

April 22, 1952

L. FERRAND

2,593,741

PROCESS FOR THE ELECTROLYTIC PRODUCTION OF ALUMINUM

Filed July 16, 1946

2 SHEETS—SHEET 1

Fig. 2.

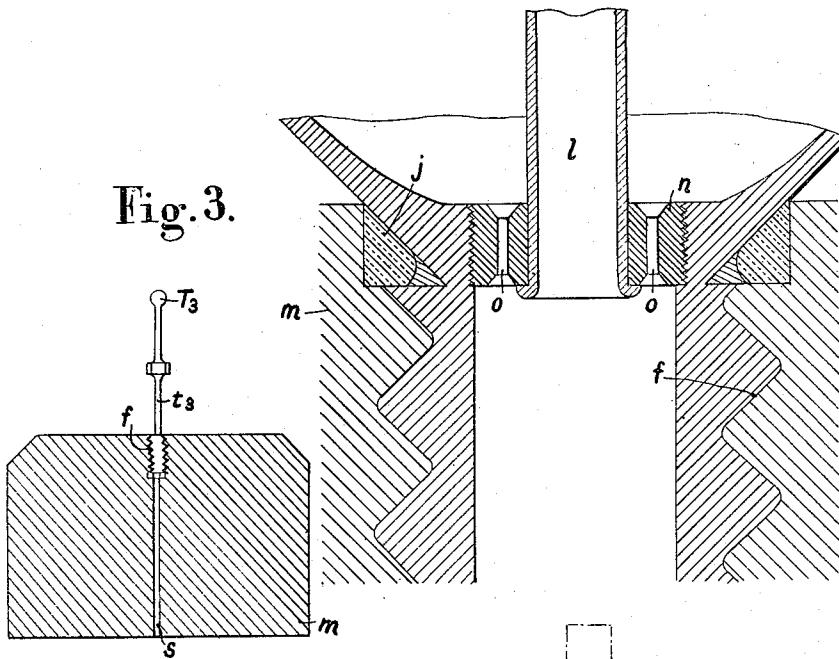
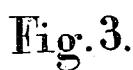


Fig. 4.

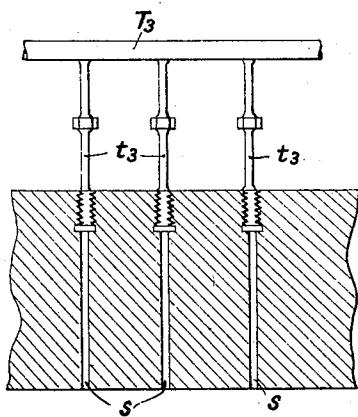
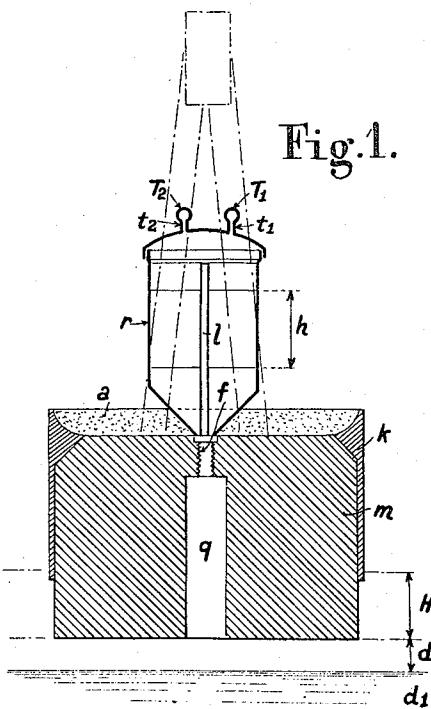


Fig. 1.



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2 SHEETS—SHEET2

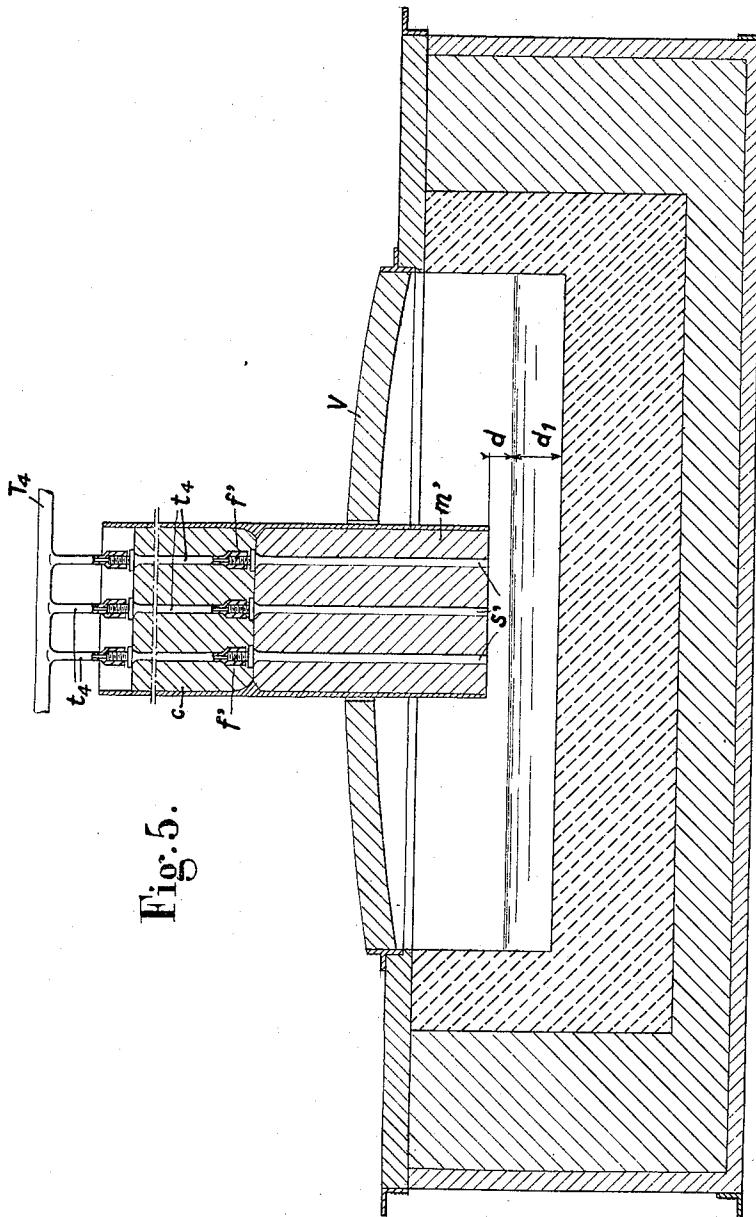


Fig. 5.

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## UNITED STATES PATENT OFFICE

2,593,741

PROCESS FOR THE ELECTROLYTIC  
PRODUCTION OF ALUMINUM

Louis Ferrand, Paris, France

Application July 16, 1946, Serial No. 683,902  
In France July 17, 1943Section 1, Public Law 690, August 8, 1946  
Patent expires July 17, 1963

4 Claims. (Cl. 204—67)

1

2

The French patent, Ser. No. 962,781 filed by the applicant on the 30th of June 1942 for "A Method for the Automatic Operation of Ovens for Melt-Electrolysis and Arrangements thereof" is concerned essentially with a method according to which the amount of material dissolved in the bath of melted salts subjected to electrolysis is maintained constant or substantially so and concurrently, as the percentage of dissolved material is being restored, the anodes are removed as early as possible from the exhausted portions of the bath.

The principal object of these improvements is to maintain the amount of material dissolved in the bath of melted salts subjected to electrolysis substantially constant and concurrently or separately to provide for adjustment in the interpolar distance and finally for a decrease in the consumption of electrodes and electric power.

A first feature of the invention consists in continuously distributing the alumina into the anodic dissolution chambers and to convey it into the bath with the aid of an auxiliary reducing gas fed at regulatable rate and pressure; preferably, such distribution is effected through calibrated apertures; the leak flow of conveyor gas moreover serves as means to reduce the lumps of alumina.

A characteristic modification of the invention consists in distributing the alumina continuously as an intimate mixture with the auxiliary reducing gas; said mixture may advantageously be distributed through calibrated tubes and orifices.

A characteristic of the invention that is a consequence of the preceding ones consists in using the pressure of the reducing gas (methane or any other gaseous hydrocarbon) in the dissolution chambers, or the pressure of the mixture of dissolved material with reducing gas, as a means to regulate the interpolar distance.

These various improvements will now be described in detail hereinafter, reference being had to the appended drawing in which:

Figures 1 and 2 are diagrammatic sectional views, drawn to different scales, of a first embodiment.

Figures 3 and 4 are sectional views of a modification.

Figure 5 illustrates applications to Soderberg anodes.

The arrangement illustrated in Fig. 1 is designed more especially for aluminum production taken as an example. It comprises a dissolution chamber *q*, circular in section, bored in the

anode *m*, on which the anode-carrying shaft and the electric leads are indicated in dotted lines. Secured in fluid-tight manner on top of said chamber *q* by a nipple *f* (Fig. 2) with the interposition of an asbestos gasket *j* is a reservoir *r*, which is also circular in section and into which the alumina to be dissolved in the bath is fed at regular intervals through a tube *t* branched off from a manifold *T* through which the alumina is conveyed pneumatically in well known manner.

The upper end of nipple *f* carries a removable steel or gunmetal plate *n* drilled with one or more calibrated orifices such as *o* designed to let alumina flow therethrough at the desired rate. Of course, the diameter of the hole or holes *o* should be ascertained experimentally with great care in order that with the mean head corresponding to the level differential *h* between two successive loadings the rate of flow of the alumina shall be obtained in accordance with the load of the electrolytic oven and the number of dissolution chambers available.

Said chambers might have an oblong section or even be replaced, in one and the same anode, by one single elongated and narrow chamber without the principle of the invention being altered thereby in itself.

The mere spraying of the alumina onto the surface of the bath, although the latter is maintained in the liquid state by the heat-insulating action of the alumina layer *a* contained in known manner in an aluminum sheath *k* designed to protect the anodes against oxidization by the air, would however be insufficient to provide for dissolution of the alumina unless dissolution chambers were resorted to having an exceedingly large section by which the sectional area for the passage of the current through the anode would become too narrow. A complementary arrangement is thus necessary.

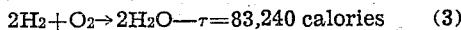
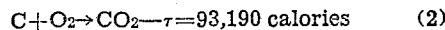
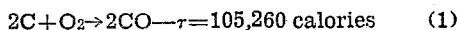
The said additional arrangement of the invention consists in the use of a tube *t* connected with a manifold *T* and of a narrow central tube *l*, through all of which a neutral or preferably a reducing gas may be flowed into the chamber *q*, e. g. methane or some other hydrocarbon gas.

Another embodiment of the invention whereby still more important additional technical effects can be secured is illustrated in Figs. 3 and 4.

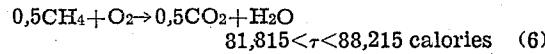
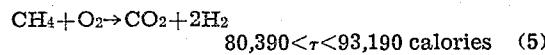
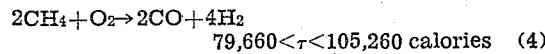
In the said embodiment, the alumina which first is de-gassed in a vacuum to strip it from the air therein, is mixed intimately, prior to its being introduced into the oven with the aid of an injector or a small gas turbine or some other

suitable apparatus that is not comprehended in the invention, with a reducing gas flowed at such rate that the atomic carbon resulting from its dissociation at the temperature of the electrolysis will be sufficient instead of carbon from the anode to sustain the secondary reactions of anodic oxidation. The very principle of this aspect of the invention, together with the selection of the reducing gases to be employed (as a rule readily dissociable hydrocarbons) are justified by established thermodynamic considerations and by the latest theories about aluminum electrolysis in the melt, according to which the primary electrolysis does not take place at the expense of the alumina itself but does it at the cost of the components of the fluorinated electrolyte to which said alumina is admixed. The anodic oxygen itself thus would not be concerned in the conveyance of the current and would merely be a product of secondary reactions.

For instance, with methane gas whose available energy is already low at 25° C. ( $\tau=12,800$  calories) and should be still lower if not null at 950° C., it can be estimated that the reactions at the expense of the anodic oxygen, separately or simultaneously, are as follows:



or else,

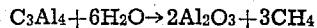


for that portion of the methane gas that escaped dissociation. One is aware that reactions (4) and (5) take place secondarily, as the methane gas is being cracked, at 850° C.

Of course, such reactions, which all take place between gases or with highly divided carbon, are likely to happen rather than such as would involve the much more compact carbon of the anode. An inoxidizable anode is thus obtained without sacrificing the recovery of electro-motive force arising from the heat liberated by these exothermic reactions.

As to the excess gas (H<sub>2</sub> or CH<sub>4</sub>) that would escape oxidation within the electrolyte, it will be burned as it comes into contact with the surrounding air, which is to be entered upon the credit-side of the thermo-chemical balance-sheet for the electrolytic reaction as a whole, this allowing to cut down power consumption materially provided the current density employed is properly adjusted.

It should be mentioned that said methane gas, of which natural sources are to be found only in Rumania and in the United States, can be produced most easily by availing one's self of the method for obtaining alumina from bauxites which consists in reducing the metal impurities therein with coal and then carburizing the alumina to obtain aluminum carbide according to a known method. Said carbide stripped from the metal impurities thus reduced, by its combination with water or steam, will give methane gas and alumina according to the known reaction:



Methane gas is thus obtained as a paying by-product which in turn will furnish the reducing carbon necessary for the anodic reactions, and this, in chemically pure state although generated from ordinary coal, without the necessity of resorting, as usual for the obtainment of pure aluminum, to high-purity and consequently costly carbon varieties such as petroleum coke.

The methane gas is preparatorily re-heated if necessary by passing the same through sole or wall tubes such as described in the French addition No. 46,398, dated Feb. 22, 1935, to Patent No. 782,136 in order to facilitate its dissociation, whereafter it is mixed with the alumina in the proportion of about 400 liters per kilogram of the latter, after which the mixture is distributed through the manifolds T<sub>3</sub> and the tubes t<sub>3</sub> to the various anodes through vertical orifices S, which are larger in number and smaller in section than the dissolution chambers in order that a more satisfactory dispersion of the gases below the anode surface may be obtained. Fluid-tightness in the fit of said tubes t<sub>3</sub> in the corresponding orifices is secured similarly with the aid of a screw-threaded nipple f and an asbestos gasket.

It will be appreciated that such method of constant distribution of dissolved material is independent of the shape of the anode system and is applicable notably to continuous so-called Soderberg anodes. Figure 5 is a sectional view of a Soderberg anode m' provided with vertical aluminum tubes s' connected by screw-thread engagement at f' with the tubes t<sub>4</sub> to be screwed in proportion as the anode is consumed and which are surrounded with carbon c maintained by the aluminum sheath of the anode. Said tubes t<sub>4</sub> are connected with the manifolds T<sub>4</sub> through which the mixture of alumina with reducing gas is led down to the bath. It will be observed that with the anode equipment described hereinbefore and the cathode equipment described in the French patent filed by the applicant on the 11th of August 1943 under the proc. No. 482,247, for "A Melt-Electrolysis Oven Designed for Very Small Voltage Drop and Continuous Running-Off" it becomes possible to shut off the oven in fluid-tight manner with the aid of an arch V since the bath has no longer to be taken care of. The use of a neutral or a reducing gas to flush the alumina or to form an intimate mixture therewith according to one of the above-described features leads to a twofold result:

(a) With suitable adjustment of the gas pressure by means of a pressure regulator controlling the feed into each oven the level of the bath in each dissolution chamber will sink until balance is obtained between the pressure of the gas within the chamber and the height H of liquid bath that surrounds the anode above the bottom of the latter. It will be found that such balance is reached or slightly exceeded as soon as the meter arranged on each anode indicates a very low rate of flow. The occurrence of such low rate of flow only at one anode indicates that same is higher than the adjacent ones, and once said anode has been set horizontal according to the procedure already described in the aforesaid patent it will only be necessary to sink the same until leak flow appears at some other anode, and so on. The simultaneous existence of such a leak flow at all the anodes in one and the same oven attests that they all are immersed by an equal amount in the bath, which means that the interpolar distance d between their bot-

toms and the metal layer  $d_1$  is the same at all the anodes (Fig. 1 and even Fig. 5 where two or more Soderberg anodes are provided).

A highly reliable way is thus afforded to adjust said interpolar distance instead of the rough methods usually resorted to. Incidentally, such condition is of capital importance in the efficient performance of the electrolysis.

That a preparatory adjustment of the interpolar equidistance is indispensable will be appreciated readily since, due to the fact that the pressure of the reducing gas or mixture in the supply line is constant everywhere, it is necessary that the back-pressure below each anode should be the same to ensure equality in the amounts of alumina fed to each of them.

(b) Where the alumina is fed in by gas flush, the leak flow (that can be adjusted at any desired value) will also be effective to drive away alumina lumps encased in the cryolite and to bring them below the active surface of the anode into impoverished regions of the bath where their dissolution will be accelerated by the turbulent action of the gases from the electrolysis. In these conditions, with proper regulation of the flow of alumina through the orifices  $\sigma$  (Figs. 1 and 2), a practically constant percentage of alumina in the bath is obtained and the occurrence of the anode effect is avoided. Moreover, such conveyance effect cannot but be aided by the increase in weight of the superficial layers of the bath at the outlet of the dissolution chambers as soon as the percentage of alumina exceeds 10%, with an attendant drop in the melting point, and reaches 24%, which corresponds to the cryolite-alumina eutectic.

Last, the method of flushing or mixing the alumina with gas is advantageous in that light alumina varieties now become available that usually cannot be dealt with by hand-feed methods on account of the excessive amounts of dust raised.

I claim:

1. The method of producing electrolytic aluminum in an oven having a carbon anode suspended in a layer of molten alumina electrolyte comprising dispersing finely powdered alumina in an atmosphere of gaseous methane, and discharging the resulting suspension directly into the space between the anode and the molten layer, the proportion of alumina to methane in said suspension being such that the methane is sufficient in amount to combine the entire oxygen content of each particle of alumina therein; whereby to obviate oxidation of the carbon anode.

2. The method in accordance with claim 1 in which the suspension is discharged into said space through a duct in the anode.

3. The method in accordance with claim 2, in which the formation of said suspension takes place prior to introduction of the materials into said anode duct.

4. The method in accordance with claim 2, in which the formation of said suspension is carried out within the anode.

LOUIS FERRAND.

#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

| Number    | Name            | Date          |
|-----------|-----------------|---------------|
| 527,848   | Gooch et al.    | Oct. 23, 1894 |
| 1,837,070 | Roth            | Dec. 15, 1931 |
| 1,851,817 | Dow             | Mar. 29, 1932 |
| 2,231,030 | Scofield et al. | Feb. 11, 1941 |

#### FOREIGN PATENTS

| Number  | Country       | Date          |
|---------|---------------|---------------|
| 9,676   | Great Britain | of 1901       |
| 318,431 | Great Britain | Sept. 5, 1929 |
| 511,076 | Great Britain | Aug. 14, 1939 |
| 115,749 | Switzerland   | July 1, 1926  |