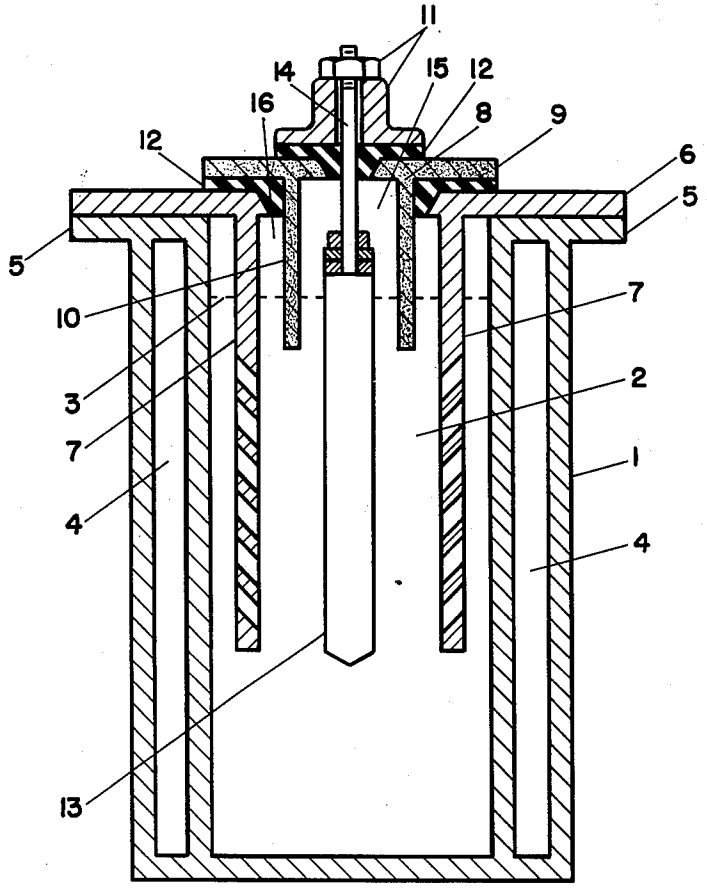
March 20, 1956 J. F. GALL ET AL 2,739,115

FLUORINE CELL

Filed June 19, 1952



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United States Patent Office 2,739,115 Patented Mar. 20, 1956

2,739,115

FLUORINE CELL

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Application June 19, 1952, Serial No. 294,396

7 Claims. (Cl. 204—243)

This invention relates to electrolytic apparatus for the manufacture of fluorine and more particularly to improvements in gas barriers in electrolytic cells of this type, the present application being a continuation-in-part of copending application Serial No. 773,918, filed September 13, 1947, now abandoned.

In electrolytic fluorine cells of recent design there has been an increasing tendency to use a solid gas barrier in place of the screens or diaphrams which were formerly used to separate the gaseous fluorine and gaseous hydrogen, which were the anode product and the cathode product respectively. Cells are generally designed to operate in temperature ranges of —15 to +30° C., 75 to 110° C., or 250 to 275° C. Since the gas barrier extends down into the electrolyte, which is an anhydrous mixture of potassium fluoride and hydrogen fluoride, it is necessary to form the gas barrier of material resistant to these corrosive substances at the temperature of cell operation.

Metals such as iron, copper and nickel, when in contact with fluorine, have formed in their surfaces protective coatings of metal fluorides which prevent further substantial attack. Since other materials sufficiently resistant to fluorine attack were not known, it had been the practice, prior to applicants' present invention, to form the gas barriers in fluorine cells of one of these metals. However, metallic gas barriers are objectionable as the metals are relatively good conductors of electricity. Due to their electrical conductivity, great care must be taken to electrically insulate the metal gas barriers from both the anode and the cathode, since the barrier must remain electrically neutral. Any break in insulation results in the barrier acting as a cathode or anode, depending on where the leak occurs, with resulting explosions due to mixing of the hydrogen and fluorine formed.

Another objection to having the gas barrier formed of a conducting material is that, particularly under faulty operation of the cell, a bipolar action is set up on the gas barrier with one side of the conducting barrier acting as the anode and the other side acting as the cathode. This results in attack of the metal and, particularly where the bipolar voltage is sufficiently high, in hydrogen being formed on the fluorine side with erosion of iron on the hydrogen side of the barrier with resulting explosions due to the mixture of the hydrogen with the fluorine.

We have now discovered that gas barriers free from the above mentioned objections and highly resistant to corrosion under the operating conditions of the cell will be obtained if the gas barriers are formed of certain metal phosphate compositions, namely compositions having at least a matrix of a cupric phosphate, an aluminum phosphate or an iron phosphate in which the average valence of the iron is less than 3.

In the drawing, which is a cross-sectional view of a fluorine cell having a gas barrier formed of one of the above mentioned metal phosphate compositions, reference numeral 1, indicates a jacketed tank forming a body of the cell. The interior 2 of the tank is filled with electrolyte comprising potassium fluoride and hydrogen fluoride up to the level indicated by reference numeral 3. The jacketed space 4 is employed for circulation of either a heating medium or cooling medium depending on conditions of operation. The tank has a flange portion 5 on which rests partial lid 6 from which cathodes 7 are suspended. The lid 6 holding the cathodes may be insulated from the tank 10, if desired, but this is not necessary. The electrical connection to the cathode may be made through suitable connectors (not shown) on the cathode lid portion 6. A gas barrier 8 having laterally extending flanges 9 and a downwardly extending barrier portion 10 is supported on the lid 6. The portion 10 of the barrier is of suitable length to extend slightly under the electrolyte liquor.

In accordance with the present invention, the gas barrier, including both the flange portion 9 and the downwardly extending barrier portion 10, is formed of the metal phosphate compositions herein described. Though it is not necessary to insulate the gas barrier from the cell cover 6 or the anode supporting means 11, gaskets 12 are preferably used to prevent escape of hydrogen and fluorine from the cell. These gaskets may be made of a soft metal such as copper or lead, or of some material relatively resistant to fluorine attack, such as a packing structure as disclosed in our Patent No. 2,571,560. The anode 13 in the modification shown in the drawing is suspended by a conducting rod 14 from supporting members 11 which are supported on the upper portion of the barrier member 8. The anode conducting rod 14 is connected to the source of current by any suitable means.

The downwardly extending portion 10 of the gas barrier divides the vapor space above the electrolyte into an anode compartment 15 and a cathode compartment 16. By making the gas barrier 8 of one of the metal phosphate compositions herein described, danger of that portion of the barrier extending below the electrolyte acting as an electrode due to failure of insulation or through bipolar action is eliminated. Also, due to the especially high resistance of the metal phosphate compositions herein described to attack by fluorine and acid fluorides, the life of the barrier member is substantially that of the cell, the barrier giving substantially no trouble.

The gas barrier can be readily formed by first preparing the metal phosphate and then molding the plastic mass into the desired shape before the same hardens. Due to the thermoplastic properties of the aluminum phosphate compositions, these compositions may, if desired, be permitted to set before being formed into the desired shape of the gas barrier and, after setting, heated to a sufficiently high temperature to become sufficiently plastic for molding into the desired form.

It is obvious that many structural modifications might be made in the gas barrier while still forming the gas barrier of one of the phosphate cements in the manner herein described. The invention, therefore, should not be limited to the specific structure, given by way of illustration, but consists broadly in the discovery that substantially improved fluorine cells are obtained if the gas barrier of the cell is made of one of the phosphate cements herein described rather than of a conducting metal as has heretofore been the practice.

We have found it desirable in making metal phosphate gas barriers to employ aqueous phosphoric acid of 70 to 100% acid concentration; preferably, 80% orthophosphoric acid is employed. This is mixed with 1 to 10 parts by weight of metal oxide for each part by weight of phosphoric acid; preferably, 2 parts by weight of oxide are employed for each part by weight of acid.

The metal oxide is preferably employed in powder form which may range in particle size from 35 mesh to 250 mesh. Preferably about 50% of the solid should be of a particle size ranging from about 60 to 150 mesh. Two

or more of the metal oxides named may be used in admixture in preparing these compositions. Since there is generally more metal oxide present than will react with the phosphoric acid, a part of the metal oxide reacts to form a matrix enclosing or cementing together particles of unreacted metal oxide. Particles of any filler that is added are similarly held. A composition of particularly advantageous plastic properties may be made by employing both magnetite and aluminum oxide as the metal oxides and employing rouge (ferric oxide) as a filler. One such composition is described in Example 5 below.

We have further found that the setting time of these compositions may be controlled by the degree of calcination of the metal oxide prior to mixing with the phosphoric acid. Thus, when uncalcined copper or iron oxides were employed, setting times ranging from one-half minute to several minutes were observed in many instances. When these materials were calcined by heating in air at 1000° C. for 20 minutes, the setting time was usually increased more than one hundred fold, i. e., setting times ranged from around one hour to several hours. Intermediate degrees of calcination may be employed to obtain intermediate setting times.

The following examples are illustrative of various phosphate cement compositions that can be used for making the gas barrier in accordance with our present invention.

Example 1

A copper phosphate plastic was prepared by mixing two parts by weight of calcined copper oxide (CuO) of such particle size that 25% by weight ranged from 35 to 60 mesh, 50% by weight ranged from 60 to 150 mesh and 25% ranged from 150 to 250 mesh, with one part by weight of an 80% phosphoric acid. Part of the copper oxide reacted slowly with the phosphoric acid to form a copper phosphate, and the plastic hardened over a period of a few hours to form a rigid solid mass that consisted essentially of a matrix of solid copper phosphate enclosing particles of the unreacted metal oxide.

Example 2

An iron phosphate plastic mix was prepared exactly as described in connection with the copper phosphate of Example 1 except that magnetite (naturally occurring Fe_3O_4) was used in place of copper oxide. The particle size of the solid, the acid concentration and the ratio of acid to powder were exactly as specified in Example 1.

The iron phosphate composition was found particularly desirable for insulation of the anode when the cover of the electrolytic cell was made of ferrous metal.

Example 3

The composition described in Example 2 may also be made using black oxide of iron (manufactured Fe_3O_4) instead of the magnetite.

Example 4

A material which has the property of being resistant to fluorine and fluorides and the additional property, unusual in the field of inorganic products, of showing a reversible thermoplasticity, i. e., the property of softening when its temperature is raised and of hardening again upon lowering the temperature, was made by employing a powder of alumina (for example, the hydrated oxide called "Aluminum Hydroxide"—$Al_2O_3 \cdot xH_2O$), instead of the copper oxide or Fe_3O_4. In this case, 1 part by weight of hydrated aluminum oxide was added to 2 parts by weight of 80% phosphoric acid which had been heated to about 100° C. and the aluminum oxide was stirred in. A product was formed which was hard below 20° C., but which was soft and plastic above this temperature. A similar product which softened above −5° C. was made by using a ratio of 5 parts by weight of acid to one of the hydrated oxide. On the other hand, a product made in the same way but using a ratio of 1 part by weight of acid to one part by weight of the hydrated oxide did not soften below 100° C., at temperatures at which they are rigid solids these aluminum phosphate compositions are excellent for preparing the gas barriers of fluorine cells in accordance with the present invention.

Example 5

As above stated, more than one of the metal oxides named may be employed at one time in preparing the plastic from which the structures of our invention are made. Thus for example, three parts by weight of magnetite of particle size as described in Example 2, one part by weight of the aluminum oxide powder and four parts by weight of rouge were mixed with 80% phosphoric acid in the proportion of one part by weight of total solid to two parts by weight of acid.

In this particular mixture the rouge is used principally as a filler but it apparently also acts somewhat as a plasticizer. That is, it adds to the mixture's unique plastic properties whereby the composition can withstand severe mechanical shock without cracking or shattering.

We have found that it is feasible to vary the proportions of the three solids employed in this particular mixture so that for every three parts by weight of magnetite there may be employed from 0 to 8 parts by weight of rouge, and from 0 to 3 parts by weight of aluminum oxide. Similarly the phosphoric acid concentration and the ratio of acid to solid may be varied as described above.

Since many modifications are possible in the structure and process of our invention as above described without departure from the scope of the invention, it is intended that the above description of our invention should be interpreted as illustrative, and the invention should, therefore, not be limited thereby.

Having thus described our invention, we claim:

1. In an electrolytic cell for the production of fluorine, a cell cover having an opening passing therethrough and a substantially vertically disposed anode and cathode, a gas barrier having a downwardly extending portion extending through said cover opening and between said anode and cathode, said gas barrier being supported by said cover and being formed from a self-hardening plastic made by mixing phosphoric acid with at least one metal oxide selected from the group consisting of cupric oxide, iron oxide in which the average valence of iron is less than 2, and aluminum oxide.

2. In an electrolytic cell for the production of fluorine, a cell cover having an opening passing therethrough and a substantially vertically disposed anode and cathode, a gas barrier having a downwardly extending portion passing through said opening and between said anode and said cathode and a laterally extending portion adapted to rest on said cover, said gas barrier being formed of a self-hardening plastic made by mixing phosphoric acid with at least one metal oxide selected from the group consisting of cupric oxide and iron oxide in which the average valence of iron is less than 3, the ratio by weight of metal oxide to phosphoric acid in said mixture being 1 to 10 parts oxide per part phosphoric acid.

3. In an electrolytic cell for the production of fluorine a substantially vertically disposed anode and cathode and a gas barrier extending downwardly between said anode and cathode so as to separate said anode and cathode at the top portions thereof to prevent gases generated at the anode from coming in contact with gases generated at the cathode when said cell is in operation, said gas barrier being formed of a metal phosphate cement the metal radical of which is selected from the group consisting of copper, aluminum and iron of average valence less than 3.

4. In an electrolytic cell for the production of fluorine a substantially vertically disposed anode and cathode and

a gas barrier extending downwardly between said anode and cathode so as to separate said anode and cathode at the top portions thereof to prevent gases generated at the anode from coming in contact with gases generated at the cathode when said cell is in operation, said barrier having a laterally extending flange for supporting the same and being formed of a metal phosphate cement the metal radical of which is selected from the group consisting of copper, aluminum and iron of average valence less than 3.

5. In an electrolytic cell for the production of fluorine a substantially vertically disposed anode and cathode and a gas barrier extending downwardly between said anode and cathode so as to separate said anode and cathode at the top portions thereof to prevent gases generated at the anode from coming in contact with gases generated at the cathode when said cell is in operation, said gas barrier being formed of an aluminum phosphate cement.

6. In an electrolytic cell for the production of fluorine a substantially vertically disposed anode and cathode and a gas barrier extending downwardly between said anode and cathode so as to separate said anode and cathode at the top portions thereof to prevent gases generated at the anode from coming in contact with gases generated at the cathode when said cell is in operation, said gas barrier being formed of cupric phosphate.

7. In an electrolytic cell for the production of fluorine a substantially vertically disposed anode and cathode and a gas barrier extending downwardly between said anode and cathode so as to separate said anode and cathode at the top portions thereof to prevent gases generated at the anode from coming in contact with gases generated at the cathode when said cell is in operation, said gas barrier being formed of an iron phosphate in which the average valence of iron is less than 3.

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