

Specification No. 124214. Application No. 124214, dated 28th November 1969. Complete Specification left on 13th May 1970. (Application accepted 10th November 1970.)

Index at acceptance 70c6 [LVIII(5)].

PROVISIONAL SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC PREPARATION OF SODIUM CHLORATE LIQUOR OF HIGHER CONCENTRATION.

COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, RAFI MARG, NEW DELHI, 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, Director, Kapisthalam Chetlur Narasimham, Scientist and Narayanaswamy Sarma Thiagarajan, Senior Scientific Assistant, all of Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, all Indians.

This invention relates to the improvements in or relating to the electrolytic preparation of sodium chlorate liquor of higher concentration suitable for the production of chlorine dioxide or sodium chlorite using graphite substrate lead dioxide anode.

Hitherto it has been the practice to prepare sodium chlorate of larger concentration by electrolysis of sodium chloride by employing two stage electrolysis viz., (1) the use of graphite or magnetite anodes till the concentration of chloride was about 100 g/l and (2) the use of platinum or platinised metal anodes for further reduction of the concentration of sodium chloride.

The objections to the current practice are as follows :

1) The process requires two different cells with two different anodes.

2) In the first stage of electrolysis (i) the concentration of the sodium chloride in the cell liquor will have to be maintained between 70 and 100 g/l in order to avoid the disintegration of the anode to a larger extent and the concentration of sodium chlorate will be between 421 and 375 g/l. (ii) The use of graphite and magnetite anodes limits the operating condition of electrolysis such as current density and temperature. (iii) The loss of graphite or magnetite due to disintegration amounts to 25 to 45 kg/tonne of sodium chlorate, depending upon the operating conditions. (iv) The graphite slurry obtained using graphite anode presents a difficult handling problem and contaminates the product. (v) Iron as an impurity can be eliminated from the product only after elaborate processing methods. (vi) The bath voltage will be

changing due to variation of the inter-electrode distance caused by the gradual disintegration of graphite or magnetite anodes.

3) In the second stage of electrolysis, (i) the loss of platinum during the electrolysis of chloride is bound to be more costly and (ii) at this high concentration of chlorate, the formation of perchlorate is inevitable with platinum anode.

The object of this invention is to obviate these disadvantages by adopting the following modified procedure developed.

The electrolysis is carried out for the preparation of sodium chlorate of higher concentration in a single cell using lead dioxide anode and stainless steel cathode at a temperature ranging from 35 to 40°C. An anode current density of 1-6 amp/dm² is used.

A saturated solution of sodium chloride containing about 300-320 g/l and 2 g/l of sodium chromate was electrolysed in an electrolytic cell consisting of lead dioxide anode and stainless steel cathode and employing the operating conditions described above till the sodium chloride concentration came down to a definite value (for e.g., between 5 and 150 g/l of sodium chloride). The solution at this stage was subjected to further saturation with solid sodium chloride and the electrolysis was further continued till the sodium chloride concentration was less than 5 g/l. The current efficiency was calculated on the basis of both chloride converted and chlorate formed. A concentration of 630 to 700 g/l of sodium chlorate with less than 5 g/l of sodium chloride was obtained and no perchlorate formation was observed in the liquor. The liquor itself can be used for the preparation of sodium chlorite or chlorine dioxide without isolating the sodium chlorate as solid crystals.

	Example I	Example II	Example III
1. Concentration of liquor before saturation with sodium chloride :			
NaCl (g/l)	2.1	105.8*	50.3*
NaClO ₃ (g/l)	575	467.3	551.0

Price : TWO RUPEES

TABLE—Contd.

	Example I	Example II	Example III
2. Concentration of liquor after saturation with sodium chloride	75.7 584.5	147.6 475.0	104.6 547.5
3. Anode	Lead Dioxide coated graphite anode	Lead Di-oxide coated graphite anode	Lead dioxide coated graphite anode
4. Cathode	Stainless Steel	Stainless Steel	Stainless Steel
5. Addition agent : Na ₂ Cr ₂ O ₇ (g/l)	2	2	2
6. Current (amps)	30	30	30
7. Voltage (volts)	3.7-3.8	3.7	3.5-3.7
8. Anode current density (amp/dm ²)	5	5	5
9. Current concentration (amp/l)	1.8	1.8	1.8
10. Temperature (°C)	35-40	35-40	35-40
11. pH	6.2-6.8	6.2-6.8	6.2-6.8
12. Concentration of liquor after completion of electrolysis :			
NaCl (g/l)	2.5	0.6	3.8
NaClO ₃ (g/l)	678	667	690.8
13. Current efficiency on the basis of chlorate formed (%)	51.1	57	54.6
14. Energy consumption for chlorate after saturation with sodium chloride (kwh/kg of NaClO ₃)	10.8	13	11.5

* The solution is earlier saturated when sodium chloride concentration is about 150 g/l along with corresponding conversion of sodium chloride.

The following are the main advantages of the invention :

1) The electrolysis for the preparation of sodium chlorate of higher concentration is carried out in the same cell using graphite substrate lead dioxide anode and stainless steel cathode and employing an anode current density of 1-6 amp/dm² and a temperature of 35-45°C.

2) The concentration of sodium chloride in the final sodium chlorate liquor is brought down to less than 5 g/l.

3) The lead dioxide protects the graphite substrate and prevents its disintegration thereby prolonging the life of graphite anode at least by 3 to 4 times.

4) The graphite substrate lead dioxide anode eliminates the platinum which is used in the second stage of existing process.

5) The cell effluent is clear and free from suspended impurities unlike that obtained with graphite or magnetite anodes in which the graphite slurry or iron presents a difficult handling problem.

6) The cumulative current efficiency is maintained well above 50% even when the concentration of chloride is very low during last stages of electrolysis.

7) There is no change of inter-electrode distance with duration of electrolysis and consequently the bath voltage does not change unlike cells using either magnetite or graphite anodes.

8) There is no perchlorate formation even at this higher concentration of chlorate in presence of chromate.

Signed-Illegible

Patents Officer,

Council of Scientific & Industrial Research,

Dated this 20th day of November, 1969.

COMPLETE SPECIFICATION.

IMPROVEMENTS IN OR RELATING TO THE ELECTROLYTIC PREPARATION OF SODIUM CHLORATE LIQUOR OF HIGHER CONCENTRATION.

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, RAJI 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 Udapa, Director, Kapisthalam Chetlur Narasimham, Scientist and Narayanaswamy Sarma Thiagarajan, Senior Scientific Assistant, all of Central Electro-chemical Research Institute, Karaikudi-3, Tamil Nadu, India, all Indians.

1. This invention relates to the improvements in or relating to the electrolytic preparation of sodium chlorate liquor of higher concentration suitable for the production of chlorine dioxide or sodium chlorite using graphite substrate lead dioxide anode.

2. Hitherto it has been the practice to prepare sodium chlorate liquor of larger concentration by electrolysis of sodium chloride by employing two stage electrolysis viz., (1) the use of graphite or magnetite anodes till the concentration of chloride was about 100 g/l and (2) the use of platinum or platinised metal anodes for further reduction of the concentration of sodium chloride.

3. The main objections to the current practice are as follows :

i) the process requires two different cells with the different anodes.

ii) in the first stage of electrolysis (a) the concentration of the sodium chloride in the liquor will have to be maintained between 70 to 100, g/l in order to avoid the disintegration of the anode to a larger extent and the concentration of sodium chlorate will be between 421 and 315 g/l. (b) The use of graphite and magnetite anodes limits the operating conditions of electrolysis such as current density and temperature. (c) The loss of graphite or magnetite due to disintegration amounts to 25 to 45 kg/tonne of sodium chlorate depending upon the operating conditions. (d) The graphite slurry obtained using graphite anodes presents a difficult handling problem, and contaminates the product. (e) Iron as an impurity can be eliminated from the product only after elaborate processing methods. (f) The bath voltage will be changing due to variation of the inter electrode distance caused by the gradual disintegration of graphite or magnetite anodes.

iii) In the second stage of electrolysis, (a) the loss of platinum during the electrolysis of chloride is bound to be more costly and (b) at this high concentration of chlorate, the formation of perchlorate is inevitable with platinum anode.

4. The main object of the invention is to obviate the disadvantages given above and find a suitable and convenient method of preparing sodium chlorate liquor of higher concentration.

5. The electrolysis is carried out for the preparation of sodium chlorate liquor of higher concentration in a single cell using lead dioxide coated graphite anode and stainless steel cathode.

6. A saturated solution of sodium chloride containing about 300 to 320 g/l and 2 g/l of sodium dichromate was electrolysed in an electrolytic cell consisting of lead dioxide anode and stainless steel cathode and employing a temperature of 35° to 40°C, anode current density of 1 to 6 amp/dm², pH 6 to 7, till the sodium chloride concentration came to a definite value (for e.g. between 5 and 150 g/l of sodium chloride). The solution at the stage was subjected to further saturation with solid sodium chloride and the electrolysis was further continued till the sodium chloride concentration was less than 5 g/l. The current efficiency was calculated on the basis of both chloride converted and chlorate formed. A concentration of 630 to 700 g/l of sodium chlorate with less than 5 g/l of sodium chloride was obtained and no perchlorate formation was observed in the liquor. The liquor itself can be used for the preparation of sodium chlorite or chlorine dioxide without isolating the sodium chlorate as solid crystals.

7. The lead dioxide protects the graphite substrate and prevents its disintegration thereby prolonging the life of graphite anode at least by 3 to 4 times. The graphite substrate lead dioxide anode not only provides easy electrical contact to the anode but also increases the mechanical strength of the brittle lead dioxide. The graphite substrate lead dioxide anode eliminates the platinum which is used in the second stage of existing process. The cell effluent is clear and free from suspended impurities unlike that obtained with graphite or magnetite anodes in which the graphite slurry or iron presents a difficult handling problem. There is no change of interelectrode distance with duration of electrolysis and consequently the bath voltage does not change unlike cells using either magnetite or graphite anodes. A change of bath voltage from 2.8 to 3.6V at 2 amp/dm² for graphite anodes in chlorate cells has been reported.

The cumulative current efficiency is maintained well above 50% even when the concentration of chloride is very low during the last stages of electrolysis.

8. According to the present invention there is provided a process for the preparation of sodium chlorate liquor of higher concentration (viz., 630 to 700 g/l sodium chlorate) to be directly used for the production of sodium chlorite or chlorine dioxide which consists in electrolyzing a concentrated solution of sodium chloride in a cell using graphite substrate lead dioxide anode and stainless steel cathode at a temperature ranging from 35–40°C and an anode current density of 1 to 6 amp/dm² and 2 g/l sodium dichromate to the electrolyte. The electrolyzing is done upto a certain stage (viz., 5 to 150 g/l sodium chloride) and then further resaturating the electrolyte with solid sodium chloride in order to obtain finally a solution containing 630–700 g/l sodium chlorate with less than 5 g/l sodium chloride.

9. The concentration of sodium chloride in the final sodium chlorate liquor is brought down to less than 5 g/l by employing graphite substrate lead dioxide anode and the liquor itself can be used for the preparation of sodium chlorite or chlorine dioxide.

10. The flow sheet of the process is shown in the attached drawings.

11. A few typical examples to illustrate the process are given in Table I (attached).

Anode : Lead dioxide coated graphite ; Cathode, stainless steel ; Addition agent, $\text{Na}_2\text{Cr}_2\text{O}_7$ (2 g/l) ; Current, 30 amps ; Current concentration, 1.8 amp/l.

	Example I	Example II	Example III	Example IV	Example V
1. Concentration of liquor before saturation with solid sodium chloride :					
NaCl (g/l)	2.1	105.8*	50.3*	114.6	50.3
NaClO ₃ (g/l)	575	457.3	551.0	337.5	455
2. Concentration of liquor after saturation with solid sodium chloride					
NaCl (g/l)	75.7	147.6	104.6	189	122.8
NaClO ₃ (g/l)	584.5	475.0	547.7	337.5	455.0
3. Voltage (volts)	3.7-3.8	3.7	3.5-3.7	3.7-3.8	3.7-3.8
4. Anode current density : (amp/dm ²)	5	5	5	5	5
5. Temperature (°C)	35-40	35-40	35-40	35-40	35-40
6. pH	6.2-6.8	6.2-6.8	6.2-6.8	6.2-6.8	6.2-6.8
7. Concentration of liquor after the completion of electrolysis :					
NaCl (g/l)	2.5	0.6	3.8	1.26	3.77
NaClO ₃ (g/l)	678	667	690.8	615	623
8. Current efficiency on the basis of chlorate formed (%)	51.1	57	54.6	63.4	65.6
9. Energy consumption for chlorate after saturation with sodium chloride (kwh/kg of NaClO ₃)	10.8	13	11.5	8.8	8.52

*The solution is earlier saturated when sodium chloride concentration is about 150 g/l along with corresponding conversion of sodium chlorate

12. The following are the main advantages of the invention: The electrolysis for the preparation of sodium chlorate liquor of higher concentration is carried out in the same cell using graphite substrate lead dioxide anode and stainless steel cathode and employing an anode current density of 1-6 amp/dm² and a temperature of 35- 5°C. The concentration of sodium chloride in the final sodium chlorate liquor is brought down to less than 5 g/l. The lead dioxide protects the graphite substrate and prevents its disintegration thereby prolonging the life of graphite anode at least 3 to 4 times. The graphite substrate lead dioxide anode eliminates the platinum which is used in the second stage of existing process. The cell effluent is clear and free from suspended impurities unlike

that obtained with graphite or magnetite anodes in which the graphite slurry or iron presents a difficult handling problem. There is no change of interelectrode distance with duration of electrolysis and consequently the bath voltage does not change unlike cells using either magnetite or graphite anodes. There is no perchlorate formation even at this higher concentration of chlorate in presence of chromate.

13. The present invention relates to the production of sodium chlorate liquor of higher concentration to be directly used, for the production of sodium chlorite and chlorine dioxide, in a single cell having graphite substrate lead dioxide and stainless steel cathode at a temperature ranging from

35-40°C and an anode current density of 1-6 amp/dm². After operating the cell till the chloride concentration reached a definite value, the solution was further saturated outside the cell with solid sodium chloride and again the electrolysis was continued with this resaturated solution till the chloride concentration was less than 5 g/l.

We claim :

1. A process for the production of sodium chlorate liquor of higher concentration (viz., 630 to 700 g/l sodium chlorate) to be directly used for the production of sodium chlorite or chlorine dioxide which consists in electrolysing a concentrated solution of sodium chloride in a cell using graphite substrate lead dioxide anode and stainless steel cathode at a temperature ranging from 35-40°C and an anode current density of 1 to 6 amp/dm² and 2 g/l sodium dichromate to the electrolyte.

2. A process as claimed in Claim (1) wherein the sodium chlorate concentration of the electrolyte is made to increase by further saturation of the electrolyte with solid sodium chloride after certain stage of electrolysis and then continuing the electrolysis till the final chloride content is less than 5 g/l.

3. A process as claimed in Claim (1) wherein the lead dioxide deposited over graphite is used as anode for the production of sodium chlorate liquor of higher concentration.

4. A process as claimed in Claim (1) wherein stainless steel is used as cathode.

5. A process as claimed in Claim (1) wherein the electrolytic cell can be operated using an anode current density range of 1 to 6 amp/dm².

6. A process as claimed in Claim (1) wherein the electrolytic cell can be operated at a temperature of 35 to 40°C.

7. A process as claimed in Claim (1) wherein the addition of 2 g/l, sodium chromate or dichromate is made to prevent the perchlorate formation at higher chlorate concentrations.

8. A process as claimed in Claim (1) wherein the graphite substrate lead dioxide anode can be used to bring down the concentration of chloride to less than 10 g/l in a single cell and thereby avoiding the use of platinum in the second stage.

9. A process claimed in Claims (1) and (8) wherein the sodium chlorate liquor of higher concentration containing less than 5 g/l sodium chloride can be directly used for the preparation of sodium chlorite or chlorine dioxide, without isolating the sodium chlorate as solid crystals.

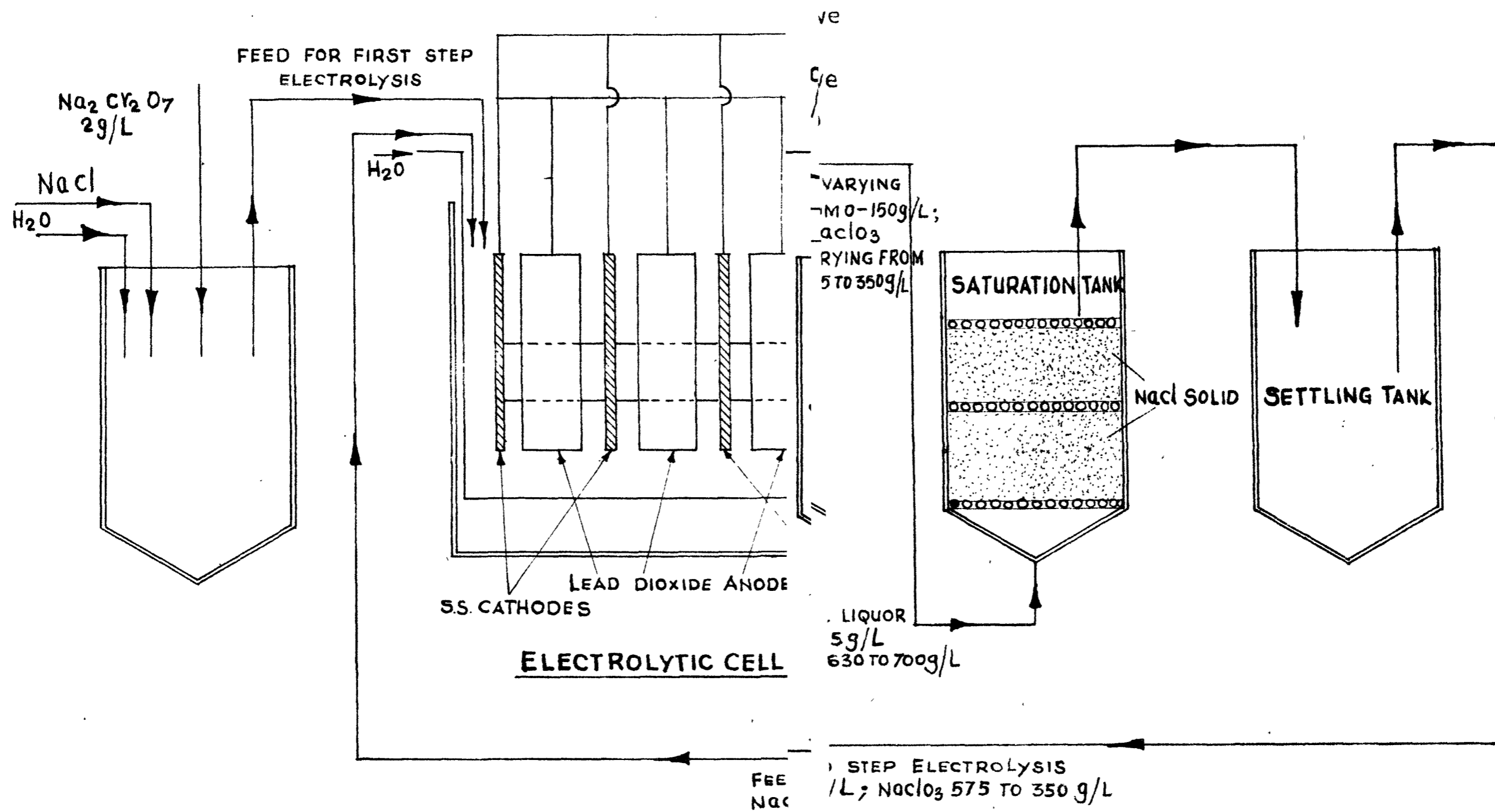
10. A process for the electrolytic production of sodium chlorate liquor of higher concentration, as substantially hereinbefore described.

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Patent Officer

Council of Scientific & Industrial Research.

Dated this 7th day of May, 1970.



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