22359/88

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

0 0 5 4 4 8

CONVENTION APPLICATION FOR A PATENT

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address (es).

I/We (1) ALUMINIUM PECHINEY

of 23, rue Balzac, 75008 Paris, France

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)

PROCESS FOR REGULATING THE ACIDITY OF ~~AN ELECTROLYTIC BATH BY RECYCLING FLUORINATED PRODUCTS EMITTED BY THE~~ HALL-HEROULT ELECTROLYTIC CELLS

(3) Here insert number(s) of basic application(s)

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered (3)

8713543

(4) Here insert Name of basic Country or Countries, and basic date or dates

for a patent or similar protection made in (4) France

on 18th September 1987

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 4-10-90

My/Our address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys, 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 15th day of September 19 88

(5) Signature (s) of Applicant (s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association.

(5) ALUMINIUM PECHINEY

by

Louis C. Gebhardt

Registered Patent Attorney

MQ02873 16/09/88

To:

THE COMMISSIONER OF PATENTS.

AUSTRALIAN PATENT OFFICE MBS

Edwd. Waters & Sons, Melbourne.

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

(1) Here insert (in full) Name of Company.

In support of the Convention Application made by(1) ALUMINIUM PECHINEY

(hereinafter referred to as the applicant) for a Patent

(2) Here insert title of Invention.

for an invention entitled:(2) PROCESS FOR REGULATING THE ACIDITY OF AN ELECTROLYTIC BATH BY RECYCLING FLUORINATED PRODUCTS EMITTED BY THE HALL-HEROULT ELECTROLYTIC CELLS

(3) Here insert full Name and Address, of Company official authorized to make declaration.

I,(3) CLAUDE PASCAUD

of 23, rue Balzac, 75008 Paris, France

do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in(4) France

(4) Here insert basic Country or Countries followed by date or dates and basic Applicant or Applicants.

on the 18th day of September 19 87, by ALUMINIUM PECHINEY

on the XXXXX day of XXXXX 19 XXXXXXXXX, by

(5) Here insert (in full) Name and Address of Actual Inventor or Inventors.

3.(5) JEAN-LUC BASQUIN, 396, avenue Henri Falcoz, 73300 St. Jean De Maurienne, France and BENOIT SULMONT, rue Florimont Truchet, 73300 St. Jean De Maurienne, France

is/are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of the said actual inventors

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Paris, France

this 18th day of August 19 88

(6) Signature.

(6) Claude PASCAUD

To: THE COMMISSIONER OF PATENTS.

Edwd. Waters & Sons, Melbourne.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-22359/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 605448

(Modified Examination)

(54) Title
PROCESS FOR REGULATING THE ACIDITY OF HALL-HEROULT ELECTROLYTIC CELLS

International Patent Classification(s)
(51)[4] C25C 003/20

(21) Application No. : 22359/88 (22) Application Date : 16.09.88

(30) Priority Data

(31) Number	(32) Date	(33) Country
87 13543	18.09.87	FR FRANCE

(43) Publication Date : 23.03.89

(44) Publication Date of Accepted Application : 10.01.91

(71) Applicant(s)
ALUMINIUM PECHINEY

(72) Inventor(s)
JEAN-LUC BASQUIN; BENOIT SULMONT

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS, Locked Bag 5, HAWTHORN VIC 3122

(57) Claim

1. Process for regulating the acidity of the electrolytic bath of electrolytic cells by recycling fluorinated effluents emitted by Hall-Heroult electrolytic cells for the production of aluminium, in which these fluorinated effluents are collected, by a dry route, on alumina in an effluent treatment apparatus, characterized in that it comprises the following stages:

establishing a reference value for the F/Al_2O_3 weight ratio in connection with the alumina leaving the effluent treatment apparatus, while continuously measuring the fluorine and alumina quantities entering the effluent treatment apparatus;

regulating the alumina flow rate to maintain the F/Al_2O_3 ratio at the reference value;

passing the fluorinated alumina into a storage means with a predetermined capacity and equipped with a level measuring means;

supplying the electrolytic cells with fluorinated

.../2

alumina taken from the storage means; and adjusting the acidity of each cell by the addition of aluminium fluoride and/or varying the power dissipated in the cell.

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL) 605448

Class Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :

This document contains the amendments made under Section 49 and is correct for printing.

Name of Applicant : ALUMINIUM PECHINEY

Address of Applicant : 23, rue Balzac, 75008 Paris, France

Actual Inventor: JEAN-LUC BASQUIN and SULMONT BENOIT

Address for Service : EDWD. WATERS & SONS,
50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

PROCESS FOR REGULATING THE ACIDITY OF ~~AN ELECTROLYTIC BATH BY RECYCLING FLUORINATED PRODUCTS EMITTED BY THE~~ HALL-HEROULT ELECTROLYTIC CELLS

The following statement is a full description of this invention, including the best method of performing it known to : us

AUSTRALIAN PATENT OFFICE MVS

PROCESS FOR REGULATING THE ACIDITY OF ~~AN ELECTROLYTIC BATH BY RECYCLING FLUORINATED PRODUCTS EMITTED BY THE~~ HALL-HEROULT ELECTROLYTIC CELLS

Technical Field of the Invention

The present invention relates to a process for regulating the acidity of the cryolite bath of Hall-Héroult cells by the controlled recycling of the fluorinated effluents emitted by said cells. Thus, it relates to the technical field of the production of aluminium by igneous electrolysis of alumina dissolved in a bath based on cryolite melted at a temperature of approximately 930 to 970°C.

State of the Art

The production of aluminium by the Hall-Héroult process makes use of an electrolyte essentially constituted by sodium cryolite Na_3AlF_6. It is standard practice to add to the cryolite various additives with a view to somewhat reducing its melting point, the most important of these being aluminium trifluoride AlF_3. This leads to an electrolyte, whereof the NaF/AlF_3 mass ratio is below 1.5 and can e.g. reach 1. The term acid is often used in connection with an electrolyte having a NaF/AlF_3 mass ratio below 1.5 and its acidity is expressed by the value of this ratio, called the bath ratio.

An operating Hall-Héroult cell emits fluorinated gaseous effluents, essentially in the form of hydrofluoric acid. Fo example, this emission can reach 30 kg (counted in fluorine) per tonne of aluminium produced and therefore substantially for two tonnes of alumina consumed.

In most modern installations, this fluorine is collected by fixing on the pure alumina, which is then used for supplying electrolytic cells. As a function of he particular case, part or all said alumina is used for fixing the fluorinated emissions collected on the cells. The thus fluorinated alumina is stored in bins and the electrolytic cells are supplied therefrom.

The problem which arises is that in the existing collecting systems, the fluorine content of the alumina having traversed the gas defluorination system fluctuates between extreme values of approximately 0.5 and 3% (by weight of F). However, it is essential that the fluorine supplies to the electrolyte are perfectly controlled so as to maintain its acidity, in the manner defined hereinbefore, at a predetermined constant value and this will not be the case if the alumina has a fluctuating fluorine content.

European patent application EP 195142 A1 proposes a method for indirectly controlling the NaF/AiF_3 mass ratio based on monitoring the temperature of the electrolyte. Thus, for a constant electrolysis intensity, there is a relationship between the (measured) temperature of the bath and its acidity. The process consequently consists of fixing a reference temperatue Tc and a reference rate for the addition of the pure AlF_3 to the bath, permanently comparing the measured values with the reference values and adjusting the AlF_3 additions in kg/24 h in order to bring the parameters to the reference value. However, this process only considers the pure AlF_3 additions and does not take account of the recycling levels of the fluorine emitted by the electrolytic cells and does not suggest any means for solving this problem.

Object of the Invention

The object of the invention is a process for regulating the acidity of the electrolytic bath for the production of aluminium by controlling the addition of fluorinated products and recycling of the fluorinated effluents fixed to the alumina in a fumes treatment installation, characterised in that it comprises the following stages:

a reference value is fixed for the fluorine/alumina weight ratio for the alumina leaving the effluent treatment apparatus, the quantity of fluorine and alumina entering the

effluent treatment apparatus is measured continuously or at predetermined intervals, the alumina flow introduced into the effluent treatment apparatus is regulated so as to maintain the F/Al_2O_3 ratio at its reference value, homogeneously fluorinated alumina is passed into a storage means with a predetermined capacity and which is equipped with a level measuring means, the electrolytic cells are supplied in homogeneous manner with fluorinated alumina taken from the storage means and the acidity of each cell is adjusted on the basis of the addition of aluminium fluoride and/or the variation of the electric power dissipated in the cell.

For performing this process, a number of parameters is used as a basis and certain of these are imposed by the electrolytic process: the alumina supply rate, imposed from the time when the electrolytic intensity is fixed and which is e.g. 4 tonnes/day/cell for cells operating under 280,000 amperes,

the fluorine emission by the cell (over a 24 hour period), approximately 30 ($\pm$10) kg per tonne of aluminium, i.e. approximately 15 kg per tonne of alumina introduced into the cell;

whereas others can be modified within certain limits:

the acidity of the electrolytic bath (NaF/AlF_3 mass ratio), the pure alumina quantity introduced into the device for collecting the fluorinated emissions of a group of cells (series or part of the series) and it is essentially the latter parameter which is to be influenced.

Description of the Invention

The stages of the process are as follows:

1) A reference value is fixed for the F/Al_2O_3 weight ratio for the alumina leaving the effluent processing apparatus, said ratio being between approximately 0.5 and 3% and preferably close to 1.5%, which corresponds to the collecting of 30kg of fluorine per tonne of aluminium produced or approximately 2 tonnes of alumina introduced into the cell.

2) A continuous determination takes place of the fluorine flow rate in milligrams per second entering the effluent processing system and coming from the group of cells connected to said system by simultaneously measuring the fluorine concentration in the collected gases and their mass flow. The concentration measurement can be carried out by different processes, e.g. by an electrochemical method with a specific electrode, whose potential is linked with the fluorine flow rate by a prior calibration.

3) A continuous measurement takes place of the pure alumina quantity introduced into the effluent treatment apparatus and which is brought into contact with the fluorinated gases. This measurement is also carried out by per se known processes, e.g. by passing the alumina onto an articulated blade supported by an elastic means, whereof the restoring torque is removed and which is linked with flow rate by a relationship established by a prior calibration.

4) The alumina is introduced into the effluent treatment apparatus by a device having a regulatable flow rate, so that action takes place on the latter so as to maintain or bring the value of the F/Al_2O_3 ratio to the reference value. The variable flow rate alumina distributor may but need not be that according to french patent 2575734 (= EP 190082) in the name of ALUMINIUM PECHINEY and which is based on the "potential fluidisation" principle.

5) The homogeneously fluorinated alumina is passed into an intermediate storage means having a predetermined capacity and which is equipped with a level measuring means. The group of cells in question is supplied therefrom with fluorinated alumina having a constant, known fluorine content.

6) In addition, the following complimentay stage is introduced into the process. The storage capacity of the homogeneously fluorinated alumina is not unlimited. Thus, over a certain period, it may arise that the fluorine emissions have increased in such a way that, for a fixed

reference value F/Al_2O_3, the fluorinated alumina stock increases to the point of saturating the bin. If it is wished to avoid costly manipulations and transfers of fluorinated alumina, it is preferable to increase the reference value of F/Al_2O_3 in order to make the fluorinated alumina production equal to its consumption, whilst adopting the opposite procedure when the bin is becoming exhausted. For example, it is possible to fix a high reference value and a low reference value for the fluorinated alumina level in the silo, whereby passing beyond one of these limits leads to an alarm as a result of which the reference value can be manually or automatically modified. Preferably, the upper limit is fixed at 90% of the capacity of the storage means and the lower limit is fixed at 10% of said capacity.

7) With the control of the fluorine addition by the fluorinated alumina supplying the cells being assured, it is possible to individually adjust the acidity of each cell as a function of its individual disturbances, such as thermal variations and states, anode effect and anode change.

Realization of the Invention

The invention was realized on a group of 105 electrolytic cells belonging to a series of 120 operating under an intensity of 280,000 amperes, said 105 cells being connected to a gaseous efluent collecting and treatment apparatus and independent from the remainder of the series. The acidity of the bath was fixed at the outset at 1.09 (bath ratio) corresponding to a melting point of 950°C and the F/Al_2O_3 ratio in the apparatus was fixed at 1.50%.

The cells were supplied exclusively with fluorinated alumina and it was found that over the first few days the alumina level in the storage bin tended to increase. The reference value was then lowered to 1.55 and this value ensured a quasi-stability of the level for several weeks.

At the end of the trial period, the means acidity level was established at 1.09 (bath ratio) with a standard deviation of 0.1. During this period the individual distrubances to each cell were taken into account by tables known to the Expert.

Advantages resulting from the Invention

The realisation of the invention leads to a certain number of advantages in the operation of the electrolytic cells:

the operation of the cells is more stable, due to the fact that the bath acidity remains constant and therefore so does its melting point, which at the same time ensured the dimensional stability of the lateral slopes constituted by solidified electrolytic bath,

the cells of the same series remain homogeneous because they are supplied with the same fluorinated alumina with a substantially constant fluorine content and

a consequence of this improved stability is a slight increase in the Faraday efficiency, which is estimated at approximately 1/2 point.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for regulating the acidity of the electrolytic bath of electrolytic cells by recycling fluorinated effluents emitted by Hall-Heroult electrolytic cells for the production of aluminium, in which these fluorinated effluents are collected, by a dry route, on alumina in an effluent treatment apparatus, characterized in that it comprises the following stages:

establishing a reference value for the F/Al_2O_3 weight ratio in connection with the alumina leaving the effluent treatment apparatus, while continuously measuring the fluorine and alumina quantities entering the effluent treatment apparatus;

regulating the alumina flow rate to maintain the F/Al_2O_3 ratio at the reference value;

passing the fluorinated alumina into a storage means with a predetermined capacity and equipped with a level measuring means;

supplying the electrolytic cells with fluorinated alumina taken from the storage means; and

adjusting the acidity of each cell by the addition of aluminium fluoride and/or varying the power dissipated in the cell.

2. Process according to claim 1, characterized in that the reference value for the F/Al_2O_3 weight ration is between about 0.5 and about 3%.

3. Process according to claims 1 or 2, characterized in that when the alumina level in the storage means passes beyond a predetermined upper or lower value, the F/Al_2O_3 reference value is modified to bring said level to a value between the upper and lower limits.

4. Process according to claim 3, characterized in that the upper limit is fixed at about 90% of the capaicty of the storage means and the lower limit at about 10% of said capacity.

DATED this 1st day of March, 1990

ALUMINIUM PECHINEY

WATERMARK, PATENT & TRADEMARK ATTORNEYS
2ND FLOOR, 290 BURWOOD ROAD
HAWTHORN VICTORIA 3122
AUSTRALIA

al:lcg:(4.8)