

March 17, 1936.

W. S. CALCOTT ET AL

2,034,458

PROCESS AND APPARATUS

Filed Oct. 31, 1932

3 Sheets-Sheet 1

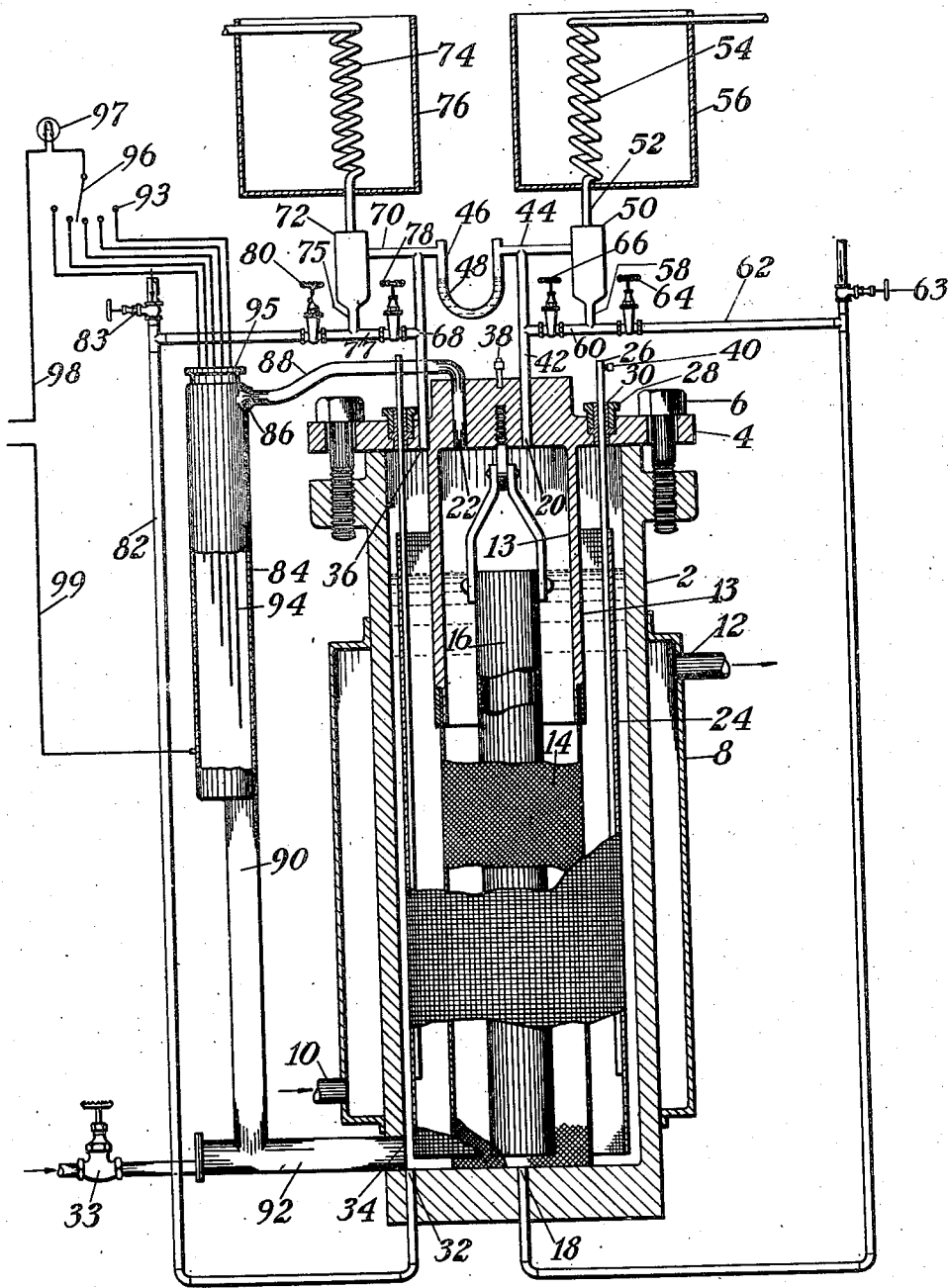


Fig. 1

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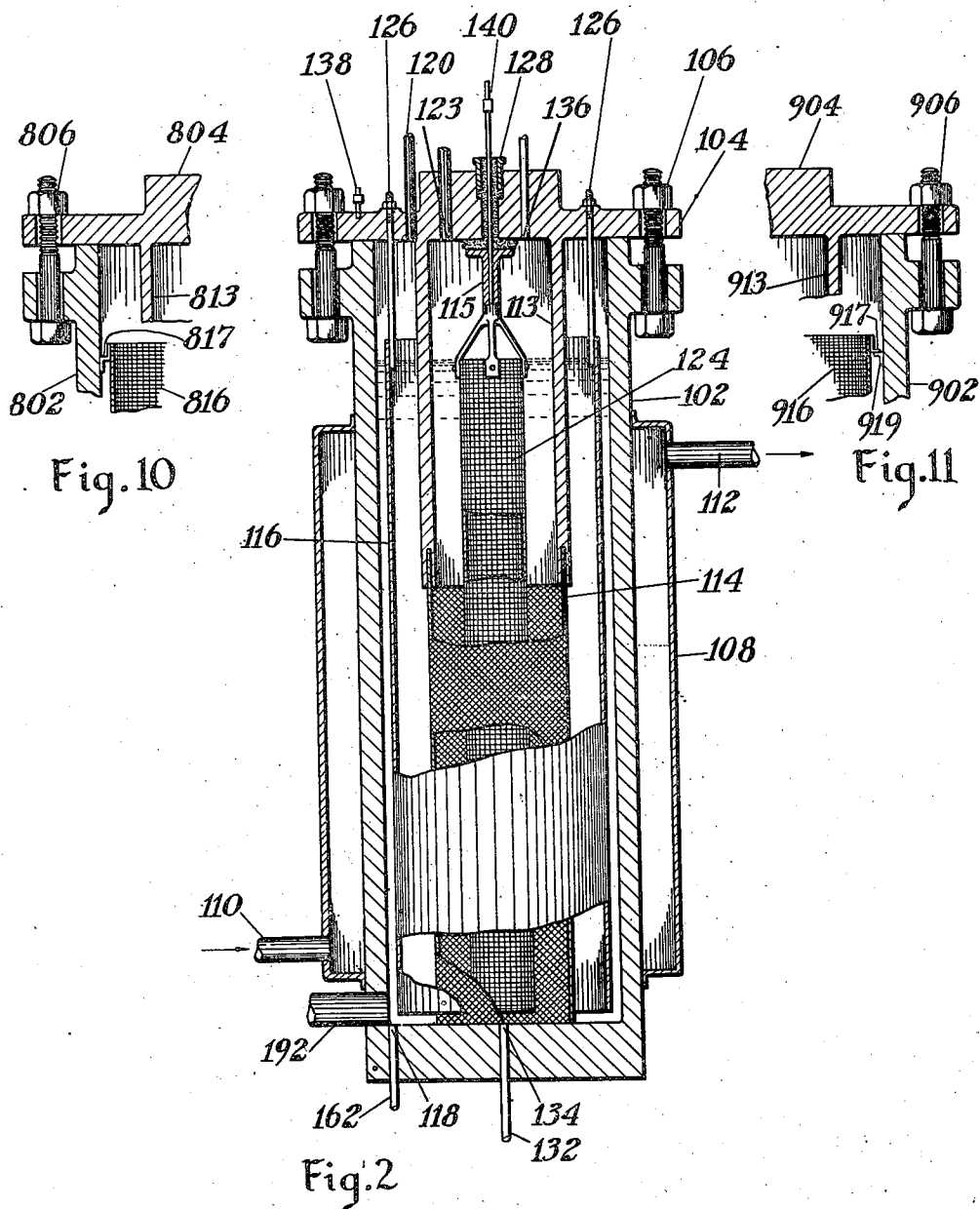
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3 Sheets-Sheet 2



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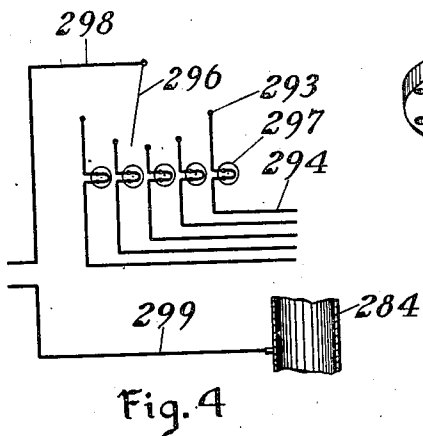
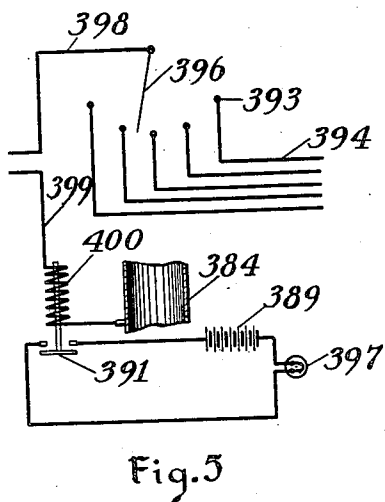
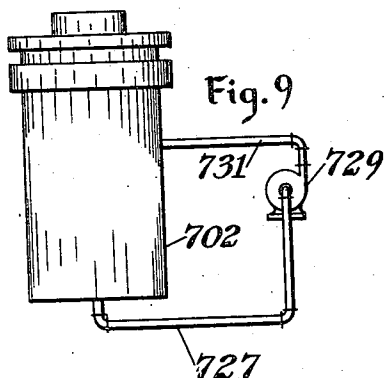
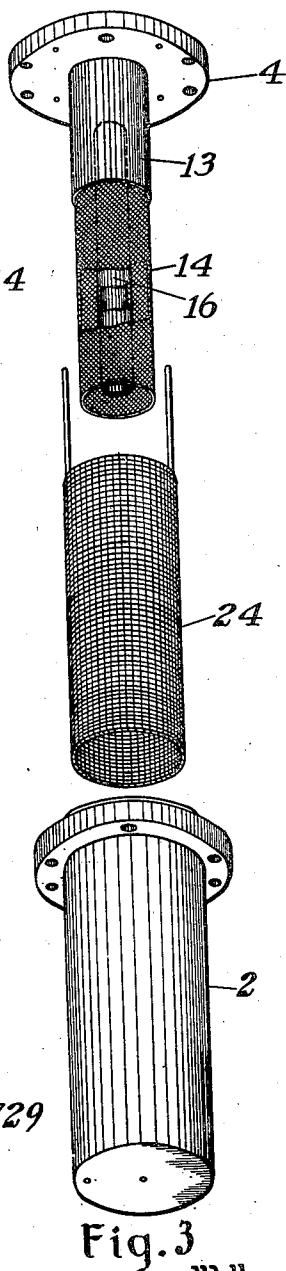
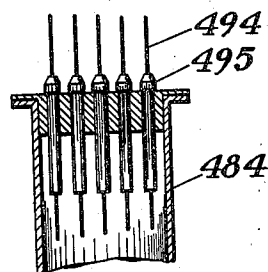
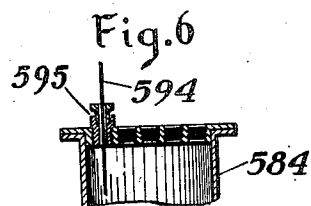
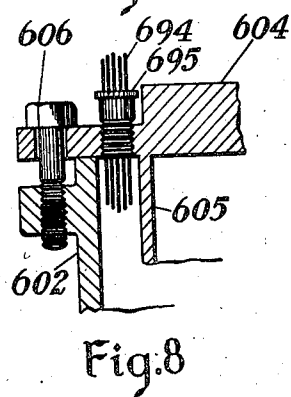
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PROCESS AND APPARATUS

Filed Oct. 31, 1932

3 Sheets-Sheet 3



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UNITED STATES PATENT OFFICE

2,034,458

PROCESS AND APPARATUS

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Application October 31, 1932, Serial No. 640,554

27 Claims. (Cl. 204—9)

This invention relates to fluorine, and a process for the production thereof. It further relates to an apparatus suitable for the production of fluorine.

It is an object of the invention to provide a new and improved type of apparatus suitable for the production of fluorine. A further object is the provision of a new and improved process for the production of fluorine. Other objects are the provision of a practical fluorine cell, the construction of an apparatus for the electrolysis of substantially anhydrous hydrofluoric acid, the construction of an apparatus in which anhydrous hydrofluoric acid can be electrolyzed by an intermittent and/or continuous process, and the construction of new and useful indicating and safety devices for a fluorine cell. Other objects will appear hereinafter.

These objects are accomplished by the electrolysis of substantially anhydrous hydrofluoric acid in an electrolytic cell in which the electrodes are not substantially attacked by fluorine and/or hydrofluoric acid.

The character of the apparatus falling within the invention is subject to considerable variation and modification in the manner of its practical construction but may be illustrated by the various forms of apparatus shown in the accompanying drawings, in which similar numbers refer to similar parts throughout the several views and the description thereof.

In the drawings:

Fig. 1 is a side view partly in section and somewhat diagrammatic of one form of the apparatus for carrying out the invention.

Fig. 2 is a view partly in section of a modified form of a portion of the apparatus shown in Fig. 1.

Fig. 3 is a perspective view partly in section of certain portions of the apparatus shown in Fig. 1.

Fig. 4 is a modified form of a portion of the indicating apparatus shown in Fig. 1.

Fig. 5 is another modification of the indicating apparatus shown in Fig. 1.

Fig. 6 is a view partly in section of a portion of the indicating apparatus shown in Fig. 1.

Fig. 7 is a modification of a portion of the indicating apparatus shown in Figs. 1 and 6.

Fig. 8 is a view partly in section showing a modified arrangement of a portion of the indicating and electrolyzing apparatus illustrated in Fig. 1.

Fig. 9 is a perspective view showing means for the circulation of the liquids within the apparatus illustrated in Fig. 1.

Fig. 10 is a sectional view of a portion of the

apparatus illustrated in Fig. 2 showing a modified means for maintaining one of the electrodes in position.

Fig. 11 is another sectional view showing a still further modified arrangement for maintaining one of the electrodes, illustrated in Fig. 2, in position.

Referring to Fig. 1 of the drawings, the apparatus illustrated comprises a container 2 in which the electrolyte is held. A removable top or cover 4 is attached to the outer casing of container 2 by a suitable fastening means, such as indicated at 6. The casing 2 is surrounded by a jacket 8 having an inlet 10 and an outlet 12 which permit the circulation of a heating or cooling fluid in heat exchange relationship for the purpose of maintaining the desired temperature within the cell. The cover 4 has a depending annular partition consisting of a solid metal wall 13 from which there depends a diaphragm in the form of screen 14. This annular partition divides the cell into two compartments. Within the inner compartment and attached to the top by suitable means is an anode 16. The anode compartment has an opening at 18 for the entry of electrolyte material, an opening 20, for the escape of liberated fluorine and an opening 22 which is connected with the electrolyte level indicating device herein described. Within the outer compartment and attached to the top by suitable insulating means is a cathode 24 shown in the drawings as a screen attached to vertical rods, such as indicated at 26. These rods are held in position by suitable stuffing box devices indicated at 28. A packing substance 30 within the stuffing box device serves to insulate the cathode 24 from the cover 4. The cathode compartment has openings 32 and 34 for the admission of the electrolyte substance and an opening 36 for the escape of liberated hydrogen.

In normal operation, the cell is preferably filled with the electrolyte to about the level indicated in Fig. 1, although the liquid level may vary widely. An electrolyzing current is supplied to the cell walls and top at a convenient terminal such as shown at 38 to cathode 24 by a suitable connection 40. Fluorine is liberated at the anode and escapes through opening 20 into a connecting line 42. This line is branched as shown at 44, one branch connecting with a U shaped manometer tube 46, containing a suitable fluid such as, for example, anhydrous hydrofluoric acid saturated with a soluble fluoride. The other branch is connected to a trap 50. The fluorine leaving the anode compartment passes through

opening 20 and line 42 into trap 50 and thereafter through line 52 into coil 54 to a suitable storage container (not shown). Coil 54 is surrounded by a cooling substance (not shown) held in container 56. Coil 54 is preferably sufficiently large in internal diameter so that fluorine may pass through and at the same time may allow any substance liquefying in the coil, for example, hydrofluoric acid to return to the trap 50. Trap 50 has a bottom outlet 58 branching into two lines 60 and 62. If it is desired to return the condensate to the top of the anode compartment, valve 64 in line 62 is closed and valve 66 in line 60 is opened, causing the condensate to enter the anode compartment through line 42 and opening 20. If desired, by closing valve 66 and opening valve 64, the condensed material may be passed through line 62, so that it enters the bottom of the anode compartment through opening 18.

The hydrogen liberated in the cathode compartment together with other gases or vapors present, such as hydrofluoric acid, passes upwards through opening 36 and line 68 into line 70, which is connected at one end with manometer 46 and at the other with trap 72. From line 70, the vapors pass into trap 72 and then into coil 74 which is surrounded by a suitable cooling medium (not shown) held in container 76. The temperature of coil 74, as well as that of coil 54 is preferably such as to condense vapors of hydrofluoric acid. Coil 74, as in the case of coil 54, is preferably sufficiently large to allow gases to pass upward and the condensate to flow downward at the same time. The condensate collected in trap 72 may be returned to the cathode compartment through the bottom outlet 75, line 77, valve 78, line 68 and opening 36 (valve 80 being closed). If desired, all or a part of the condensate from trap 72 may be returned to the bottom of the cathode compartment instead of the top by closing valve 78 and opening valve 80, thereby causing the condensate to pass through line 82 and enter the cathode compartment through opening 32.

A liquid level indicating device is provided to indicate the level of the electrolyte in the cell. This device consists of a well 84 having an opening at the top 86 connected to the opening 22 at the top of the anode compartment by means of a line 88 and also having an opening at the bottom through line 90 which connects with line 92, entering the cathode compartment through opening 34 so that the level of the electrolyte in well 84 is the same as the electrolyte level in the container 2. Extending different depths into well 84 are a series of wires generally indicated at 94 which are separately connected to terminals 93. The wires generally indicated at 94 are insulated in a suitable manner from the well at the top 95. A current source (not shown) is connected to indicator 97 through line 98 and also to the wall of well 84 through a wire 99. The depth of the electrolyte is then determined by moving the selector switch 96 in contact with the terminals 93 until a current through the electrolyte in well 84 is shown on indicator 97.

The cell operation may be intermittent or continuous, as desired. The design of the apparatus may be varied considerably. It may be desirable, for instance, to force the condensate from condensers 54 and 74 through lines 62 and 82, respectively, by means of pumps (not shown) connected in said lines. If desired, the electrolyte may be introduced into the cell or replenished, for example, by the addition of hydrofluoric acid, through valved inlets 33, 63 and 83.

The modification of apparatus shown in Fig. 2 shows the anode and the cathode reversed, i. e., the cathode compartment in the central portion of the cell with the anode compartment surrounding it. In Fig. 2, the container 102 is provided with a cover 104 held in place by a suitable fastening means, such as indicated at 106. As in Fig. 1, the container is surrounded by a jacket 108 having an inlet 110 and an outlet 112 which permit the circulation of a fluid in heat exchange relationship for the purpose of maintaining the desired temperature within the cell. The top or cover 104 has a depending annular partition consisting of a wall 113 having a depending screen 114, dividing the cell into two compartments. Within the inner compartment and attached to the top by a suitable means, such as indicated at 115 is a cathode 124 shown in the form of an annular screen or grid extending nearly to the bottom of the cell. The cathode is insulated from the cover by means of a suitable insulating medium held in a stuffing box 128. The cathode compartment has an opening 123 connected to a liquid level indicating device (not shown) such as described with reference to Fig. 1, and a second opening 136 for the escape of the gases formed during operation of the cell. This second opening 136 is connected to a condenser (not shown) such as described with reference to Fig. 1, and if desired, the condensate from said condenser may be allowed to run into the cathode compartment through this opening. Alternatively, as indicated in the description of Fig. 1, the condensate may be returned to the cathode compartment at the bottom through line 132 and opening 134.

Within the outer compartment and attached to the top 104 is an anode 116 attached to vertical rods 126. The anode compartment has an opening at the top through line 120 which serves as an outlet for fluorine liberated at the anode. Line 120 may be connected to a suitable trap and condenser (not shown) such as described with reference to Fig. 1, and if desired, the condensate may be returned to the anode compartment through this line. Alternatively, the condensate may be introduced into the bottom of the anode compartment through line 162 and opening 118. Line 192 is similar to line 92 in Fig. 1 and extends to a liquid level indicating device (not shown) and a reservoir of the electrolyte (not shown) as in Fig. 1. The cell is operated by an electrolyzing current introduced through conveniently placed terminals, as shown, for example, at 138 and 140. The features of the apparatus of Fig. 2, which are not shown, may be similar to those described in Fig. 1. The operation of the cells described in Figs. 1 and 2 may be substantially the same as regards the kind and amount of electrolyte, the current density, and the temperatures and pressures of operation.

In Fig. 3, certain portions of the apparatus illustrated in Fig. 1 are shown in perspective. These are the container 2, the cathode 24, and the partition between the cathode and the anode which consists of an annular wire screen 14 depending from a metal wall 13 attached to the cover 4. The anode in Fig. 3 is indicated at 16.

The modification of the liquid level indicating device shown in Fig. 4, differs from that shown in Fig. 1, in that the wires 294 which are connected to terminals 293 and extended different depths into the electrolyte well 284 each contain indicating devices 297, as for example electric light bulbs. Wires to a source of current are shown at 298 and 299, said wires being connected

to the selector switch 296 and the well 284, respectively. For convenience of illustration, portions of the well 284 and the wires 294 are broken away. The wires 294 are insulated from well 284 by any suitable means, e. g., as hereinafter described with reference to Figs. 6 and 7. The operation of this liquid level indicating device is substantially the same as that shown in Fig. 1.

In the modification of the electrolyte level indicating device shown in Fig. 5, a solenoid 400 is connected at one end to the electrolyte well 384 (shown with parts broken away) and at the other to a source of current by means of a wire 399. The other wire from the source of current is connected to a selector switch 396 by means of a wire 398. Selector switch 396 may be moved in order to contact the terminals 393 of the wires generally indicated at 394, which extend different depths into the electrolyte well 384. Wires 394 are insulated from well 384 by any convenient method. When a current passes through the solenoid, the piston 391 is drawn inward closing a battery circuit 389 connected to an indicator 397.

Figure 6 illustrates a method of insulating the wires 494 which extend to different depths into the electrolyte well 484. This insulation is effected in any suitable manner, e. g., by means of plugs consisting of a mixture of powdered aluminum fluoride and a wax such as ceresin generally indicated at 495. A modification of the method of insulation is shown in Fig. 7 wherein the wire indicated at 594 leading into the electrolyte well 584 passes through a packing box 595 containing the insulating composition. The remaining wires (not shown) may be similarly insulated.

If desired, the liquid level indicating device may be included directly in the cell container. This is illustrated, for example, in Fig. 8 which shows an upper corner of the cell partly in section and with parts broken away. In Fig. 8, the cell container is indicated at 602 and the top 604 is suitably fastened, for example, by means of bolts such as shown at 606. A depending wing 605 forms an electrolyte well with the casing 602. The wires 694 connected to a suitable indicating device, e. g., such as described in Figs. 1, 4 and 5, extend different depths into this electrolyte well through an insulator 695.

It may be desirable to agitate the electrolyte to prevent local concentration. This may be effected by suitable mechanical means or by circulation of the electrolyte, e. g., as illustrated in Fig. 9. In Fig. 9 a line 727 is shown leading from the bottom of the cell 702 to a pump 729 which in turn connects to a point higher in the cell through a line 731. The electrolyte may thus be circulated intermittently or continuously.

In Fig. 10, an upper corner of the cell is shown partly in section and with parts broken away, illustrating a modification of the apparatus described in Fig. 2. The portions shown are a part of the casing 802 and a part of the top 804 which is held in position by a fastening device such as indicated at 806. A part of the partition wall 813 is also shown with parts broken away. According to this modification, the anode, shown with parts broken away at 816, is welded to a projecting fastening device 817 which in turn is welded to the casing 802.

Another modification of the method of fastening the anode within the cell of Fig. 2 is shown in Fig. 11 in which the casing is indicated at 902, the top at 904, the partition at 913 and the anode at 916, all with parts broken away. The top is

held in position by a fastening means such as shown at 906. In this modification, an L shaped piece such as shown at 917 is fastened to the anode and another L shaped piece 919 in inverted position is fastened to the casing 902. By allowing the L piece 917 to rest on the inverted L 919, the anode may be held in position and at the same time be easily removable, as desired.

It will be recognized that the design of the apparatus above described may be varied widely as to mechanical details.

The anode may be constructed of any electrically conducting solid material which is non-polarizing under the conditions of operation and, at the same time, is resistant to the action of hydrofluoric acid and fluorine. Nickel has given very highly desirable results. In practice, we have found that a cell having a substantially pure nickel anode may be operated continuously or intermittently over a long period of time. Nickel alloys, preferably containing materials other than nickel in relatively small amounts, may be used as anode materials. Metals which may be alloyed with nickel for this purpose are, for example, iron, chromium, and/or cobalt. The amount of nickel which should be present in a nickel alloy to give desirable results may be determined by empirical tests. In general, the proportion of nickel should be sufficiently high to render the alloy non-polarizing under the conditions of reaction. The use of an anode containing nickel in a cell of this type is apparently novel. It should be noted that many materials of construction such as platinum or graphite which are useful as anode materials in many types of electrolytic cells are practically worthless for the commercial electrolysis of anhydrous hydrofluoric acid since they are not sufficiently resistant to the action of hydrofluoric acid and fluorine.

The cathode may be constructed of any electrically conducting solid material which is resistant to the action of anhydrous hydrofluoric acid and hydrogen. As specific examples of materials of construction which may be employed may be mentioned: iron (including grey and white cast iron), nickel, cobalt, copper, chromium, magnesium and alloys of any two or more of these metals. In operating the cell with a nickel anode and an iron cathode, it has been noted that the nickel may plate out on the iron at the beginning of the operation. If desired, a nickel plated cathode may be used initially. In general, it is preferable to use a cathode constructed of iron or an iron alloy.

The partition separating the anode and cathode compartments may be constructed of any non-anodic material resistant to the action of anhydrous hydrofluoric acid, fluorine and hydrogen. As indicated by the foregoing description with reference to the drawings, this partition above the level of the electrolyte should preferably be a non-pervious or gas-tight wall, since it is desirable at all times to prevent the combination of gaseous fluorine and hydrogen, which may occur with explosive violence. Below the level of the electrolyte, the partition between the anode and cathode compartments should preferably be in the form of a pervious diaphragm, as for example, a screen or grid having sufficiently small apertures to prevent the passage of large bubbles of fluorine. The whole partition is preferably constructed of a metal resistant to the action of hydrofluoric acid, fluorine and hydrogen. That part of the partition above the surface of the electrolyte may or may not be of the same mate-

rials as that part extending below the surface of the electrolyte. If desired, the partition may be insulated from the cell casing. In general, however, it is preferable to employ a metal partition connected directly to the top of the cell, as illustrated in the drawings and previously described. As examples of metals of construction for the partition may be mentioned iron (including white and grey cast iron), steel, cobalt, chromium or anodically passive alloys of these metals with each other and/or nickel. Especially desirable results have been obtained in the use of partitions constructed of iron and steel. Where a cast iron has been used slightly better results have been obtained with white cast iron than with grey cast iron.

The container or casing of the cell and the cover may likewise be constructed of any non-anodic materials resistant to the action of anhydrous hydrofluoric acid, fluorine and hydrogen. Very highly desirable results have been obtained in the use of metals for this purpose. As specific examples of metals which may be employed may be mentioned iron, steel, cobalt, chromium, magnesium, copper and alloys of any two or more of these metals, or anodically passive alloys of any one or more of these metals with nickel. Particularly desirable results have been obtained in the use of iron, steel and alloys thereof. In operation, the container may be electrically insulated from the anode or from the cathode or from both. For convenience of construction, as well as from the standpoint of corrosion, however, it has been found that especially desirable results are obtained in the construction of a cell consisting of a metal container, an anode, a cathode and a metal partition between the anode and cathode compartments of the character described, in which the anode and the metal partition are always electrically connected to the metal casing of the container and the cathode is always electrically insulated. Certain of the specific metals which have been described as being useful in the construction of the metal container and the partition between the anode and cathode compartments are characterized by the property that they become passive or polarize when an electrolyzing current is passed through them in contact with anhydrous hydrofluoric acid. Hence, by having the metal container and the partition connected to the anode and constructed of metals of this character, these portions of the apparatus are always anodically passive. The use of anodically passive metals apparently tends to minimize corrosion. Insofar as is known, this type of construction is novel in an electrolytic cell.

The size and shape of the various portions of this cell, including the casing or container, the anode, the cathode and the partition wall between the anode and the cathode may vary widely to meet the convenience and requirements of the application of the cell. The container may be square, circular or of any other suitable design as to cross section. The same is true of the anode, cathode and partition separating the anode and cathode compartments. The anode, for example, may be solid, grooved or made of screen. It may be cylindrical or of any other suitable design. The same is true of the cathode.

In general, the object of the design is to obtain high current and power efficiency which is largely dependent upon the surface of the electrodes and the nearness of the electrodes to each other. These factors may be regulated and adapted to the desired production of fluorine.

Very desirable results have been obtained in cells of the character illustrated in Figs. 1 and 2. In cells of this type good results have been obtained by placing the anode and cathode approximately equi-distant from the partition wall and preferably about one-half to about one and one-half inches therefrom.

Where it is desired to electrically insulate any portion of the apparatus, as for example the cathode, the insulating material should preferably be a substance which is not appreciably attacked by hydrofluoric acid and/or fluorine. In the construction of the apparatus, we have found that very desirable results are obtained in using as insulating materials inorganic solids which are insoluble in anhydrous hydrofluoric acid, are not attacked by hydrofluoric acid or fluorine, and are not electrically conducting. As specific examples of such insulating materials may be mentioned: aluminum fluoride, cupric fluoride, cupric nitrate, cobalt nitrate, zinc sulfate, silver sulfate, fused silver chloride, silver bromide, tungsten trioxide and stannic oxide. In general, metallic oxides and salts, the metal of which has a specific gravity equal to or greater than that of aluminum (2.7), are preferably employed. Compounds of the type described may be employed as such or in mixtures with each other or with certain other materials, as for example, waxes. Very highly advantageous results have been obtained in the use of fused silver chloride as an insulating material and also in the use of a mixture of aluminum fluoride and a wax such as ceresin. A specific composition of the latter type which may be mentioned consists of 30 parts of aluminum fluoride and 70 parts of ceresin. The method by which the insulation is held in place may vary widely. In insulating the cathode and wires of the electrolyte level indicating device, good results have been obtained by the methods described in connection with the drawings.

As indicated by the description with reference to the drawings, in operating the cell it is desirable, although not necessary, to provide control devices such as a device for indicating the level of the electrolyte in the cell. It is further desirable and highly important for the continuous operation of the cell to add substantially anhydrous hydrofluoric acid to the electrolyte to replace that which has been vaporized and/or decomposed by the electrolysis. It will be recognized that the devices employed for these purposes may vary considerably. In the various devices for measuring the electrolyte level described in connection with the drawings, the wires which extend to different depths in the electrolyte well should be made of a material not substantially attacked by anhydrous hydrofluoric acid, preferably nickel. The power source connected to the well and having its circuit completed through the selector switch should preferably be alternating current.

The process of the invention is susceptible of considerable variation and modification in the manner of its practical application, particularly as regards the character of the electrolyte, the current density and the temperature and pressure of operation. It will be further understood by reference to the following examples.

Example I

An electrolyte consisting of approximately 40% by weight of potassium acid fluoride (KHF_2) and 60% by weight of substantially anhydrous

hydrofluoric acid was introduced into a cell of the type described in Fig. 1, the liquid level being about that indicated in Fig. 1. The anode of the cell was constructed substantially of nickel. The container and cathode were constructed of iron, the cathode being electrically insulated from the top of the container by means of an insulating composition consisting of about 30 parts of aluminum fluoride and 70 parts of ceresin. The wires extending different depths into the well of the liquid level indicator were made of nickel and insulated from the well by the same material used in insulating the cathode. The liquid level indicator was operated on an alternating current. The partition between the anode and the cathode was constructed substantially of iron. That part of the partition below the level of the electrolyte and extending to the bottom of the cell was constructed of about 40 mesh iron screen. The cathode was constructed of about 8 mesh iron screen. The partition was equi-distant, about one-half inch, from the anode and cathode. A direct current was applied to the container and cathode corresponding to an anode current density of about 200 amperes per square foot. The temperature of the electrolyte was maintained at about 30° C. to about 35° C. Fluorine was evolved at the anode and hydrogen at the cathode. The evolved gases were passed separately through condensers where the hydrofluoric acid was condensed and continuously returned to the electrolyte. Fresh anhydrous hydrofluoric acid was added to the electrolyte continuously in order to replace that which was decomposed by the electrolysis.

Example II

The apparatus and process were the same as in Example I except that the electrolyte comprised substantially 30% potassium acid fluoride and 70% anhydrous hydrofluoric acid. The current density employed was about 300 amperes per square foot and the temperature of the cell was maintained at about 15° C.

Example III

The apparatus and process were the same as described in Example I except that the cathode was made of nickel instead of iron.

Example IV

The process and apparatus were the same as described in Example I except that the diaphragm separating the anode and cathode was constructed substantially of cobalt instead of iron.

Example V

The process and apparatus were the same as described in Example I except that the diaphragm separating the anode and cathode was constructed substantially of magnesium instead of iron.

Example VI

The process and apparatus were the same as described in Example I except that the anode was constructed of a non-polarizing alloy comprising substantially nickel and iron.

Example VII

In the process and apparatus described in Example I the metal container and the diaphragm separating the anode and cathode were rendered anodically passive prior to operation of the cell.

Example VIII

The process and apparatus were the same as described in Example I except that fused silver chloride was used as an electrical insulating material instead of the aluminum fluoride-wax composition.

The character of the electrolyte may vary within relatively wide limits. In general, the electrolyte comprises hydrofluoric acid containing a material capable of imparting electrical conductivity thereto but which does not enter into the electrolytic action. It is preferable to employ hydrofluoric acid containing a soluble fluoride. The hydrofluoric acid should be of high purity and preferably substantially anhydrous. As specific examples of soluble fluorides which may be used may be mentioned rubidium fluoride, cobalt fluoride, potassium fluoride, potassium acid fluoride, chromium fluoride, sodium fluoride and silver fluoride. Especially desirable results have been obtained in the use of an electrolyte comprising substantially anhydrous hydrofluoric acid and an alkali metal fluoride, particularly potassium fluoride or potassium acid fluoride.

The composition of the electrolyte should preferably be such that it is fluid at the temperature of operation. In general, conductivity increases with increased proportions of dissolved fluoride. The higher the proportion of dissolved fluoride, therefore, the greater the conductivity of the electrolyte and the better the efficiency of the cell. On the other hand, a decrease in the proportion of fluoride decreases the conductivity of the electrolyte and the efficiency of the cell. In order to obtain the maximum conductivity at the temperature of operation without substantial precipitation of fluoride, it is preferable to employ an electrolyte composed of substantially anhydrous hydrofluoric acid containing sufficient soluble fluoride in solution to be saturated at a temperature slightly lower than the temperature of operation.

The temperature may vary within relatively wide limits depending largely upon the composition of the electrolyte and the results desired. The upper limit is fixed by the critical temperature (about 230° C.) of hydrofluoric acid. The lower temperature of operation is more or less determined by the solubility of the fluoride in the hydrofluoric acid, since it is desirable that the temperature be sufficiently high to prevent separation of the fluoride to such an extent as to make the electrolyte too thick for efficient operation. For this purpose the temperature should preferably not be lower than about -20° C. Since hydrofluoric acid boils at about 19.5° C., relatively high temperatures tend to cause rapid volatilization of the hydrofluoric acid. Hence, in operating under atmospheric pressure where it is desired to recover the vaporized hydrofluoric acid, the higher the temperature the greater is the condenser capacity required. Generally speaking, therefore, it is preferable to operate the cell at temperatures below about 100° C. and preferably within the range of about 15° C. to about 50° C. Under these temperature conditions especially desirable results have been obtained in the use of electrolytes comprising substantially anhydrous hydrofluoric acid containing about 30% to about 50% of an alkali metal fluoride, as for example potassium acid fluoride.

The pressure at which the cell is operated is

subject to considerable variation. In general, super-atmospheric pressures may be used to advantage in regulating the volatilization of the hydrofluoric acid from the electrolyte. By employing pressures greater than the partial pressure of the hydrofluoric acid in the electrolyte, the cooling capacity of condensers used to condense hydrofluoric acid vaporized from the electrolyte may be greatly reduced. Thus, the temperature of a condenser employed to condense hydrofluoric acid under atmospheric pressure (B. P. 19.5° C.) is lower than the temperature required for condensation under an absolute pressure of 20 pounds per square inch gauge (B. P. 47° C.) or 75 pounds per square inch gauge (B. P. about 82° C.). Condensers may be omitted from the construction of the apparatus, particularly in operating at relatively low temperatures or under super-atmospheric pressures; or, if desired, partial condensation may be effected. In any case, it is desirable to replenish the electrolyte with anhydrous hydrofluoric acid in order to maintain it in a fluid condition. Super-atmospheric pressures may be obtained in any suitable manner, e. g., by closing or partly closing the cell outlets so that the total vapor pressure of the electrolyte at the temperature of operation is greater than atmospheric; or an outside source of pressure, as for example inert gas pressure, may be introduced.

The current density used in operating the cell may vary widely depending largely upon the production of fluorine desired. Other things being equal, a low current density will give a low production of fluorine, while a high current density will give a high production of fluorine. A high current density also tends to give a high heating effect so that it may be desirable to regulate the current density in accordance with the desired temperature of operation. Generally speaking, it is preferable to employ a current density below about 300 amperes per square foot and preferably within the range of about 100 to 250 amperes per square foot.

The invention has the advantage that it provides a commercially practical process for the production of fluorine. Insofar as is known fluorine is not produced on a commercial scale at the present time. Previously proposed methods for the production of fluorine have been impractical for various reasons. The so-called "fused salt cells", that is, electrolytic cells, using as an electrolyte a fused fluoride, have the disadvantage that they operate at exceptionally high temperatures as, for example, 150 to 400° C. Such cells have the further disadvantage that the electrolyte is made up and dried before using and when depleted of hydrogen fluoride is reworked. In general, "fused salt" fluorine cells may be defined as those in which the electrolyte is of such a composition that a metal fluoride will separate on cooling but hydrogen fluoride will not separate as such, whereas the electrolytes contemplated by the process of the present invention are those from which hydrogen fluoride will eventually separate as such on cooling. No anodic materials have heretofore been proposed which would withstand the action of hydrofluoric acid and fluorine to such an extent that they would be used commercially. As previously indicated, the anodic materials herein discussed are characterized by greater resistance to the action of anhydrous hydrofluoric acid and fluorine than materials such as platinum and graphite. The extent to which various anodic materials will be attacked by fluor-

ine and hydrofluoric acid may vary widely, depending upon the composition of the electrolyte, the temperature, and other conditions of the electrolysis. It will be understood that even the anodic materials of the present invention may be attacked to some extent by hydrofluoric acid and/or fluorine, but the amount of metallic fluoride formed by such attack is not substantial enough to prevent their use in commercial operations, whereas the contrary is true in the case of materials such as platinum. To illustrate, under a given set of electrolyzing conditions using an electrolyte of the character herein described, an anodic material such as nickel may allow the recovery of 80% to 90% of the fluorine liberated by the electrolysis while platinum will allow the recovery of only 20% to 30% of the liberated fluorine, the remainder reacting with the platinum and going into solution as a fluoride of platinum.

The type of cell construction described is considered to be broadly new not only for the electrolysis of hydrofluoric acid but for other electrolytic processes. Insofar as is known it has not been customary heretofore to construct a cell having a metal container and a metal diaphragm between the anode and cathode, both the container and metal diaphragm being anodically passive. This design of a cell is particularly advantageous in that it eliminates insulation of the anode from surrounding parts and may cause a decided reduction in the amount of corrosion of the container and metal diaphragm. A further advantage of the invention is the use of inexpensive materials for the construction of the various portions of the apparatus. Other advantages are the provision of a means for the continuous replacement of hydrofluoric acid which has been volatilized or decomposed, the provision of a means for the circulation of the electrolyte to prevent concentration changes, the provision of suitable electrical insulating means, and the use of a multi-length electrical contact level indicator on a fluorine cell.

As many apparent and widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that we do not limit ourselves to the foregoing examples or description except as indicated in the following claims.

We claim:

1. In an electrolytic fluorine cell suitable for the electrolysis of anhydrous hydrofluoric acid, the construction of an apparatus including a non-polarizing anode not substantially attacked by anhydrous hydrofluoric acid and fluorine, electrically connected to an anodically passive container for the electrolyte and a cathode electrically insulated from the anode and the metal container for the electrolyte.

2. In an electrolytic fluorine cell suitable for the electrolysis of anhydrous hydrofluoric acid, the construction of an apparatus including an anode comprising substantially nickel, electrically connected to an anodically passive container for the electrolyte and a cathode electrically insulated from the anode and the metal container for the electrolyte.

3. In an electrolytic fluorine cell suitable for the electrolysis of anhydrous hydrofluoric acid the combination of: an anodically passivated metal container for the electrolyte; a non-polarizing anode not substantially attacked by anhydrous hydrofluoric acid and fluorine inside of said container in contact with the electrolyte; a

cathode not substantially attacked by anhydrous hydrofluoric acid and hydrogen inside of said container in contact with the electrolyte and electrically insulated from the anode, and a means of withdrawing gases liberated at the anode and cathode without bringing them together.

4. In an electrolytic fluorine cell suitable for the electrolysis of anhydrous hydrofluoric acid the combination of: an anodically passivated metal container for the electrolyte; a non-polarizing anode not substantially attacked by anhydrous hydrofluoric acid and fluorine inside of the container in contact with the electrolyte; a cathode not substantially attacked by anhydrous hydrofluoric acid and hydrogen inside of the container in contact with the electrolyte and electrically insulated from the anode; a means of withdrawing gases liberated at the anode and cathode without bringing them together; and a means for replenishing the electrolyte during the operation.

5. In an electrolytic fluorine cell suitable for the electrolysis of anhydrous hydrofluoric acid, the combination of: an anodically passivated base metal container for the electrolyte not substantially attacked by anhydrous hydrofluoric acid and fluorine; a non-polarizing metal anode not substantially attacked by anhydrous hydrofluoric acid and fluorine inside of said container in contact with the electrolyte; a metal cathode not substantially attacked by anhydrous hydrofluoric acid and hydrogen inside of said container in contact with the electrolyte and electrically insulated from the anode; a means of withdrawing gases liberated at the anode and cathode without bringing them together; and a means for replenishing the electrolyte during operation.

6. In an electrolytic fluorine cell suitable for the electrolysis of anhydrous hydrofluoric acid, the combination of: a base metal container for the electrolyte which is anodically passivated; a non-polarizing metal anode not substantially attacked by anhydrous hydrofluoric acid and fluorine inside of said container in contact with the electrolyte; a metal cathode not substantially attacked by the action of anhydrous hydrofluoric acid and hydrogen inside of said container in contact with the electrolyte and electrically insulated from the container and from the anode; and a means of withdrawing gases liberated at the anode and cathode without bringing them together.

7. In an electrolytic fluorine cell suitable for the electrolysis of anhydrous hydrofluoric acid, the combination of: a metal container for the electrolyte constructed of a metal which is anodically passive and unreactive in anhydrous hydrofluoric acid; a non-polarizing anode not substantially attacked by anhydrous hydrofluoric acid and fluorine inside of said container in contact with the electrolyte and electrically connected to the container; a metal cathode not substantially attacked by anhydrous hydrofluoric acid and hydrogen inside of said container in contact with the electrolyte and electrically insulated from the container; an anodically passive metal partition inside of the container between the anode and cathode out of contact therewith and joined with the container so as to divide it into an anode compartment and a cathode compartment, said partition being substantially gas-tight above the electrolyte but sufficiently pervious in the electrolyte to allow pas-

sage thereof from one compartment to another; means for withdrawing gases from the anode and cathode compartments; and means for continuously replenishing the electrolyte.

8. The apparatus of claim 7, in which the anode comprises substantially nickel.

9. The apparatus of claim 7, in which the anode comprises substantially a non-polarizing nickel alloy.

10. The apparatus of claim 7, in which the cathode is constructed substantially of a metal selected from the group consisting of iron, nickel, cobalt, copper, chromium, magnesium and alloys of any two or more of these metals.

11. The apparatus of claim 7, in which the metal container is constructed substantially of a metal selected from the group consisting of iron, steel, cobalt, chromium, magnesium, copper, alloys of any two or more of these metals and anodically passive alloys of one or more of these metals with nickel.

12. The apparatus of claim 7, in which the metal partition between the anode and cathode compartments is constructed substantially of a metal selected from the group consisting of iron, steel, cobalt, chromium and anodically passive alloys of these metals with each other or with nickel.

13. In an electrolytic fluorine cell suitable for the electrolysis of anhydrous hydrofluoric acid, the combination of: a metal container for the electrolyte constructed substantially of iron; an anode constructed substantially of nickel situated inside of the container in contact with the electrolyte and electrically connected to the container; a cathode constructed substantially of iron situated inside of the container in contact with the electrolyte and electrically insulated from the container; an iron partition inside of the container between the anode and cathode out of contact therewith and joined to the metal container dividing it into an anode compartment and a cathode compartment, said partition being substantially gas-tight above the electrolyte but sufficiently pervious in the electrolyte to allow passage thereof from one compartment to another; means for withdrawing gases from the anode and cathode compartments; and means for continuously replenishing the electrolyte.

14. In a relatively low temperature process for the production of fluorine, the step which comprises passing an electrolyzing current through a non-polarizing nickel-containing anode which is not substantially attacked by the action of hydrofluoric acid and fluorine in contact with an electrolyte composed of substantially anhydrous hydrofluoric acid containing sufficient soluble fluoride in solution to be saturated at a temperature slightly lower than the temperature of operation, and maintaining a temperature of operation below about 100° C.

15. In a relatively low temperature process of producing fluorine, the step which comprises passing an electrolyzing current through an anode constructed substantially of nickel and in contact with an electrolyte composed of substantially anhydrous hydrofluoric acid containing sufficient soluble fluoride in solution to be saturated at a temperature slightly lower than the temperature of operation, and maintaining the temperature of operation below about 100° C.

16. The process of claim 14 in which the electrolyte is composed of an unsaturated solution of a soluble fluoride in substantially anhydrous hydrofluoric acid and the amount of hydro-

fluoric acid corresponds to at least 50% by weight of the electrolyte.

17. In a process of producing fluorine, the step which comprises passing an electrolyzing current through an anode comprising substantially nickel and a cathode comprising substantially iron in contact with an electrolyte composed substantially of about 30% to 50% potassium acid fluoride and about 50% to about 70% anhydrous hydrofluoric acid maintained at a temperature within the range of about 15° C. to about 50° C., continuously withdrawing fluorine liberated at the anode and hydrogen liberated at the cathode without bringing them together in the gas phase, maintaining a current density below about 300 amperes per square foot and adding anhydrous hydrofluoric acid to the electrolyte during the operation in order to keep the electrolyte level substantially constant.

18. The process of claim 17 in which the electrolysis is carried on under superatmospheric pressure.

19. In an electrolytic fluorine cell suitable for the production of fluorine, electrical insulation means comprising substantially a material selected from the group consisting of non-conducting, inorganic compounds of metals having a specific gravity of at least 2.7 and which are substantially insoluble in anhydrous hydrofluoric acid and are not attacked by hydrofluoric acid or fluorine and mixtures of such solids with waxes.

20. In an apparatus according to claim 19, fused silver chloride as an insulating means.

21. In an electrolytic fluorine cell suitable for the electrolysis of anhydrous hydrofluoric acid, the construction of an apparatus including a metal container for the electrolyte which is anodically passivified.

22. In an electrolytic fluorine cell suitable for the electrolysis of anhydrous hydrofluoric acid, the construction of an apparatus including a container for the electrolyte which is constructed of anodically passivified iron.

23. In an electrolytic fluorine cell for the production of fluorine by electrolysis of substantially anhydrous hydrofluoric acid containing a soluble fluoride, the combination of: a metal container for the electrolyte constructed of a metal which is anodically passive and unreactive in anhydrous hydrofluoric acid; a non-polarizing anode not substantially attacked by anhydrous hydrofluoric acid and fluorine inside of said container in contact with the electrolyte and electrically connected to the container; a cathode not substantially attacked by anhydrous hydrofluoric acid and hydrogen inside of said container in contact with the electrolyte; and an insulating means between the cathode and the container comprising substantially a material selected from the group consisting of non-conducting inorganic compounds of metals having a specific gravity of at least 2.7 and which are substantially insoluble in anhydrous hydrofluoric acid and are not attacked by hydrofluoric acid and fluorine and mixtures with waxes; and anodically passive metal partition inside of the container between the anode and the cathode out of contact therewith and joined with the container so as to di-

vide it into an anode compartment and a cathode compartment, said partition being substantially gas-tight above the electrolyte but sufficiently pervious in the electrolyte to allow passage thereof from one compartment to another; and means for withdrawing gases from the anode and cathode compartments.

24. In an electrolytic fluorine cell suitable for the electrolysis of anhydrous hydrofluoric acid, the combination of: an anodically passive metal container for the electrolyte; a non-polarizing anode not substantially attacked by anhydrous hydrofluoric acid and fluorine inside of the container in contact with the electrolyte; a cathode not substantially attacked by anhydrous hydrofluoric acid and hydrogen inside of the container in contact with the electrolyte and electrically insulated from the anode; a means of withdrawing gases liberated at the anode and cathode without bringing them together; and a means for indicating the liquid level of the electrolyte including current conducting means disposed at different depths within and above the electrolyte corresponding to the desired liquid level and electrically insulated from the container, a current indicating means, the current source in turn being connected to the container and the current conducting means disposed in the electrolyte, whereby the indicating device registers when the circuit is closed by contact of the current conducting means with the electrolyte.

25. In an electrolytic fluorine cell suitable for the electrolysis of an electrolyte comprising substantially anhydrous hydrofluoric acid and a soluble fluoride, the construction of an apparatus including an anodically passivified metal container for the electrolyte, an anode and a cathode compartment in said container formed by a metal partition constructed of an anodically passivified metal, said anode, partition and metal container being electrically connected, and a cathode which is insulated from said other metal parts of the cell and from the anode.

26. In an electrolytic fluorine cell suitable for the electrolysis of substantially anhydrous hydrofluoric acid containing a soluble fluoride, the construction of an apparatus including a non-polarizing nickel-containing anode, an iron container for the electrolyte, an anode and a cathode compartment in said container formed by an iron partition, said container and said partition being electrically connected to the anode, and a cathode which is insulated from said other metal parts of the cell.

27. In a process of producing fluorine, the step which comprises passing an electrolyzing current through an anode comprising substantially nickel, and a suitable cathode in contact with an electrolyte composed of substantially anhydrous hydrofluoric acid containing insufficient soluble fluoride to be saturated at the temperature of operation, maintaining said electrolyte at a temperature of about 15° C. to about 50° C., and withdrawing fluorine liberated at the anode and hydrogen liberated at the cathode without bringing them together.

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