

GOVERNMENT OF INDIA, THE PATENT OFFICE  
214, ACHARYA JAGADISH BOSE ROAD  
CALCUTTA-700017.

Complete Specification No. 152858 dated 4th August, 1979

Application No. 557/Del/79 dated 4th August, 1979

Acceptance of the complete specification advertised on *21st April, 1984*.

Index at acceptance — 39 C /III/.

International Classification — C01c 1/00.

" AN IMPROVED CYCLIC ELECTROCHEMICAL PROCESS FOR THE  
PRODUCTION OF AMMONIUM PERCHLORATE FROM SODIUM CHLORIDE".

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New Delhi-110001, 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 :-

PRICE : TWO RUPEES

This is an invention by Handady Venkatekrishna Udape, Kapisthalem Chetim Narasimham, Reappagounder Palanisamy and Pallickal Ulahannan John, Scientists of Central Electrochemical Research Institute, Karaikudi-623,006, Tamil Nadu, India, all Indians.

This invention relates to an improved cyclic electrochemical process for the production of ammonium perchlorate from sodium chloride. The ammonium perchlorate is obtained by double decomposition of sodium perchlorate solution with a slurry of ammonium chloride at  $90^{\circ}$  to  $105^{\circ}\text{C}$  and isolating the same. The perchlorate content is not lost in waste liquor and the complete recovery of perchlorate is achieved by expelling ammonia with sodium hydroxide, and reusing this as cell feed with proper adjustment of sodium chloride.

Hitherto it has been the practice to prepare ammonium perchlorate by passing hydrogen chloride and ammonia gases through sodium perchlorate solution and recovering ammonium perchlorate by evaporation and chilling (procedure adopted by M/s Western Electrochemical Company, U.S.A.).

Another method for the production of ammonium perchlorate consists in the double decomposition of sodium perchlorate solution with ammonium chloride solution and recovery of perchlorate by expelling ammonia after removing the solid ammonium perchlorate (procedure adopted by M/s Pacific Engineering and Production Company, Nevada, U.S.A.).

In the third method ammonium sulphate is employed for double

decomposition of sodium perchlorate to get ammonium perchlorate and sodium sulphate.

The objection to the first procedure described above is that it involves the loss of material and also inclusion of large quantity of sodium chloride in the crude ammonium perchlorate thereby necessitating a number of recrystallisation steps.

The details of the quantitative data of the second procedure are not available.

Ammonium perchlorate obtained by the third method has been giving higher sulphated ash in the final analysis and sodium sulphate has been a byproduct involving disposal problem.

According to this invention there is provided an improved cyclic electrochemical process for the production of ammonium perchlorate from sodium chloride which is characterised in subjecting the sodium chloride to electrolytic oxidation in a cell using lead dioxide as anode, treating the used electrolyte containing sodium perchlorate thus formed by double decomposition with ammonium chloride to form ammonium perchlorate, cooling the reaction product to precipitate ammonium perchlorate formed, boiling the resultant liquor with sodium hydroxide to remove ammonia and reusing the regenerated sodium chloride as cell feed in the electrolytic cell.

Sodium perchlorate solution containing 600 to 800 g/l obtained from the perchlorate cell by the oxidation of sodium chloride, is double decomposed with the desired quantity, ranging from 70% to

152858

stoichiometric quantity based on perchlorate content, of solid ammonium chloride made into a slurry with calculated quantity of water at 90 to 105°C and the hot liquor is cooled to room temperature. After separating the precipitated ammonium perchlorate by filtration, the filtrate is subjected to further cooling up to 5°C when the second crop of ammonium perchlorate is precipitated. The liquid obtained after filtering the second crop is boiled with the required quantity of sodium hydroxide to expel ammonia thereby getting a solution containing sodium salts free from ammonia suitable for reuse (after adjusting the concentration of sodium chloride) as cell feed in the oxidation of chloride to perchlorate using lead dioxide anodes. The ammonia gas is absorbed in dilute hydrochloric acid and recovered as ammonium chloride which can also be used for double decomposition.

The double decomposition of sodium perchlorate solution of 600 to 800 g/l is effected with the desired quantity ranging from 70% to stoichiometric quantity of solid ammonium chloride (based on perchlorate content) made into a slurry with calculated quantity of water so as to have the sodium chloride concentration in the final liquor between 200 and 230 g/l and the recovery of ammonium perchlorate being from 75 to 95%. The ammonia from the filtrate after separation of ammonium perchlorate is boiled off with sodium hydroxide and absorbed in dilute hydrochloric acid. The ammonium chloride so obtained can be used in the subsequent double decompositions. The mother liquor after expelling ammonia can be reused as cell feed in the oxidation of chloride to

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perchlorate after adjusting the concentration of sodium chloride.

The present invention consists of a process for the production of ammonium perchlorate by the double decomposition of 600 to 800 g/l sodium perchlorate solution with the desired quantity ranging from 70% to stoichiometric quantity (based on perchlorate content) of ammonium chloride made into a slurry with calculated quantity of water at 90 to 105°C, wherein 75 to 95% of the salt is obtained by cooling the liquor to 5°C and the filtrate after separation the salt is boiled with calculated (stoichiometric) quantity of sodium hydroxide to get a solution containing sodium chloride and sodium perchlorate free from ammonia which can be reused as cell feed in the oxidation of sodium chloride to perchlorate in the electrolytic cell using lead dioxide anode and the ammonia gas is absorbed in dilute hydrochloric acid to recover the same as ammonium chloride for reuse.

The use of ammonium chloride slurry with calculated quantity of water keeps the volume of filtrate almost constant thereby getting maximum yield of ammonium perchlorate (in the first crop). the process can be worked out as a cyclic one. A flow sheet of the process is attached.

A few typical examples are given to illustrate how the invention is carried out in actual practice.

Example 1

Volume of sodium perchlorate (l)	24
Concentration of sodium perchlorate (g/l)	756.5

Wt. of ammonium chloride (Con. 98.3%) (Kg)	7.95
Volume of water for making $\text{NH}_4\text{Cl}$ slurry (l)	12
Wt. of ammonium perchlorate obtained in I crop (cooling upto $30^\circ\text{C}$ ) (Kg)	10.72
Wt. of ammonium perchlorate obtained in II crop (cooling from $30$ to $5^\circ\text{C}$ ) (Kg)	1.9
Recovery of ammonium perchlorate (%)	73
Ammonium content in the filtrate as $\text{NH}_4\text{ClO}_4$ (Kg)	2.95
Sodium chloride in the filtrate (Kg)	7.83
Sodium hydroxide taken (Kg)	1.03
Time of boiling (hr)	1.00
Ammonia recovery as $\text{NH}_4\text{Cl}$ (%)	93

Example 2

Volume of sodium perchlorate (l)	35
Concentration of sodium perchlorate (g/l)	756.5
Wt. of ammonium chloride (Kg)	11.6
Volume of water for making $\text{NH}_4\text{Cl}$ slurry (l)	20
Wt. of ammonium perchlorate obtained in the I crop (cooling upto $30^\circ\text{C}$ ) (Kg)	15.9
Wt. of ammonium perchlorate obtained in the II crop (cooling from $30$ to $5^\circ\text{C}$ ) (Kg)	3.6
Recovery of ammonium perchlorate (%)	76.6
Ammonium content in the filtrate as $\text{NH}_4\text{Cl}$ (Kg)	3.77
Sodium chloride in the filtrate (Kg)	12.1
Sodium hydroxide taken (Kg)	1.3
Time of boiling (Hr.)	1.5
Ammonia recovered as $\text{NH}_4\text{Cl}$ (%)	94

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Volume of sodium perchlorate (l)	30
Concentration of sodium perchlorate (g/l)	688.4
Wt. of ammonium chloride (Con. 98.3%) (Kg)	9.0
Volume of water for making $\text{NH}_4\text{Cl}$ slurry (l)	11
Wt. of ammonium perchlorate obtained in I crop (cooling upto $30^\circ\text{C}$ ) (Kg)	14.2
Wt. of ammonium perchlorate obtained in II crop (cooling from $30$ to $5^\circ\text{C}$ ) (Kg)	1.84
Recovery of ammonium perchlorate (%)	79.3
Ammonium content in the filtrate as $\text{NH}_4\text{ClO}_4$ (Kg)	4.21
Sodium chloride in the filtrate	9.25
Sodium hydroxide taken (Kg)	1.5
Time of boiling (Hr.)	1-1.5
Ammonia recovery (%)	93

Example 4

Volume of sodium perchlorate (l)	1.5
Concentration of sodium perchlorate (g/l)	704.7
Wt. of ammonium chloride taken (g)	350
Volume of water (ml)	390
Wt. of ammonium perchlorate obtained (g) (cooling upto $5^\circ\text{C}$ )	780
Recovery of ammonium perchlorate (%)	94.1
Ammonium content in the liquor (g)	6.5
Sodium chloride in filtrate (g)	332.3

(The boiling off ammonia is same as in Example 1 to 3).

The main advantages of the process are as follows :

1. The sodium perchlorate solution obtained from electrolytic cells by oxidation of sodium chloride can be directly used for double decomposition.
2. The addition of slurry of ammonium chloride does not allow the system to get diluted too much.
3. The perchlorate content remaining after the separation of solid ammonium perchlorate is recovered as sodium salt by boiling with sodium hydroxide.
4. The liquor obtained after boiling off ammonia is suitable for reuse after adjusting the concentration of sodium chloride as cell feed in the oxidation of sodium chloride to perchlorate using lead dioxide anode.
5. The expelled ammonia is recovered as ammonium chloride by absorbing the same in dilute hydrochloric acid which can be used in further processing.
6. The procedure avoids any possible effluent disposal problem since the entire process is made cyclic.

Sodium perchlorate solution containing 600 to 800 g/l obtained from the cell is double decomposed with the desired quantity ranging from 70% to stoichiometric quantity of ammonium chloride made into a slurry with calculated quantity of water at 90 to 105°C and cooled to room temperature. After separating the precipitated ammonium perchlorate, the filtrate is further cooled



to 5°C when the second crop of ammonium perchlorate is precipitated. The ammonia content in the resultant liquor is boiled off with required quantity of sodium hydroxide for reuse as cell feed in the oxidation of sodium chloride to perchlorate using lead dioxide anode. The ammonia is recovered as ammonium chloride by absorbing in dilute hydrochloric acid.

As shown in the flow sheet of the drawings of the cyclic process, the sodium chloride feed solution is fed from the feed preparation tank to the electrolytic cell. Sodium perchlorate ( $\text{Na ClO}_4$ ) solution obtained from the cell is fed to a reactor where it is treated with  $\text{NH}_4 \text{Cl}$  slurry at 90-105°C. The reaction liquor is cooled in a crystalliser at room temperature and  $\text{NH}_4 \text{ClO}_4$  crystals separated in a centrifuge. The filtrate is further cooled to 5°C and the crude ammonium perchlorate along with the first crop is purified by treatment in a recrystalliser with water and cooling to 5°C, the pure  $\text{NH}_4 \text{ClO}_4$  crystals are separated in a second centrifuge, dried and ground to desired size in a drier and grinder respectively. The filtrate is boiled with NaOH in a second reactor to expell ammonia which is absorbed in diluted HCl in an absorbing tank and  $\text{NH}_4 \text{Cl}$  formed is reused as a slurry in the first reactor. The liquor freed from ammonia in the second reactor is fed back to feed preparation tank for reuse as cell feed in the electrolytic cell.

We Claim:

1. An improved cyclic electrochemical process for the production of ammonium perchlorate from sodium chloride characterised in

subjecting the sodium chloride to electrolytic oxidation in a cell using lead dioxide as anode, treating the used electrolytic containing sodium perchlorate thus formed by double decomposition with ammonium chloride to form ammonium perchlorate cooling the reaction product to precipitate ammonium perchlorate formed, boiling the resultant liquor with sodium hydroxide to remove ammonia and reusing the regenerated sodium chloride as cell feed in the electrolytic cell.

2. A process as claimed in claim 1 wherein the double decomposition reaction is carried by treating the electrolyte containing sodium perchlorate with 70% to stoichiometric quantity of ammonium chloride (based on perchlorate content) at a temperature of  $90^{\circ}$  to  $105^{\circ}\text{C}$ .

3. A process as claimed in claim 1 wherein the sodium perchlorate solution obtained from the electrolytic cell has a concentration of 600 to 800 g/l and the same is directly used for treatment with ammonium chloride.

4. A process as claimed in any of the preceding claims, wherein the separation of ammonium perchlorate crystals from the liquor is effected in two stages, firstly by cooling the liquor to room temperature, separating the precipitated ammonium perchlorate by filtration and further cooling the filtrate to  $5^{\circ}\text{C}$  to obtain a second crop of ammonium perchlorate.

5. An improved cyclic process for the production of ammonium perchlorate substantially as herein before described particularly

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**with reference to the drawings.**

**Dated the 3rd day of August, 1979.**

**Sd/-**

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