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COMPLETE SPECIFICATION

Manufacture of Sodium Chlorate

We, SOCIETE D'ELECTRO - CHIMIE, D'ELECTRO-METALLURGIE ET DES ACIERIES ELECTRIQUES D'UGINE, a body corporate organised under the laws of France, of 10, rue du General, Foy, Paris, France, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention concerns the manufacture of sodium chlorate by means of an electrolytic method.

It is known that, for obtaining sodium chlorate by this means, an electrolysis is made of a solution of sodium chloride. The decomposition of this salt, which is effected with a yield in current close to 100% first provides chlorine which is formed at the anode and sodium hydroxide which is formed at the cathode.

The first chlorine fractions are generally nearly entirely lost since the sodium chloride solution is rapidly saturated therewith. The sodium hydroxide thereafter diffusing in the electrolyte, chlorine is absorbed and sodium hypochlorite is formed in accordance with the reaction:

$$2NaOH + Cl_2 \rightarrow NaClO + NaCl + H_2O$$

This hypochlorite is then transformed into a chlorate, by two ways:

First by a chemical process, in accordance with a slow reaction, the complex mechanism of which may thus be summarized:

$$3NaClO \rightarrow NaClO_3 + 2NaCl$$

The yield may reach 100%; there is no loss of oxygen.

Secondly by electrolysis. Experience shows that the operation then leads to oxygen being released at the anode, together with the formation of chlorate, this being attributed to the reaction:

$$6ClO^- + 3H_2O + 6(+) = 2\,ClO_3^- + 4Cl^- + 1.5O_2 + 6H^+$$

The energy used for the formation of free oxygen is uselessly spent and the gases released by the electrolysis are charged with oxygen, which constitutes an additional drawback.

In usual processes, these two transformations are simultaneously effected. Their respective actions affect the total yield which is all the lower the more important the electrolytic transformation. If the chemical process were alone involved, this yield, on the contrary, would reach 100%.

Various means have been studied with a view to improving the efficiency of the electrolytic transformation of the chloride into chlorate. It has thus been suggested to increase the density of the electric current and to equalize its distribution over the whole area of the electrodes, to maintain the acidity of the solution within the required limits, or to use salts such as chromates for avoiding the cathode reduction of the hypochlorite. It has also been proposed to cause a motion of the electrolyte either upwards or downwards, and even to use the release of hydrogen which results from the electrolysis, for aiding the circulation of the electrolyte. Finally, anodes connected with a bottom plate have been used while the brine was being moved upwards.

The operations according to these various methods are generally carried out in a turbulent disturbed medium, inside the electrolysis space, without any possible control of the various reactions or of the flow of electrolyte. The improvements in efficiency, which were thus sought were obtained in a purely empirical manner.

The object of the present invention is a process which makes it possible to obviate these drawbacks and to considerably increase the efficiency of the preparation of sodium chlorate.

This process fundamentally consists in causing a solution of sodium chloride to circulate in the interpolar space created between an anode and a cathode immersed in said solution, at a speed sufficiently high so that the OH^- ions formed at the cathode cannot, as an average reach the anode, in maintaining in contact outside of the interpolar space the sodium hydroxide solution and the chlorine resulting from the electrolysis over a sufficiently long period of time to ensure the fixation, by sodium hydroxide, of all the chlorine present, then in allowing the solution of hypochlorite and sodium chloride thus obtained to rest for a sufficiently long time and at a sufficiently high temperature in order that the chemical transformation of the hypochlorite into chlorate could take place.

The speed of migration of the OH^- ions formed at the cathode is perfectly known and it is easy, taking into account the distance between the electrodes and the potential drop in the electrolyte to determine and control the speed of passage of the electrolyte in the field, so that, by composition of the latter speed with the speed of migration of the OH^- ions, the latter take such trajectories that the lowest possible number of them reach the anode. Due to this feature on the one hand, and, on the other hand, to the fact that, the solution of sodium hydroxide and the chlorine formed being removed from the interpolar space as they are formed, the formation of hypochlorite takes place only outside said space, the formation of oxygen is avoided and consequently, as well, a useless expense of current and the production of a detonating mixture with the hydrogen resulting from the electrolysis.

This hydrogen may easily be separated from the products of electrolysis after fixation of the chlorine by the formation of sodium hypochlorite.

The solution of hypochlorite is then poured into a container where the transformation of the hypochlorite into chlorate is chemically effected. This transformation is all the more rapid the higher the temperature. The speed of the transformation is also promoted by adding an acid.

The volume of the container in which the operation is effected is calculated according to the duration of the transformation and the rate of flow of the solution, in such a manner that the latter remains in the container over long enough a period of time for the reaction to be effected at the desired rate.

The solution of sodium chlorate and sodium chloride thus obtained is preferably again subjected, once or several times, to the sequence of operations according to the invention: electrolysis, separate formation of hypochlorite, transformation of the hypochlorite into chlorate. It is thus possible to transform the major part of the sodium chloride and to finally obtain a solution with a high concentration in sodium chlorate.

The process according to the invention may be worked by means of an apparatus comprising an electrolysis cell with immersed electrodes, in direct connection with a reaction container, the dimensions of which are so calculated that the period of time during which the products resulting from the electrolysis remain in this container is sufficiently long to allow the total fixation of the chlorine in the form of hypochlorite. This container is provided with means for evacuating hydrogen, and connected with a reaction tank so dimensioned as to allow the substantially complete transformation of the hypochlorite into chlorate to take place in said tank. Means are provided for ensuring the circulation of the electrolyte inside the electrolysis apparatus and the container which follows it and for evacuating the solution obtained in the reaction container.

The installation thus constituted may be designed for ensuring a continuous re-cycling of the products issuing from the reaction tank or again several similar installations may be arranged in series, in parallel or in series-parallel.

The appended drawing shows an example of an embodiment of such an apparatus.

Referring to said drawing, the apparatus for the production of sodium chlorate according to the invention, comprises an electrolysis apparatus consisting, on the one hand, of an electrolysis cell comprising a tubular cathode 1 surrounding an anode 2, of graphite for instance, and, on the other hand, of a container 3 arranged immediately above the cell, and in which the tubular cathode 1 opens directly with the interposition of a sealing gasket. The cell is held, at its lower portion, in a base 4 which comprises an inlet chamber 5 for the electrolyte, in communication with the annular space provided between the cathode 1 and anode 2 and to which a level indicator 6 is connected. At the upper portion of the container 3, a tube 7 is arranged for the evacuation of gases. Below the level of this tube 7 there opens, into the container 3, an overflow pipe 8 connected, through a level regulator 9, of a type known *per se*, with a reaction container 10.

A level indicator 11, connected with pipe 8, makes it possible to control the liquid level in tank 10. The latter is connected through an overflow pipe 12 with a tank 13 from the bottom of which a conduit 14 extends, on which a motor driven pump 15 is interposed (not shown). The conduit 14 reaches a vat 16, placed higher than the electrolysis apparatus 1—3. A conduit 17, issuing from the lower portion of the vat 16 extends, through a flowmeter 18, to the feeding chamber 5 for the electrolytic cell 1—2. Return conduits 19, 20, 21, to tank 13 are respectively connected to pipe 8, vat 16 and conduit 17 and a level indicator 22 is connected to conduit 14, between pump 15 and tank 13, for controlling the level therein.

Finally, the apparatus comprises a heat exchanger, consisting of a tank 23, in which a circulation of a hot fluid may be set up by piping 24 and which contains tubes 25 connected in series, the first tube 25 being connected through a conduit 26 with the conduit 12 connecting the tank 10 with the tank 13, while the last tube 25 is connected with the upper portion of tank 13 through a conduit 27 in which a level regulator 28 is interposed.

The initial solution of sodium chloride, placed in the tank 13 is sent into the vat 16 by the pump 15 which keeps a constant level of solution inside said vat. From the vat 16, the solution is directed to the electrolytic cell 1—2, the electrodes of which have been placed under voltage, and it flows through this cell at a uniform speed controlled by the adjustment of the flowmeter 18, said speed being determined, in accordance with the invention, so that there results from its composition with the migration speed of the OH^- ions from cathode 1 towards anode 2, for these ions, such a trajectory that on an average they do not reach said anode 2.

The products of the electrolysis, consisting of a solution of sodium hydroxide and chloride which are not electrolytically decomposed, together with chlorine and hydrogen, then flow through container 3, the dimensions of which are determined as a function of the circulation speed of the electrolyte and of the respective amounts of sodium hydroxide and chlorine provided by electrolysis, amounts which, in turn, depend upon the intensity of the current, determined in accordance with usual rules, as a function of the nature and size of the surface of the anode, in order that all the chlorine formed may be fixed by the sodium hydroxide as hypochlorite.

The electrolysis gases, other than chlorine, which almost exclusively consist of hydrogen, are evacuated through tube 7 while the hypochlorite solution reaches tank 10. The dimensions of the latter are calculated, as a function of the flow of electrolyte through the electrolysis apparatus, of the speed of transformation of the hypochlorite into chlorate and of the hypochlorite content of the solution issuing from container 3, so that this hypochlorite may be transformed entirely into chlorate.

The solution of sodium chlorate and sodium chloride thus obtained flows constantly into tank 13, after having or having not gone through exchanger 23—25, according to whether the valve 29 is closed or not, said exchanger making it possible to control the electrolyte temperature. The contents of tank 13 are then taken by pump 15 and the cycle is repeated.

When the solution, issuing from tank 10, has reached the desired concentration of sodium chlorate, it may be evacuated through tap 31, and a new amount of fresh sodium chloride solution may be introduced at 30.

Instead of providing for a re-cycling of the solution of sodium chlorate and chloride, several similar installations might be arranged in series, the pump 15 of one installation delivering, for instance, into the vat 16 of the next one.

The temperature at which the electrolysis takes place, which may be adjusted by means of the exchanger 23—25, must be compatible with the material which constitutes the anode 2.

If the latter is made of graphite, for instance, one may operate at temperatures which are all the higher the lower the concentration of the solution in residual hypochlorite, supplying the electrolysis apparatus 5. One may thus reach 50° C. for example.

The temperature in the reaction container 10 is generally the same as that of the solution issuing from container 3, namely 40 to 50° C. approximately, in the above considered case. The reaction temperature in tank 10 may be raised, however, by providing the latter with heating means so as to increase the speed of reaction which makes it possible to decrease the dimensions of tank 10.

The speed of chemical transformation of the hypochlorite into chlorate increases with the acidity of the solution introduced into tank 10, but the residue which cannot be transformed into chlorate, which consists in hypochlorous acid increases at the same time. A value must thus be calculated or established by experience for the pH of the solution in reaction in container 10 making it possible to obtain the greatest possible speed of transformation which is compatible with a minimum of residue.

During the transformation the percentage of hypochlorous acid remains constant while the percentage of hypochlorite continuously decreases. The pH value is determined by the equilibrium of the dissociation of the hypochlorous acid and the following equation exists between the concentrations of the acid and the hypochlorite:

$$(1) \qquad \frac{(ClO-)(H+)}{(ClOH)} = K_1$$

where

(ClO−) stands for the concentration of hypochlorite ions

(ClOH) for the concentration of hypochlorous acid

(H) for the concentration of hydrogen ions, i.e., e^{-pH} and

$K_1 = e^{-3020\ 1/T-6}$, where T is the temperature of the reaction in degrees absolute.

Further it has been verified experimentally that the speed of transformation of the hypochlorite into chlorate is proportional to the square of the concentration in hypochlorous acid ions and to the concentration in hypochlorite ions.

Said relation may be written as follows:

$$(2) \qquad v = -\frac{dx}{dt} = K_2C^2x$$

where

C = the concentration of hypochlorous acid = (ClOH)

x = the quantity of hypochlorite present at the time *t* and

$K_2 = e^{-8640\ 1/T+25.7}$.

By comparison of both equations (1) and (2), one obtains

$$(3) \qquad v = -\frac{dx}{dt} = \frac{K_2}{K_1{}^2}(H_+)^2\ x^3$$

which is the relation existing between pH, temperature, concentration in hypochlorite ions, and time, during the considered transformation.

It will be noted that an increase of the temperature of the reaction (i.e. where the hypochlorite is chemically transformed) increases the speed of the reaction and makes it possible to work in the presence of a lower concentration of hypochlorous acid. Also the untransformable residue, which is constituted by hydrochlorous acid is reduced and the transformation into chlorate is more complete.

The corrosion of the materials of the installation increases however with increase of temperature and thus it is preferred to work at a temperature not exceeding about 50° C. The pH value decreases during the transformation but its average value remains within the limits of about 7.5—5.5.

The adjustment of the pH value of the solution may be obtained by any known means, for instance by adding hydrochloric acid before the introduction into tank 10, at 9 for instance. The volume of tank 10, or, in case this volume is determined in advance, the rate of flow and the period of time during which it remains in said tank, are then determined according to the choice of this pH.

Even when the process according to the invention is applied, there may occur a small loss in active oxygen, due to the decomposition, with evolution of gaseous oxygen, of the hypochlorous acid present. This oxygen does not appear in the electrolysis gases but is formed inside the reaction tank 10. Thus, there is no risk of explosion. Besides, an accurate adjustment of the pH, as set forth above, makes it possible to avoid this loss.

By way of example, an apparatus has been used, similar to the one described above, in which the cathode -1-anode 2 assembly had a height of 64 cms. and an interpolar distance of 1 cm., with a graphite anode having a 6 cm. diameter. The current applied was 36 amperes. The various calculation principles stated above led to a minimum flow of electrolyte of 2 litres per hour. However, in order to take into account the disturbances caused by the evolution of gas in the electrolyte subjected to electrolysis, a flow of 10 litres per hour was adopted.

With such a rate, it was necessary, to ensure the fixation of all the chlorine as hypochlorite, to use a container 3 having a diameter of 10 cms. and a length of 64 cms., and, for transforming 9/10 of the hypochlorite thus obtained into chlorate, to adopt a reaction tank of 50 litres, maintaining the latter at a temperature of 40° C. and an average pH of 7.5.

These conditions being applied, a yield in current of 90% was obtained, after a long operation, under an average voltage of 2.9 V. and a power consumption of 5 kwh. per kilogram of $NaClO_3$ produced in solution.

The electrolysis gases collected had the following composition:

Hydrogen - - -	98.5%
Carbon dioxide - -	1%
Oxygen - - - -	0.5%

What we claim is:—

1. A method for the manufacture of sodium chlorate by means of electrolysis of a sodium chloride solution, characterised in that it consists in causing a solution of sodium chloride to circulate in the interpolar space which is created between the anode and cathode immersed in said solution, at sufficiently high a circulation speed for the OH— ions which are formed at the cathode not being able to reach the anode; furthermore in maintaining, in contact, outside the interpolar space, the solution of sodium and hydroxide and of chlorine resulting from the electrolysis, over a period of time which is sufficiently long for the sodium hydroxide to fix all the chlorine present as sodium hypochlorite and finally in causing the solution of hypochlorite and of sodium chloride thus obtained to rest over long enough a period of time and at sufficiently high a temperature for said hypochlorite to be transformed into chlorate by chemical means.

2. A method for the manufacture of sodium chlorate according to claim 1, characterised in that the gases resulting from the electrolysis, other than chlorine, are evacuated after the latter has been fixed.

3. A method for the manufacture of sodium chloride according to claims 1 and 2, characterised in that the temperature of the solution of hypochlorite during the transformation into chlorate is adjusted by means of a heat exchanger.

4. A method for the manufacture of sodium chlorate according to claims 1 and 3,

characterised in that the pH of the solution of hypochlorite is adjusted to the value which is necessary for obtaining the highest speed of transformation which is compatible with the formation of a minimum quantity of hypochlorous acid, for example, by adding hydrochloric acid to this solution.

5. A method for the manufacture of sodium chlorate according to claims 1 to 4, characterised in that the solution of chlorate and of sodium chloride which is finally obtained is again submitted, at least once, to the same sequence of operation.

6. A method of manufacturing sodium chlorate as claimed in any of claims 1—5 and performed in apparatus substantially as described and as shown in the accompanying drawings.

7. A method of manufacturing sodium chlorate as claimed in claim 6 and performed in the manner substantially as described with specific reference to the accompanying drawings.

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