GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, LOWER CIRCULAR ROAD, CALCUTTA-17.

Specification No. 103067, Application No. 103067, dated 17th December 1965. Complete Specification left on 14th September 1966. (Application Accepted 1st September 1967.)

Index at acceptance 70C$_4$ +6[LVIII(5)].

PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC PREPARATION OF PERCHLORATES.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification describes the nature of this invention.

This is an invention by HANDADY VENKATAKRISHNA UDUPA, Scientist, SRINIVASA SAMPATH, Scientist, KAPISTHALAM CHETLUR NARASIMHAM, Scientist, MUTHIAH NAGALINGAM, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi, CHAKKALAKKAL JACOB RAJU of the Fertilizer Corporation India Ltd., Trombay Unit, Bombay and PADMANABHAN POTTY GOVINDA RAO, Production Supervisor, Madras Rubber Factory, Tiruvottiyur, Madras, all Indians,

This invention relates to improvements in or relating to the electrolytic preparation of perchlorates directly from sodium chloride using lead dioxide anode.

Hitherto it has been the practice to employ a two-stage process for the production of perchlorates from chlorides, the first stage being the oxidation of chloride to chlorate using graphite, magnetite or lead dioxide anodes and the second stage consisting of the oxidation of chlorate to perchlorate, using platinum or lead dioxide anodes. In between the stages, the solutions have to be processed to isolate the chlorate and recover the unconverted chloride. Japanese research workers have studied the direct oxidation of chloride to perchlorate using lead dioxide anode, avoiding the intermediate processing of liquors but there are two discrete electrochemical stages where the conditions of electrolysis are entirely different.

The objections to the current practices are that graphite gets disintegrated to a considerable extent and magnetite to a lesser extent when used in the production of chlorates and there is an inevitable loss of platinum due to corrosion in the perchlorate cell. The processing of the effluent from the chlorate cell introduces another complication in the method. The modification effected by the Japanese workers does not do away with two stages of electrolysis.

The object of this invention is to obviate these disadvantages by preparing the perchlorates directly from sodium chloride in a single step of electrolytic oxidation by the use of carbon or graphite substrate lead dioxide anodes (the preparation of such electrodes is covered by Indian Patent No. 66195) thus avoiding the use of graphite, magnetite or platinum and the processing of liquors halfway through the process, electrolysing a solution of sodium chloride using graphite or carbon substrate lead dioxide anode and passing adequate direct current to convert all the chloride to perchlorate, the conditions of electrolysis being maintained constant at predetermined levels throughout the period.

The following typical examples are given to illustrate the invention:

	Example I	*Example II*
Concentration of electrolyte (g/l)	290·8	291
Addition agents NAF (g/l)	2	2
Anode	Carbon substrate lead dioxide	Graphite substrate lead dioxide
Cathode	Stainless steel	Stainless steel
Current density (amp/dm^2)	10	25
Current concentration (amp/l)	18·75	25
Cell voltage (volts)	3·0—3·9	3·7—4·5
Quantity of electricity passed (amp-hrs)	1577	1565
Energy consumption (kwh/kg)	13·29	13·93

The following are among the main advantages of the invention:

(1) The electrolytic preparation of perchlorates can be carried out in a single step from chloride.

(2) The intermediate processing is avoided.

(3) The cell can be operated using a wide range of current densities (for *e.g.*, 5 amp/dm^2 to 40 amp/dm^2).

(4) The cell can be operated using a wide range of temperatures (30° C. to 60° C.).

(5) The lead dioxide is the only material which can be used as an anode in both stages of electrolysis.

(6) Addition of sodium fluoride gives a high current efficiency.

(7) The energy consumption for the preparation of perchlorates compares favourably with the two stages electrolysis.

R. BHASKAR PAI,

PATENTS OFFICER,

Council of Scientific and Industrial Research,

Dated this 10th day of December 1965.

COMPLETE SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC PREPARATION OF PERCHLORATES

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed.

This is an invention by HANDADY VENKATAKRISHNA UDUPA, Scientist SRINIVASA SAMPATH, Scientist, KAPISTHALAM CHETLUR NARASIMHAM, Scientist MUTHIAH NAGALINGAM, Senior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi, CHAKKALAKKAL JACOB RAJU of the Fertilizer Corporation of India Ltd., Trombay Unit, Bombay and PADMANABHAN POTTY GOVINDA RAO, Production Supervisor, Madras Rubber Factory, Tiruvottiyur, Madras, all Indian citizens.

This invention relates to improvements in or relating to the electrolytic preparation of perchlorates directly from sodium chloride using lead dioxide anode.

Hitherto, it has been the practice to employ a two-stage process for the production of perchlorates from chlorides, the first stage being the oxidation of chloride to chlorate using graphite, magnetite or lead dioxide anodes and the second stage consisting of the oxidation of chlorate to perchlorate, using platinum or lead dioxide anodes. In between the stages, the solutions have to be processed to isolate the chlorate and recover the unconverted chloride. Japanese research workers have studied the direct oxidation of chloride to perchlorate using lead dioxide anode, avoiding the inter-

mediate processing of liquors but there are two discrete electrochemical stages wherein the conditions of electrolysis are entirely different.

The objections to the current practice are that graphite gets disintegrated to a considerable extent and magnetite to a lesser extent when used in the production of chlorates and there is an inevitable loss of platinum due to corrosion in the perchlorate cell.

The object of this invention is to obviate these disadvantages by preparing the perchlorates directly from sodium chloride in a single step of electrolytic oxidation by the use of lead dioxide electrodes either electrodeposited anodes without substrates or deposited on such substrates as carbon or graphite (Indian Patent No. 66195, December 1958) or on any other material, thus avoiding the use of graphite, magnetite or platinum as anodes.

The processing of cell liquors halfway through the process is avoided by electrolysing a solution of sodium chloride using lead dioxide anode and passing adequate direct current to convert all the chloride to perchlorate, the conditions of electrolysis being maintained constant at predetermined levels throughout the period. Once the direct oixdation of chloride to perchlorate is attempted, none of the commonly used electrodes *viz.*, graphite, magnetite or platinum can be employed singly as anode material for this one-step process and lead dioxide is the natural choice at present. The addition of sodium fluoride made at the beginning of the electrolysis makes a profound difference on the course of electrolysis. The simultaneous formation of chlorate to perchlorate in the presence of chloride confers a beneficial influence on the performance of the electrode. The modifications introduced, forming part of the present invention, have simplified the process with consequent reduction in the energy consumption to 12-14 kwh/kg. It is also possible to further effect a saving in power for electrolysis by suitably adjusting the anode current density only at the appropriate time (*i.e.*, by increasing the anode current density from say 10 to 20 amp/dm^2 as soon as all the chloride is converted). Two sets of cells operating at two different current densities but the same circuit amperage can thus be employed and the energy consumption can be as low as 10 to 11.5 kwh/kg comparable to the present day two-step electrolytic method.

According to the present invention, the process of preparing sodium perchlorate directly from sodium chloride in a single step of electrolytic oxidation consists in passing a direct current through a bath of sodium chloride solution containing fluoride ions wherein the electrolytic oxidation is carried out in a cell having a stainless steel cathode and a lead dioxide anode using a current density range of 5 to 40 amp/dm^2 at a temperature of 30° to 60°C.

The said fluoride ions may be provided by adding sodium fluoride or hydrogen fluoride to the said bath.

The said anode may consist of massive lead dioxide or an electrode having lead dioxide electro-deposited on a substrate like graphite.

About 0.5 to 5 g/l of sodium fluoride is added to the sodium chloride solution.

The sodium fluoride added is about 2 g/l.

The conditions of electrolysis are maintained constant at predetermined levels throughout the process.

The oxidation of chloride to perchlorate is thus carried out in a single step, wherein lead dioxide (massive or electrodeposited on substrates like graphite or carbon etc.) and stainless steel are used as anodes and cathodes respectively. A current density range of 5 to 40 amp/dm^2, a temperature of 30°-60°C. and fluoride as addition agent are employed.

The intermediate processing of cell liquor is avoided.

A flow sheet of the process is given in Fig. 1 of the accompanying drawing. Typical examples:

	Example I	*Example II*	*Example III*
Concentration of electrolyte (initial) (g/l) NaCl	290.8	291	308.1
Addition agent NaF (g/l)	2	2	2
Anode . . .	Carbon substrate lead dioxide	Graphite substrate lead dioxide	Graphite substrate lead dioxide
Cathode . . .	Stainless steel	Stainless steel	Stainless steel
Current density (amp/dm^2)	10	25	19
Current concentration (amp/l) . . .	18·75	25	10
Temperature of electroyte (°C) . . .	40	40	45
Cell voltage (volts) .	3·0—3.9	3·7—4·5	3·9—4·5
Current efficiency (%) .	52·2	53·2	57·5
Energy consumption (Kwh/kg of $NaClO_4$) .	13·3	13·9	13·2

Based on the conditions arrived at in the laboratory (Examples I and II are typical of the laboratory runs), one 800 amp cell was set up and operated with lead dioxide coated graphite rod anodes and stainless steel cathodes. Example III above illustrates results obtained from this larger cell.

Advantages: The present invention envisages only one step for the production of perchlorates using lead dioxide anodes without recourse to processing in between to remove chromate or isolate solid chlorate.

Summary: The present invention consists in producing perchlorates directly from chloride using lead dioxides and stainless steel cathode and employing sodium fluoride as addition agent even at the beginning of electrolysis. A change of current density which involves conducting the electrolysis in two sets of cells in series can help to reduce the energy consmuption still further to a favourable value.

We claim:

1. A process of preparing sodium perchlorate directly from sodium chloride in a single step of electrolytic oxidation, which consists in passing a direct current through a bath of sodium chloride solution containing fluoride ions wherein the electrolytic oxidation is carried out in a cell having a stainless steel cathode and a lead dioxide anode using a current density range of 5 to 40 amp/dm^2, at a temperature of 30° to 60°C.

2. A process as claimed in Claim 1, wherein the said fluoride ions are provided by adding sodium fluoride to the said bath.

3. A process as claimed in Claim 1, wherein the said fluoride ions are provided by adding hydrogen fluoride to the said bath.

4. A process as claimed in Claim I, wherein the said anode consists of massive lead dioxide.

5. A process as claimed in Claim 1, wherein the said anode consists of an electrode having lead dioxide electro-deposited on a substrate like graphite.

6. A process as claimed in Claim 2, wherein about 0.5 to 5 g/l of sodium fluoride is added to the sodium chloride solution.

7. A process as claimed in Claim 6 wherein the sodium fluoride added is about 2 g/l.

8. A process as claimed in Claim 1, wherein the conditions of electrolysis are maintained constant at predetermined levels throughout the process.

R. BHASKAR PAI.

Patent Officer,

Council of Scientific & Industrial Research

Dated this 6th day of September 1966.

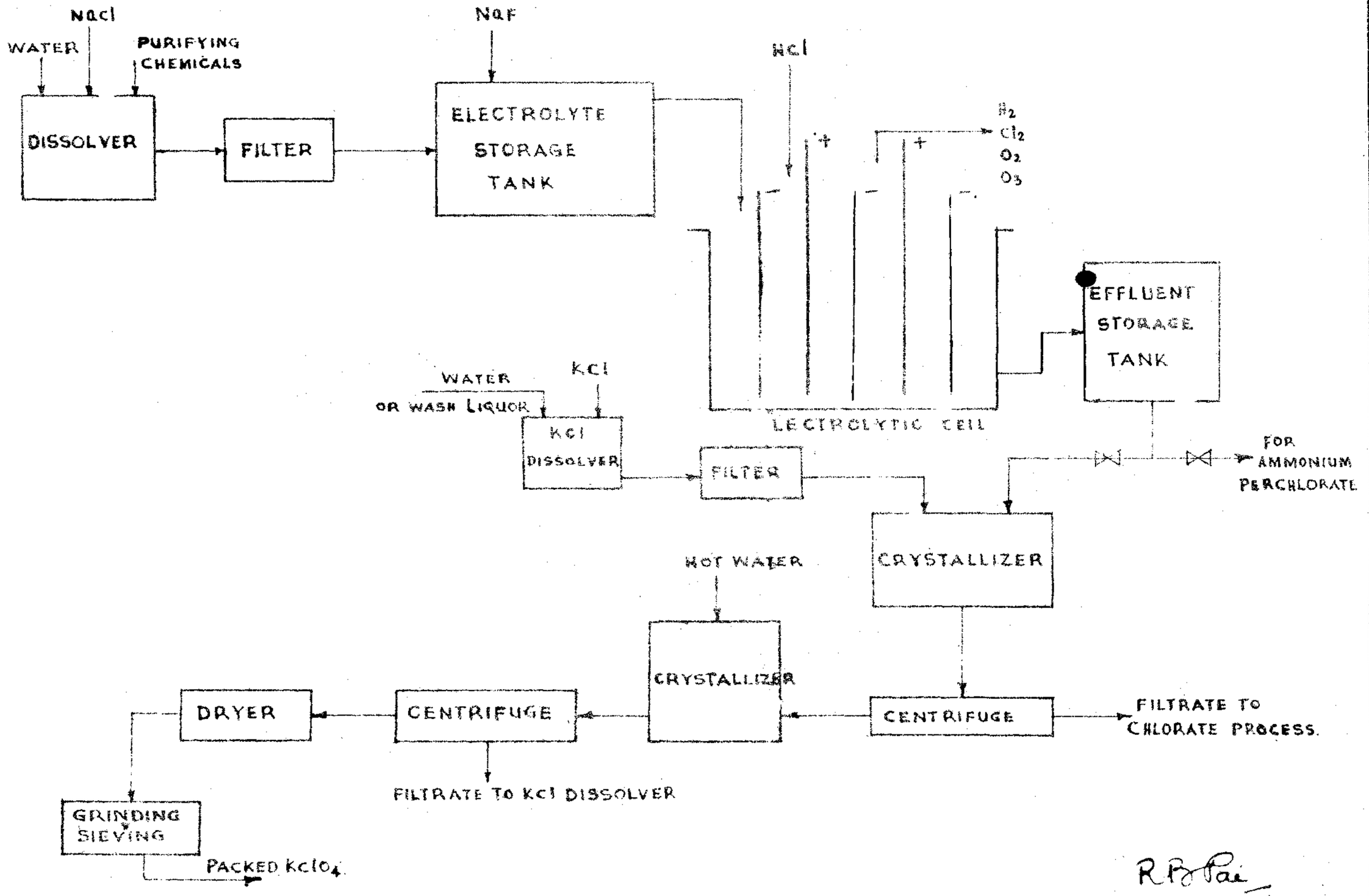
MGIP—Sant (K.S.R. Unit)—S14— Patent9/6—26-5-75—100.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

NO: 103067

NO OF SHEETS : 1

SHEET NO : 1



PRINTED BY HEADS & LITHOGRAPHIC CO. CALCUTTA-34.

Fig. 1.

R B Pai

(R.B. PAI)
PATENTS OFFICER
C.S.I.R