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G. GIN.

PROCESS OF ELECTROLYTIC MANUFACTURE OF ALUMINIUM.

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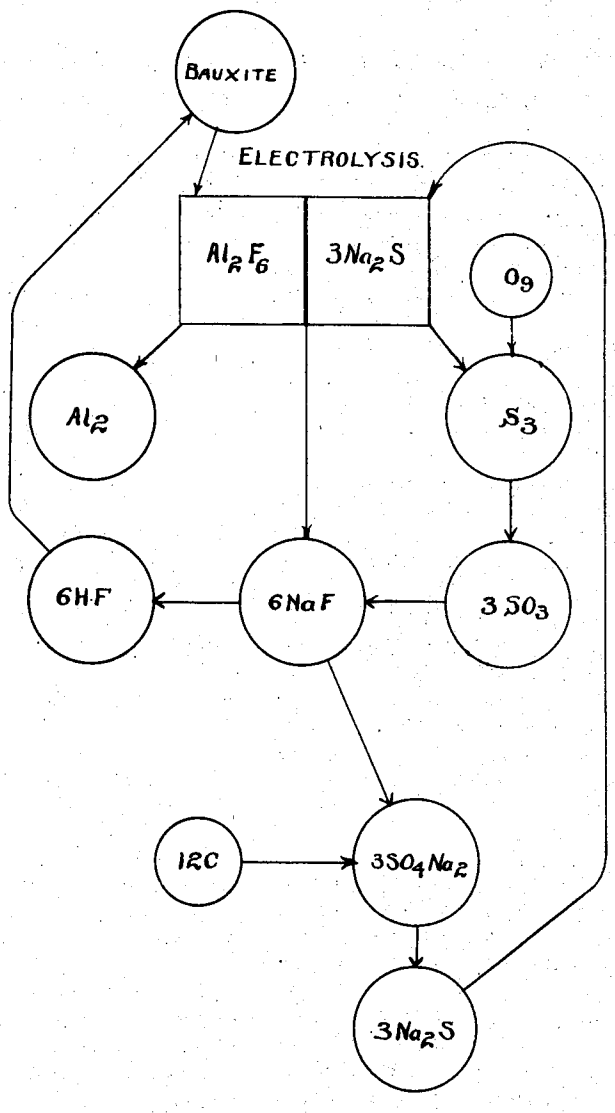
NO MODEL.



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UNITED STATES PATENT OFFICE.

GUSTAVE GIN, OF PARIS, FRANCE.

PROCESS OF ELECTROLYTIC MANUFACTURE OF ALUMINIUM.

SPECIFICATION forming part of Letters Patent No. 763,479, dated June 28, 1904.

Application filed May 14, 1903. Serial No. 157,178. (No specimens.)

To all whom it may concern:

Be it known that I, GUSTAVE GIN, a citizen of the French Republic, residing in Paris, in the Republic of France, have invented a new and useful Process of Electrolytic Manufacture of Aluminium, (for which I have obtained patent in Italy, No. 64,966, dated September 9, 1902,) of which the following is a full, clear, and exact description.

This application is a continuation of my prior application, filed October 15, 1902, Serial No. 127,421.

This invention relates to a process of manufacturing aluminium in such a manner that the electrolytic solvent and the intermediate reagents used in the process are continuously recuperated.

This invention is illustrated in a diagrammatic manner in the accompanying drawing.

My process consists in electrolyzing a mixture of definite proportions of aluminium fluorid and sodium sulfid in which one molecule of the first ingredient is in presence of three molecules of the second according to the formula:

$$(1)\quad Al_2F_3+3Na_2S.$$

The fusion of this electrolyte takes place at a temperature slightly above 700° centigrade and is facilitated by the calories disengaged during the reciprocal reactions of the elements.

The successive progression of the reactions is as follows: As soon as the mixture begins to melt the constituents react upon each other, thus causing the formation of sodium fluorid and aluminium sulfid, according to the formula:

$$(2)\quad 2(Al_2F_6+3Na_2S)=(Al_2F_6,6NaF)+(Al_2S_3,3Na_2S).$$

The formation of sodic cryolite (Al_2F_3,6NaF) disengages 39.7 calories centigrade, and that of the sulfo-salt (Al_2S_3,$3Na_2S$) about twelve calories centigrade, so that the reaction (2) is strictly exothermic and disengages 75.4 calories centigrade. The sulfo-aluminate, the heat of formation of which is much lower than that of the fluo-aluminate, is alone decomposed by the current. The aluminium goes to the cathode and the sulfur to the anode, while the sodium sulfid reacts upon the fluo-aluminate to furnish a new quantity of aluminium sulfid, which is subsequently electrolyzed.

The electrolytic decompositions and the secondary reactions take place according to the formulæ:

$$(3)\quad (Al_2F_6,6NaF)+(Al_2S_3,3Na_2S)=\underset{-}{\boxed{2Al}}+(Al_2F_6,6NaF)+3Na_2S+\underset{+}{\boxed{3S}}$$

$$(4)\quad (Al_2F_6,6NaF)+3Na_2S=Al_2S_3+12NaF$$

$$(5)\quad Al_2S_3+12NaF=\underset{-}{\boxed{2Al}}+12NaF+\underset{+}{\boxed{3S}}$$

The totality of the phenomenon is therefore summed up by the following equation:

$$(6)\quad 2(Al_2F_6+3Na_2S)=\underset{-}{\boxed{4Al}}+12NaF+\underset{+}{\boxed{6S}}$$

In reality a certain quantity of carbon sulfid is disengaged at the anode at the same time with the sulfur.

The electrolysis takes place in a furnace having, as usual, an anode, preferably a multiple anode to facilitate the elimination of gaseous products, and a cathode. The current used must be sufficiently great to cause the fusion of the electrolyte and maintain the bath at a temperature of about 850° centigrade while the electrolytic reduction takes place.

A continuous current is used of an electromotive force of five to six volts with a quantity of current of one ampere, maximum, per square centimeter of active surface of the carbon anodes, and of 2.5 amperes, minimum, per square centimeter of cathode.

In order to prevent the vapor of sulfur and of carbon sulfid to escape to the atmosphere, the furnace is closed by a cover having a single issue connecting with the conduit leading the vapors to an oxidizing apparatus. The structure bearing the anodes may slide through this cover by means of appropriate mechanism.

A very important feature of my invention consists in the mode of preparation of the

electrolyte and the recuperation of the intermediate products by a series of operations forming a continuous closed cycle, the various phases of which are linked together and the main principle of which consists in starting from bauxite as a raw material to end in metallic aluminium as a manufactured product.

I first extract the aluminium fluorid from the raw bauxite by the following process: The dried, but not calcined, bauxite is pulverized and treated at the ordinary temperature with a solution of hydrofluoric acid in a mixing apparatus the lining of which is made of lead. This brings about the formation of aluminium and iron fluorids and of aluminium fluosilicate and fluotitanate according to the reactions:

(7) $Al_2O_3+6HF=Al_2F_6+3H_2O$

(8) $Fe_2O_3+6HF=Fe_2F_6+3H_2O$

(9) $Al_2O_3+3SiO_2+18HF=(3SiF_4,Al_2F_6)+9H_2O$

(10) $Al_2O_3+3TiO_2+18HF=(3TiF_4,Al_2F_6)+9H_2O$

I eliminate the iron and the silicic and titanic acids in the following manner: In the solution containing the fluorids and the fluo salts, formed as first described, I add hydrated alumina, which precipitates the iron first, and then the silicic and titanic acids according to the exothermic reactions:

(11) $Fe_2F_6+Al_2O_3=Fe_2O_3+Al_2F_6$

(12) $3SiF_4,Al_2F_6+2Al_2O_3=3SiO_2+3Al_2F_6$

(13) $3TiF_4,Al_2F_6+2Al_2O_3=3TiO_2+3Al_2F_6$

These reactions take place at the ordinary temperature; but they are accelerated by heating the materials to a temperature of about 60° centigrade.

The chemical precipitation of which I have just spoken does not necessitate the use of pure alumina. Ordinary bauxite mixed with water acts as well, though not as rapidly.

When precipitation has taken place, the mixture contains in solution aluminium fluorid only. It is then boiled for a few minutes to gather the precipitates of peroxid of iron which may remain in suspension and then filtered in a filter-press, giving a pure solution of aluminium fluorid. This solution is concentrated by vaporization and gives after cooling a precipitate of hydrated aluminium fluorid, which is separated from the mother-liquor, dried in a centrifugal machine, and dehydrated in a muffle-furnace at a dark-red temperature. The mother-liquor is preserved to be mixed with the liquor of a new operation.

The principal element of the electrolyte having been obtained as I have described, the sodium sulfid is manufactured separately by the reduction of anhydrous sodium sulfate according to the known reaction:

(14) $SO_4Na_2+2C=Na_2S+2CO_2$

This reduction takes place in a muffle-furnace the hearth of which is made of agglomerated magnesia, this body being impervious to aluminium sulfid.

It must be noticed that the sodium sulfate used in preparing the alkaline sulfid is not borrowed from an external supply; but it is one of the intermediate products recuperated during one of the phases of a cycle in the course of which sulfuric acid, hydrofluoric acid, and sodium sulfate are successively recuperated to finally culminate in materials which are the constituents of the electrolyte. (See reaction 15.)

Although the processes of prepartion of the intermediate products which have just been mentioned are respectively known, I shall examine them successively, so as to fully bring out the manner in which they are linked and the particular circumstances which connect them with my process.

The sulfur vapor which is disengaged at the anodes is the first burned in contact with the air, and the mixture of air and sulfurous anhydrid which is the result is transformed into sulfuric acid either in lead chambers or in a contact apparatus, using the well-known catalytic action of platinized asbestos. This latter process is preferable to that of the lead chambers, for it gives immediately a properly-concentrated sulfuric acid for the treatment of sodium fluorid, which will further be described.

The hydrofluoric acid, the use of which has been indicated above for the preparation of aluminium fluorid, is obtained by the treatment with concentrated sulfuric acid of the sodium fluorid forming the residue of the electrolytic action. The operation takes place in an apparatus the sides of which are lined with bricks made of barium sulfate agglomerated by means of coal-tar and the bottom of which is heated to a temperature between 250° and 300° centigrade. The following well-known reaction is produced:

(15) $SO_4H_2+2NaF=SO_4Na_2+2HF.$

The direct treatment by means of the gaseous sulfuric anhydrid as it comes out of the oxidizing apparatus upon the sodium fluorid pulverized and slightly dampened may be substituted for the reaction by concentrated sulfuric acid.

In both cases the hydrofluoric acid is gathered and condensed by the usual means, and there remains anhydrous sodium sulfate, which is employed as I mentioned above for the preparation of sodium sulfid. As the disengaged hydrofluoric acid is utilized for the treatment of the bauxite and the production

of aluminium fluorid, it will be seen that the two products evolved in the last operation come, respectively, into play for the preparation of the two elements of the electrolyte.

To sum up, all the phases of the continuous close cycle, which is the feature of my process, may be expressed as follows:

First phase—Preparation of the electrolyte:

$$(16)\begin{cases} Al_2O_3+6HF=3H_2O+\boxed{Al_2F_6} \\ 3SO_4Na_2+6C=6CO_2+\boxed{3Na_2S} \end{cases}$$

Second phase—Electrolysis:

$$(17)\ Al_2F_6+3Na_2S=6NaF+\underset{+}{\boxed{3S}}+\underset{-}{\boxed{2Al}}$$

Third phase—Recuperation of the reagents:

$$(18)\ 3S+O_9+3H_2O=3SO_4H_2$$

$$(19)\ 6NaF+3SO_4H_2=3SO_4Na_2+6HF.$$

In reality bauxite and carbon only are consumed, and the other materials used are indefinitely recovered and recuperated. In practice there are losses by slow volatilization of sodium fluorid and the carrying down of intermediate bodies with the precipitates.

The losses are easily compensated, as far as sodium and sulfur are concerned, by introducing in the sodium-sulfid furnace a sufficient proportion of pure sodium sulate.

The elimination of fluorin is made up by the use of a supplementary apparatus for the usual preparation of hydrofluoric acid, in which fluor-spar is treated with sulfuric acid from an outside source.

I know that it has been proposed to use aluminium sulfid as the decomposable element of the electrolyte in the manufacture of aluminium; but my invention is essentially different from all the methods previously contemplated. For instance, Bucherer in his German patent, No. 63,995, employs a double sulfid of aluminium and of alkaline metal in solution with an alkaline haloid salt, and he obtains a double sulfid by treating the alkaline polysulfid by means of carbon and sulfur in excess. This mode of preparation of the electrolyte is therefore essentially different from mine. His starting-point is the electrolysis:

$$Na_6Al_2S_6+NaCl\ (or\ NaF),$$

while mine is

$$Al_2F_6+3Na_2S.$$

The two electrolytes are therefore not alike. Moreover, with the Bucherer electrolyte the double sulfid being decomposed by the current there remains a residue containing sodium sulfid mixed with a solvent haloid salt, while the residue of my operation is solely composed of sodium fluorid, which reënters the cycle of operations as I have explained above.

In the German Patent No. 68,909, November 18, 1890, to the Aluminium Industrie Gesellschaft of Neuhausen, the electrolysis of aluminium sulfid alone or mixed with haloid salts is also proposed; but this aluminium sulfid is obtained only by the use of pure alumina—that is to say, by means not only very expensive, but also completely different from those I have invented. Moreover, I produce the aluminium sulfid in the bath at the moment the electrolysis takes place, while in the patent under consideration it is prepared in advance and outside the bath, which is a very unfavorable condition, by reason of the ease with which this compound changes in contact with the air.

Gooch in his English Patent No. 16,555, August 15, 1899, has patented a process based upon the electrolysis of aluminium sulfid produced by the action of carbon sulfid upon the alumina dissolved in the bath. This method has evidently nothing in common with mine.

To sum up, these processes differ from my invention, first, by the essential constitution of the electrolyte; second, by the reciprocal reaction of the constituents; third, by the means of production and recuperation of the electrolyte.

Looking at the matter from another point of view, it must be observed that my process consists in a series of operations forming a whole starting from raw bauxite to end in metallic aluminium. Several inventors have already attempted to practice an analogous method by different means, and I shall mention them to further emphasize the novelty of my invention.

French Patent No. 230,546, June 2, 1893, to Cornelius Doelter, proposes a slightly-different process, but again comprising the electromagnetic separation of iron. French Patent No. 250,108, September 6, 1895, to the Mayer et Smidt Company, claims the purification of emery by the reduction of the oxid of iron in an electrical furnace. Finally, Hall (American Patents Nos. 677,207, 677,208, June 25, 1901, and 678,732, July 16, 1901) has disclosed an analogous means of preparing alumina from raw bauxite; but all these processes have no other object than the previous preparation of pure alumina to form an electrolyte very different from mine, and this preparation is quite independent from the process of manufacturing aluminium itself, while in my method the treatment of bauxite is inseparable from the production of the metal itself and from the other operations, which form a novel whole distinctly characterized by the means used to proceed economically from raw bauxite to metallic aluminium.

My process suppresses the delicate and expensive manufacture of pure alumina and replaces it by the much more practical prepara-

tion of aluminium fluorid. On the other hand, the counter electromotive force of polarization of the electrolyte being not above one volt, there is the same economy of electrical energy as results from the electrolysis of aluminium sulfid, while avoiding the considerable difficulties in the preparation and preservation of the compound. Finally, my electrolyte is easily handled, and it satisfies all the conditions of density, fusibility, and conductivity required for the manufacture of aluminium.

What I claim is—

1. The process of manufacturing aluminium which consists in decomposing by an electric current an electrolyte formed by a molten mixture in definite proportions of fluorid of aluminium and sulfid of sodium in which one molecule of fluorid of aluminium and three molecules of sulfid of sodium are present.

2. The process of preparation and continuous recuperation of the electrolyte and its intermediate reagents, which consists in treating bauxite with a solution of hydrofluoric acid in sufficient quantity to combine with all the component parts of the bauxite so as to form aluminium fluorid (principal element of the electrolyte) as well as iron fluorid and fluosilicates and fluotitanates of aluminium, the silica, the titanic acid and the iron being subsequently precipitated by an addition of alumina, the hydrofluoric acid being obtained by the decomposition of the sodium fluorid which is the residue of the electrolysis, this decomposition being effected by means of the sulfuric acid recuperated through the oxidation of the sulfur disengaged at the anode, the sodium sulfid (secondary element of the electrolyte) being manufactured by means of the reduction of the sodium sulfate resulting from the decomposition of sodium fluorid by sulfuric acid, the above-described operations constituting a continuous closed cycle, substantially as herein described.

In testimony whereof I have signed my name in the presence of two subscribing witnesses.

GUSTAVE GIN.

Witnesses:

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J. ALLISON BOWEN.