reason of the coning of this shield the hydrogen is caused to travel upward and pass out through a space *g* beneath the top side or cover of the cylinder B.

In order to insure that the shield shall intercept all of the hydrogen bubbles and prevent their reaching the anode or coming in contact with the evolved chlorine, the shield should extend lower down than the cathode-surface G, as shown. The hydrogen bubbles are caught in a funnel-shaped space between two tubes *h* and *i*, and the hydrogen passes up through the annular space between these tubes into a chamber *j*, and thence is conducted away through a pipe *k*. The flaring ends of the tubes *h i* extend outwardly beyond the annular level assumed by the liquid at *x* while undergoing rotation, so that there-

by a liquid seal is formed, constituting a practically-frictionless packing between the stationary tubes *i h* and the revolving cylinder. The chlorine as it is revolved against the surfaces of the anode E is by reason of its inferior specific gravity thrown inward toward the center, occupying thus the tubular space or core X, left within the body of whirling liquid, and from this tubular space it passes up through a chlorine-conduit L, consisting of a stationary tube passing down through the sleeve J, with its lower end flared or trumpet-shaped, and extending outwardly slightly beyond the annular surface *x* of the liquid to form a liquid seal. This tube L is fastened to a fixed tube L', through which the chlorine gas is conducted away.

In order to be able to continuously introduce the brine to be decomposed, a pipe M is provided leading from a suitable tank of brine and controlled by a valve *l*. This pipe enters through the pipe L' and extends down through the pipe L and core X for a greater or less distance, terminating, preferably, just above the top of a funnel-shaped casing N, which receives the entering brine. This casing is fastened to the hub *f*, so that it revolves with the cylinder, and surrounds the hub at a little distance, so as leave an annular space or conduit between, down which space the brine flows and is discharged at the bottom of the cylinder beneath the plate I.

For the discharge of the generated caustic-soda solution an outlet-orifice P is provided at the outermost portion of the cylinder B. This orifice is made adjustable by means of a screw *p*, so that the quantity of liquid discharged can be so regulated as to be commensurate with the rapidity with which the caustic soda is generated. The discharged solution is thrown radially outward in drops, which are caught by an annular stationary trough Q and conducted away through a pipe Q'.

The operation is as follows: The proper quantity of brine is first placed in the centrifugal machine and the latter is revolved until by reason of the centrifugal force the brine is thrown outward and brought up to the level denoted at *x x*. The electric current is then turned on, passing from the brush *e* through tube J, anode-carbons E E, and the body of brine to the cathode-surface G, and out through the material of the cylinder B and shaft C to the frame F, as described. All the metallic portions of the apparatus that are in contact with the electrolyte are insulated, in order to confine the current to this path. The insulating-coatings are shown in Fig. 2 in solid black. The chlorine and hydrogen generated against the anode and cathode are by reason of their inferior specific gravity thrown centripetally, and being generated on opposite sides of the shield K are kept separated by the latter. The chlorine passes out from the space X through the tubes L L', while the hydrogen passes out through

the space *g*, between the tubes *h i*, and is led away through the pipe *k*. The caustic soda as fast as it is formed seeks the outermost portion of the cylinder B. As the outer walls of the latter are preferably made flaring, the solution travels upwardly and collects annularly at the upper portion thereof, from which it is constantly discharged through the outlet P. As fast as the electrolyte wastes away by being decomposed its volume is restored by the graduated stream introduced through the pipe M.

This apparatus has many advantages over any electrolytic cell or tank heretofore employed. By reason of the centrifugal separation of the solutions of different densities, all recombination of the generated chlorine and caustic soda is absolutely prevented. By reason, also, of the arrangement of the anode and cathode surfaces on opposite sides of an intercepting shield or partition K the chlorine and hydrogen are kept out of contact, and their recombination to form hydrochloric acid is prevented. A further important advantage is that the generated soda is discharged from the machine in the condition of a very nearly pure solution of sodium hydrate in water, and almost entirely free from admixture with brine, so that but little or no subsequent treatment will be required in order to free the caustic soda of salt. Furthermore, the caustic soda is discharged in a solution of the greatest-possible density, so that the minimum amount of concentration by boiling down will be required in order to reduce it to the form of solidified or drum soda. A further advantage is that by reason of the centrifugal pressure exerted to throw the evolved chlorine and hydrogen gases toward the center the bubbles of these gases will cling for only an instant to the anode and cathode surfaces, so that these surfaces will constantly be kept free from adherent bubbles and the partial polarization thereof be prevented. Hence the internal resistance of the cell will be diminished.

My invention also contemplates the simultaneous utilization and generation of the electric currents required. To this end my improved machine is constructed as a combined dynamo and centrifugal machine, as shown in Fig. 1. The same shaft C which carries the cylinder B carries, also, the armature D' of a dynamo D, the field-magnet F' of which is mounted fixedly on the supporting-frame F. The commutator R is fixed on the shaft and its segments connected with the terminals of the armature-coils in the manner usual in dynamos, the current being taken off by positive and negative commutator-brushes *m m'*. From the positive brush *m* the current is led by a wire *p* to the brush *e*, which admits the current to the anode, while the current from the cathode passes out by the frame F, as already described, and is taken therefrom through the wire *p'* and led to the negative brush *m'*. A switch

p^2 may be provided for breaking the circuit when starting, if desired, in order that the brine may be brought fully under centrifugal action before the current is turned on. The field-coils of the dynamo may be wound in shunt or series or with a compound winding in any manner known to the art of dynamo construction, and the proportions of the dynamo should be such as to deliver at the speed determined upon such electro-motive force as is necessary to cause the required volume of current to pass through the centrifugal machine and the armature should be so wound as to admit of the passage of this current without injury, all as will be obvious to any competent electrician. By thus combining the dynamo and centrifugal machine in one the running of circuit-wires through the works is avoided and all difficulty due to the short-circuiting of the current by reason of defective insulations is overcome. Each separate machine is consequently self-contained and independent of every other, and it is only necessary to supply the requisite power for driving each at the proper speed. There is, also, the important advantage that any reduction in speed of the centrifugal machine due to accident or to a falling off in the driving-power or otherwise, whereby the separating action of the centrifugal machine is impaired, is accompanied simultaneously by a proportionate reduction in the electro-motive force, and consequently in the volume of current traversing the centrifugal electrolytic cell, so that the electrolysis is proportionately diminished and the electrolytic products are consequently reduced in volume, thereby lessening the liability of any admixture and recombination. This I consider an important feature of my invention.

My improved centrifugal electrolytic apparatus may be modified in many ways without departing from the essential features of my invention. As examples thereof I have illustrated two such modifications in Figs. 4 and 5, which I will now describe.

Fig. 4 shows a cylinder B' mounted on a shaft C' and with a carbon plate E' fastened within it, near its bottom, to constitute the anode, and an iron plate G' , fastened within it, near its top to constitute the cathode. Both these plates are insulated from the cylinder and are connected to circuit-conductors, by which the current is introduced to the anode and taken off from the cathode. The current enters through a brush e' to a cylindrical sleeve J' , insulated from the hub f' , and passes thence through a conducting-strip o and insulated bolt o' to the carbon anode. From the iron plate G' the current passes through an insulated bolt n and conducting-strip n' to an annular collar S , mounted upon and insulated from the top of the cylinder, from which the current is taken off by a brush s . The brine is introduced, as before, through a pipe M' and drips down through the chlorine-pipe L^2 into

the annular casing N' , which discharges it beneath the anode. The chlorine liberated at the anode is thrown toward the center and passes out through the tube L^2 , the trumpet-shaped lower end of which (lettered K') dips deeply into the liquid and serves the purpose of the partition K in the previous construction for keeping the chlorine and hydrogen out of contact. The hydrogen evolved from the cathode G' is thrown toward the center, passing on the opposite side of this trumpet-shaped shield K' , and passes up through the space g' between the tube L^2 and a tube i' , being conducted away through a tube k' . The caustic soda is discharged through an outlet-orifice P' , as before described. The upper part of the cylinder B' is made of larger diameter than the lower part, in order that the caustic soda solution as it is generated shall be thrown outward and shall fill this enlarged upper portion, so that its descent into contact with the anode E' , and consequently where it would recombine with the chlorine generated at the anode, is prevented.

Fig. 5 shows a centrifugal electrolytic cell revolving on a horizontal axis. The cylinder B^2 is supported on shafts C^2 and C^3 , projecting axially from its opposite sides and turning in bearings a' a^2 . The anode E^2 consists of a disk of carbon, supported as in Fig. 4, while the cathode G^2 consists of the bared inner surface of a disk q , forming part of one end of the cylinder, supplemented by wings or blades q' , arranged radially and projecting perpendicularly from this disk. The central portion of the vessel B^2 is divided by a partition K^2 , consisting of a disk fixed within it and revolving with it. The shafts C^2 C^3 are insulated from each other by being insulated from the body of the cylinder B^2 . The current enters at the bearing a' , passes through the shaft C^2 and insulated studs r^2 to the anode E^2 , thence through the electrolyte to the cathode G^2 , and out through the material of the disk q and through the shaft C^3 to the bearing a^2 . All parts necessarily insulated for confining the current to this path are insulated, as shown in the drawings. The machine is driven by a belt on a pulley a^3 , fixed on one of the shafts. Brine is introduced from a pipe M^2 into a pipe M^3 , which is bent at l^2 to form a liquid seal or trap and extends in through the tubular shaft C^2 to deliver the brine into the interior of the cylinder. The chlorine evolved from the anode is thrown inwardly and passes through the tubular shaft C^2 , being drawn off through a stationary pipe L^3 , connected with the end of the revolving shaft by means of a packed joint j' , preferably packed with asbestos. Hydrogen liberated from the cathode G^2 is thrown toward the center and flows out through the tubular shaft C^3 , being conducted off through a stationary tube k^2 , which joins the revolving end of the shaft through the medium of a packed joint j^2 . The caustic-soda solution is thrown outward as it is generated and collects in the

enlarged left-hand end of the cylinder B², from which it flows gradually inward through the narrow space or passage *t*, formed between the disk *q* and the end *t'* of the cylinder. Through the open mouth *b* of the cylinder a bent pipe Q² enters and its open end dips tangentially into the level of liquid in this space *t*. This pipe Q² is adjustable on a supporting-standard *u*, so that it may be set with its end dipping more or less deeply into the liquid in this space. As the cylinder and liquid are revolving the revolving liquid is cut by the open end of this tube and a quantity of it is caused to flow into the tube, running out from its opposite end into a stationary tube Q³, which carries it away.

The operation of the apparatus is controlled by regulating its speed and regulating the rapidity of admission of brine at M² and of drawing off the caustic soda at Q². By reason of the greater specific gravity of the caustic-soda solution the level *x*² of that solution in the space *t* will coincide with a cylinder of larger radius than the level *x'* of the brine in the interior of the cylinder B².

In all the figures I have shown a separate conduit for conducting away the hydrogen gas, but this is not strictly essential, as this gas may be permitted to escape into the atmosphere. It is better, however, to conduct it away in order to avoid the liability of the formation of an explosive mixture of hydrogen and air.

The parts of the apparatus that come in contact with the chlorine gas should be made of such materials as will withstand the corrosive action of chlorine. Likewise those portions which are brought into contact with the caustic-soda solution should be of iron or other material which is not affected by caustic soda.

I claim as my invention the following defined novel features, substantially as hereinbefore specified, namely:

1. The improved electrolytic process consisting in subjecting the electrolyte to centrifugal action during the electrolysis, whereby the resulting products of different specific gravities are separated.

2. The improved electrolytic process consisting in subjecting a liquid simultaneously to electrolysis and centrifugal action and discharging the products thereby separated through distinct conduits.

3. The improved electrolytic process consisting in subjecting a liquid simultaneously to electrolysis and centrifugal action, whereby a gaseous product of the electrolysis is separated from the electrolyte, and discharging the separated gas.

4. The improved electrolytic process consisting in subjecting simultaneously to electrolysis and centrifugal action a liquid from which two gaseous products are liberated at the respective electrodes, and discharging said gases through distinct conduits to prevent their recombination.

5. The improved electrolytic process consisting in subjecting a liquid simultaneously to electrolysis and centrifugal action, whereby the resulting gaseous products are directed inwardly and the resulting liquid product of greater specific gravity than the electrolyte is directed outwardly, and continuously discharging the respective products through distinct conduits.

6. The improved process of making caustic soda and chlorine, which consists in subjecting brine to electrolysis and to centrifugal action.

7. The improved process of making caustic soda and chlorine, which consists in subjecting brine to electrolysis while under the influence of centrifugal action, whereby the resulting caustic soda is thrown outwardly and the chlorine gas directed inwardly, so that both are separated from the electrolyte, and continuously conducting away the disengaged chlorine.

8. The improved process of making caustic soda and chlorine, which consists in subjecting brine to electrolysis while under the influence of centrifugal action, whereby the resulting caustic soda is thrown outwardly and the chlorine gas directed inwardly, so that both are separated from the electrolyte, and continuously discharging the caustic soda and conducting away the chlorine.

9. The improved process of making caustic soda and chlorine, which consists in subjecting brine to electrolysis while under the influence of centrifugal action, whereby chlorine and hydrogen are generated and thrown inwardly and caustic soda is generated and thrown outwardly, and maintaining the separation of the chlorine and hydrogen and conducting them away through distinct conduits.

10. A centrifugal machine provided with an anode and cathode, and means for passing an electric current through them, whereby the contents of the machine may be subjected to electrolysis while whirling.

11. A centrifugal electrolytic cell consisting of a cylinder mounted to revolve, an anode and cathode therein arranged to be in contact with an electrolyte while revolving, and separate outlets for the liquid and gaseous products resulting from the electrolysis.

12. A centrifugal electrolytic cell consisting of a cylinder mounted to revolve, an anode and cathode therein arranged to be in contact with an electrolyte while revolving, and a gas-discharge conduit leading from the center of the cylinder.

13. A centrifugal electrolytic cell consisting of a cylinder mounted to revolve, an anode and cathode therein arranged to be in contact with an electrolyte while revolving, and two distinct gas-discharge conduits leading from the center of the cylinder, the one adapted to conduct away the gases liberated from the anode and the other those liberated from the cathode.

14. A centrifugal electrolytic cell consisting of a cylinder mounted to revolve and an anode and cathode therein arranged to be in contact with an electrolyte while revolving, 5 whereby a liquid of greater specific gravity than the electrolyte is thrown to the outer portion of the cylinder, and an outlet for said liquid from said outer portion.
15. A centrifugal electrolytic cell consisting 10 of a revolving cylinder provided with an anode and cathode, and a partition within said cylinder arranged to receive on its opposite sides the gases liberated from the anode and cathode, respectively, and to prevent the 15 commingling of said gases.
16. A centrifugal electrolytic cell consisting of a revolving cylinder provided with an anode and cathode, a partition within said cylinder arranged to receive on its opposite 20 sides the gases liberated from the anode and cathode, respectively, and to prevent the commingling of said gases, and two distinct gaseous outlets from said cylinder leading from the spaces on opposite sides of said partition.
- 25 17. A centrifugal electrolytic cell consisting of a revolving cylinder provided with an anode and cathode, outlets for continually discharging the products of electrolysis from said cell, and an inlet for continuously ad- 30 mitting the electrolyte thereto.
18. The combination, with a centrifugal electrolytic cell, of a dynamo for generating the electric current passed through said cell, connected together to be driven from the same source of power at proportionate speeds. 35
19. The combination, with a centrifugal electrolytic cell, of a dynamo for generating the electric current passed through said cell, having its armature mounted on the same revolving shaft as said cell, whereby the two 40 are revolved at the same speed.
20. The combination, with a centrifugal electrolytic cell having terminal electric connections leading to its anode and cathode, of 45 a dynamo the armature of which is mounted on the same revolving shaft as said cell, the stationary commutator-brushes of said dynamo, and electric connections joining the positive brush thereof to the terminal communicating with the anode and the negative 50 brush thereof to the terminal communicating with the cathode.
- In witness whereof I have hereunto signed my name in the presence of two subscribing witnesses.
- HENRY BLACKMAN.
- Witnesses:
GEORGE H. FRASER,
FRED WHITE.