

June 25, 1957

W. GRAFF ET AL

2,797,192

ELECTROLYTIC PREPARATION OF ALKALINE CHLORATES

Filed June 30, 1954

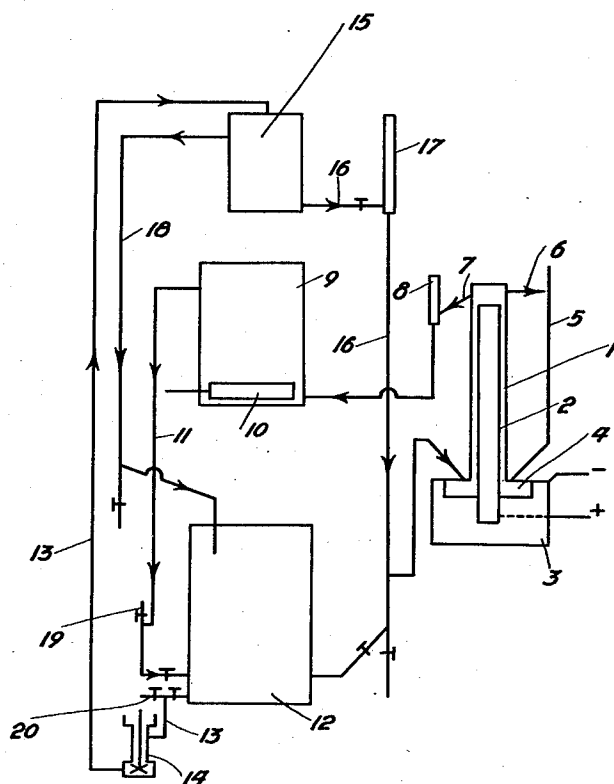


Fig 1

INVENTORS

Willy Graff

Robert Boulitrop

BY Webb, Mackay & Burden

HIS ATTORNEYS

1

2,797,192

ELECTROLYTIC PREPARATION OF ALKALINE CHLORATES

Willy Graff, Moutiers, and Robert Boulitrop, Paris, France, assignors to Societe d'Electro-Chimie d'Electro-Metallurgie et des Acieries Electriques d'Ugine, Paris, France, a corporation of France

Application June 30, 1954, Serial No. 440,398

Claims priority, application France July 2, 1953

4 Claims. (Cl. 204—95)

This invention concerns the electrolytic preparation of alkaline chlorates.

U. S. patent application No. 321,820 dated November 28, 1952, now abandoned, describes such a process for the electrolytic preparation of sodium chlorate, which comprises three steps, namely:

1. A solution of sodium chloride is circulated in the interpolar space between an anode and a cathode immersed in this solution, at such a high speed that the OH⁻ ions formed on the cathode can not, on the average, reach the anode.

2. The contact is maintained, outside of the interpolar space, between the solution of sodium hydroxide and the chlorine resulting from the electrolysis so that there be time enough for the fixation, by the sodium hydroxide, of all the chlorine present.

3. The solution of hypochlorite and sodium chloride thus obtained is allowed to rest over a sufficient period of time and at a sufficiently high temperature so that the hypochlorite may be chemically and satisfactorily transformed into chlorate.

Such a process avoids the anodic oxidation of the hypochlorite formed, and thus produces chlorate almost solely by means of the slow decomposing chemical reaction of the hypochlorite, in accordance with the following:



Simultaneously, the formation of oxygen is cut down to a minimum, and, consequently also a useless expenditure of current is avoided as well as the production of a detonating mixture with the hydrogen resulting from the electrolysis. The yield in the preparation of sodium chlorate is thus substantially increased.

The above mentioned patent application also describes an apparatus for carrying out this method.

Now, the applicant has found that it was possible, on the one hand, to considerably simplify the method described in said patent application and to reduce it to two succeeding operations instead of three and, on the other hand to apply such as improved method to the preparation of alkaline chlorates other than sodium chlorate.

The method according to the present invention fundamentally consists in circulating a solution of chloride of the alkaline metal of which it is desired to obtain the chlorate in the interpolar space created between an anode and a cathode immersed in said solution, the speed of circulation of this solution in said space and the value of the electrolysis current being so chosen, as functions of each other, the first one being sufficiently high and the second one sufficiently low, that the OH⁻ ions formed at the cathode be unable, on the average, to reach the anode, and that the entirety almost of the chlorine formed at the anode remain fixed in the electrolytic solution, either in a dissolved condition or as hypochlorite without giving rise to an important gas evolution, then in causing the solution of hypochlorite and chloride thus obtained to rest, outside of the zone of electrolysis, during a sufficiently long time and at a sufficiently high temperature

2

for the transformation of the hypochlorite into chlorate to be chemically effected.

The migrating speed of the OH⁻ ions formed at the cathode is perfectly known and it is easy, when taking into account the distance between the electrodes and the potential drop in the electrolyte, to determine and to control the speed at which the electrolyte passes through the field so that by regulating this latter speed in relation to the speed of migration of the OH⁻ ions, the latter follow such trajectories that the least possible number of them reach the anode.

The amount of chlorine formed at the anode, per time unit, depends on the intensity of the current used. It is all the smaller, all other things remaining equal, as this intensity proper is smaller.

An intensity will, therefore, be chosen as above mentioned, for a given outflow, which shall be sufficiently small so that the OH⁻ ions formed at the cathode do not reach the anode and so that almost the entirety of the chlorine formed at the anode remains in the electrolytic solution, either in a dissolved condition or in the form of hypochlorite. Thus is avoided, as far as possible, the formation of oxygen and the release of chlorine gas, hence also a useless expenditure of current and the formation of an explosive mixture with the hydrogen issuing from the cathode. This hydrogen may besides be easily removed from the electrolysis apparatus.

The value of the electrolysis current may also be predetermined and the flow may be regulated as a function of said value, so as to obtain the desired results.

Temperature conditions shall also be chosen in the electrolysis apparatus, making it possible to decrease the voltage drop across the electrodes and to cut down to a minimum the evolution of chlorine gas. To this effect, it was found that by operating around 60° C., conditions are favourable.

The method according to the present invention may be worked by means of a plant comprising an electrolysis cell with immersed electrodes which define an electrolysis zone and a reaction space distinct from this electrolysis zone and in direct communication therewith. The reaction space may consist of a tank or vat separated from the electrolysis apparatus or by a capacity which is part of the electrolysis apparatus. Means are provided for ensuring the circulation of the electrolyte in the electrolytic apparatus, and, if need be, for introducing the solution issuing from the electrolysis apparatus in the reaction space when using an independent tank.

Such an installation may be designed for the continuous recycling of the products issuing from the reaction space or again several similar installations may be arranged in parallel or in series-parallel.

When the electrolysis is completed, the solution containing hypochlorite, which is slightly basic, is sent to the reaction vat where the transformation of hypochlorite into chlorate is effected by chemical means. The temperature at which the transformation is allowed to take place is generally the same as that of the solution issuing from the electrolysis apparatus. The temperature of reaction in the vat, however, may be raised by heating means. The speed of reaction is thus increased, which makes it possible to decrease the dimensions of the vat. The capacity of this container is calculated according to the duration of the transformation and to the rate of flow of the solution, in such a manner that the solution should remain there long enough for the reaction to take place at the desired rate.

The speed of the chemical transformation of the hypochlorite into chlorate increases with the acidity of the solution which is sent to the reaction vat, but the residue, which cannot be transformed into chlorate and which is made of hypochlorous acid, increases at the same time.

3

A pH value must therefore be chosen, for this solution, either by calculation or from experience, which provides the highest speed of transformation consistent with a minimum residue. The adjustment of the pH value of the solution may be obtained by any known means, for instance by the addition of hydrochloric acid with the required concentration before sending it to the reaction vat.

The addition of acid may cause a loss, though small, of active oxygen, due to the decomposition of the hypochlorite and chlorate present with an evolution of chlorine and oxygen. A suitable dilution of this acid besides avoids this loss to a large extent. Anyhow, the oxygen evolved during the acidifying operation does not mix with the electrolysis gases which implies no possible explosion in this respect.

The solution of chlorate and chloride obtained in the vat is preferably subjected again, once or repeatedly to the cycle of operations according to the invention: electrolysis with formation of hypochlorite, then transformation of the hypochlorite into chlorate. It is thus possible to transform into an alkaline chlorate the greater portion of the chloride and to finally obtain a solution with a high percentage in alkaline chlorate.

The appended drawing shows, diagrammatically, an example of an embodiment of a plant for working the method according to the present invention.

As represented, the plant for the production of alkaline chlorate comprises an electrolysis apparatus consisting of an electrolysis cell containing a tubular cathode 1, surrounding an anode 2, of graphite for instance. The cell is maintained, at its lower portion, in a base 3 which comprises a chamber 4 for the arrival of the electrolyte, in communication with the annular space provided between the cathode 1 and the anode 2 and on which is connected a level indicator 5. At the upper portion of the cell, a tube 6 is arranged for gas evacuation. Below the level of this tube 6, an overflow conduit 7 is connected, through a level regulator 8 of a type known per se, with a reaction vat 9, provided with a heating means 10, such, for instance, as rod type electrical resistances or a steam coil.

The reaction vat proper is connected, through an overflow conduit 11, with a tank 12, the base of which is provided with a conduit 13, on which a pump 14 is interposed, driven by a motor not shown. The conduit 13 leads to a vat 15, placed higher than the electrolysis apparatus 1—2. A conduit 16, extending from the lower portion of vat 15 leads, through a flowmeter 17, to the supply chamber 4 for the electrolytic cell 1—2.

The initial solution of alkaline metal chloride, the chlorate of which is desired, is placed in tank 12 and sent to the vat 15 by the pump 14 which holds the level constant in said vat, the excess solution, by means of conduit 18 flowing back to the tank 12. From the vat 15, the solution flows to the electrolytic cell 1—2, the electrodes of which have been previously connected to a voltage source and it flows through this cell at a speed controlled by an adjustment of the flowmeter 17, this speed being so determined, according to the invention, that, by its correlation with the migrating speed of the OH⁻ ions from the cathode 1 towards the anode 2, a trajectory is obtained for these ions, so that they do not reach said anode 2, on the average.

The electrolysis gases, other than chlorine, which consist almost entirely of hydrogen, are evacuated through tube 6, while the solution of chloride and hypochlorite, formed in the electrolysis in an amount determined according to usual rules as a function of the liquid flow through the electrolysis apparatus and of the current, flows to vat 9. As already mentioned, the dimensions of the latter are calculated as a function of this flow, of the speed of transformation of the hypochlorite into chlorate and of the contents of the solution in hypochlorite so that this hypochlorite may be transformed into chlorate in a sufficient amount.

4

The solution of alkaline chlorate and chloride thus obtained flows continuously into tank 12, the contents of which are taken by the pump 14 and the cycle is repeated.

When the solution issuing from tank 12 has reached the desired contents in chlorate, it may be evacuated through the cock 20, and a new supply of fresh chloride solution may be introduced at 19.

Instead of recycling the solution of sodium chlorate and chloride, several similar plants could be arranged in series, the pump 14 of one installation delivering, for instance, into the vat 15 of the next one.

On the other hand, instead of providing a vat 9 independent of the electrolysis apparatus, the space through which flows the solution of chloride and hypochlorite resulting from the electrolysis, may be included, as already mentioned, in the electrolysis apparatus, in which a capacity, distinct from the zone of electrolysis proper has been provided.

The temperature at which the electrolysis takes place should also be compatible with the material constituting the anode 2; if the latter is made of graphite, for instance, one may operate at temperatures all the higher as the proportion of residual hypochlorite of the solution supplied to the electrolysis apparatus at 4 is lower.

By way of example for obtaining sodium chlorate, an installation has been used as described above, in which the cathode-anode assembly had a height of 16 cms. and an interelectrode distance of 2 cms., with a graphite anode of 6 cms. in diameter. The current density was 10 amps. per square decimeter. The various calculation principles stated above led to a minimum flow for the electrolyte of 2.5 litres per hour; however, in order to take into account the disturbances caused by the evolving gas in the electrolyte during electrolysis operations, and which would tend to direct the OH⁻ ions towards the anode, a flow of 10 litres per hour was adopted with a view to increasing the component driving these ions parallel to the electrodes.

With such a current density and flow, it was necessary, for transforming 1/10 of the hypochlorite thus obtained into chlorate, to use at vat 9 of 50 litres, and to maintain therein a temperature of 60° C., and a pH decreasing from 8 (at the outlet of the electrolysis apparatus) to 7.2 (after acidifying), and 6.5 (at the outlet of the reaction vat 9).

In maintaining these conditions, after a prolonged operation, a current efficiency of 90%, a mean voltage of 3.6 volts and an energy consumption of 6 kwh. were obtained per kilogram of sodium chlorate produced in solution.

The electrolysis gases collected had the following composition:

	Percent
Hydrogen -----	98.4
Oxygen -----	1.5
Chlorine -----	0.1
Carbon dioxide -----	Traces

What we claim is:

1. A method for the preparation of an alkaline metal chlorate by electrolysis of a solution of a chloride of said metal comprising the steps of circulating said chloride solution in an interelectrode space between a cathode and an anode, establishing between said cathode and said anode a current density sufficient to form chlorine near the anode and to cause OH⁻ ions which are formed at the cathode to migrate towards the anode, the circulating speed and the current density being selected, as functions of each other, such that the speed is sufficiently high and the current density sufficiently low, so that said OH⁻ ions formed near the cathode cannot, on the average, reach the anode and so that the greater portion of the chlorine formed at the anode remains fixed in the solution without causing any substantial release of chlorine gas, thus forming a solution containing a chloride and a hypochlorite of said metal, then leading said solution

5

of chloride and hypochlorite outside said interelectrode space and allowing said solution of chloride and hypochlorite to rest for a sufficiently long time and at a sufficiently high temperature for transforming the hypochlorite into a chlorate in said solution.

2. A method for the preparation of chlorate of an alkaline metal by electrolysis of a solution of a chloride of said metal comprising the steps of circulating said chloride solution in an interelectrode space between a cathode and an anode, of establishing a current density between said cathode and said anode sufficient to form chlorine and cognate gases near the anode and to cause OH^- ions formed at the cathode to migrate towards the anode, said circulation speed and said current density being chosen as functions of each other, the first one sufficiently high and the second one sufficiently low, so that said OH^- ions formed at the cathode cannot, on the average, reach the anode and so that the greater portion of the chlorine formed at the anode remains fixed in the solution without causing any substantial evolution of chlorine gas, thus forming a solution containing a chloride and a hypochlorite of said metal, then leading said solution of chloride and hypochlorite outside said interelectrode space, eliminating the cognate gases and allowing said solution of chloride and hypochlorite to rest for a sufficiently long time and at a sufficiently high temperature for transforming the hypochlorite into chlorate in said solution.

3. A method as described in claim 2 wherein the solution of chlorine and hypochlorite is allowed to rest at a temperature of about 60°C . and a sufficient pH value is maintained in the solution such that a fairly complete and rapid transformation of the hypochlorite into chlorate is accomplished while avoiding a formation of hypochlorous acid.

4. A method for the preparation of an alkaline metal chlorate by electrolysis of a solution of a chloride of

6

a metal comprising the steps of circulating said chloride solution at a rate of about 10 liters per hour in an inter-electrode space provided between an anode about 6 centimeters in diameter and a cathode surrounding the anode at a distance of about 2 centimeters, said anode and cathode having a height of about 16 centimeters, establishing a current density of about 10 amperes per square decimeter between said cathode and anode sufficient to form chlorine near the anode and to cause OH^- ions which are formed at the cathode to migrate toward the anode, the circulating speed and the current value being selected as functions of each other such that the speed is sufficiently high and the current sufficiently low so that said OH^- ions formed near the cathode cannot normally reach the anode and so that the greater portion of the chlorine formed at the anode remains fixed in solution without causing any substantial release of chlorine gases, thus forming a solution containing a chloride and a hypochlorite of said metal, then flowing said solution of chloride and hypochlorite outside said inter-electrode space and allowing the solution to rest at a temperature of about 60°C and a pH less than 8 for a time sufficient to transform the hypochlorite into a chlorate.

References Cited in the file of this patent

UNITED STATES PATENTS

1,173,346	Gibbs	Feb. 29, 1916
2,180,668	Delavenna et al.	Nov. 21, 1939

OTHER REFERENCES

Foerster: "Transactions of the American Electrochemical Society," vol. 46 (1924), article entitled "The Electrolysis of Hypochlorite Solutions" pages 23 to 50, pages 29, 30, 38, 39 pertinent.

Mantell: Industrial Electrochemistry, 1st. ed. (1931), pages 281, 282, 283 and 284.