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PREPARATION OF PERCHLORATES

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This invention relates to an improved process for making a perchlorate by the electrolysis of a chlorate solution and to the electrolyte for use therein.

Perchlorates, in particular the perchlorates of the alkali metals, are commonly made by the electrolysis of concentrated aqueous solutions of the corresponding chlorates. It has been recognized that maintenance of the electrolyte pH on the acid side in an important factor for most efficient operation. To provide an acid electrolyte for the electrolysis and maintain the pH on the acid side, the previously known commercial processes generally employed the addition of hydrochloric acid. In the absence of such acid addition, the electrolyte, because of previous processing or side reactions during subsequent electrolysis, tends to assume an equilibrium value on the alkaline side with resulting loss in electrolytic current efficiency.

Hydrochloric acid is, unfortunately, quite readily decomposed, with evolution of chlorine, when introduced into an electrolysis area. More hydrochloric acid must then be added to make up this loss. Due to the decomposition of the hydrochloric acid and the formation of chlorine, the ventilation problem is also quite acute, and persons working in proximity to the cells are subjected to noxious fumes. Large ventilation systems are required to cope with this problem, but since perchlorate cells are generally not completely gas-tight, the problem of chlorine gas in the cell room always exists. This decomposition of hydrochloric acid present in the electrolyte is especially pronounced toward the end of the run, and pH control becomes more difficult. The addition of chloride ions to the electrolyte, in the form of hydrochloric acid, lowers current efficiency, since they are preferentially electrolyzed to chlorates instead of the desired reaction of chlorate to perchlorate.

I have now discovered that by using perchloric acid instead of hydrochloric acid to maintain the electrolyte pH at the proper acid value, not only are the above disadvantages attendant upon the use of hydrochloric acid avoided but, surprisingly, as cell operation continues, a point is generally reached (generally during the final third of the electrolysis) when the addition of acid to the electrolyte can be completely discontinued. Thus, at the stage of operation when the hydrochloric acid addition of prior processes reaches a maximum and introduces the worst complications, in my process acid addition is virtually discontinued. Moreover, my process has the advantage of requiring a much smaller acid requirement for the electrolysis. For example, in a typical operation, 40 to 80 pounds of hydrochloric acid (100 percent basis) are required per ton of sodium perchlorate produced, whereas in steady operation the perchloric acid requirement of my invention is of the order of 8 to 10 pounds per ton of sodium perchlorate produced.

As is known in the art, it is generally desirable to use as the electrolyte an aqueous solution substantially saturated with sodium chlorate. Such a solution may, for example, contain about 650 grams per liter of sodium

chlorate, sodium dichromate (in an amount, for example, of the order of 3.0 to 15.0 grams per liter), and calcium or magnesium chloride (in an amount, for example, of the order of 0.5 to 1.0 gram per liter). In processes of the prior art, sufficient dilute hydrochloric acid is added to give the desired acidity before and during electrolysis.

In the preferred method of carrying out the improved process of this invention, an aqueous solution, substantially saturated with sodium chlorate, containing calcium or magnesium chloride as previously described is also used, but the quantity of sodium dichromate is reduced appreciably (being used in an amount, for example, of the order of 0.5 to 3.0 grams per liter). Further, the desired acidity or pH of the electrolyte is achieved by the addition of perchloric acid (preferably of about 50 percent concentration) instead of hydrochloric acid. A sodium dichromate concentration lower than previously described for prior processes is possible because of the greater stability of perchloric acid during electrolysis as compared to hydrochloric acid. One of the functions of sodium dichromate, when using hydrochloric acid in conventional practice, is to slow down the rate of loss of the acidity during electrolysis.

An electrolyte thus prepared may be subjected to electrolysis at a voltage of 5–8 volts, in an electrolytic cell having steel cathodes and platinum anodes.

In preferred operation, the electrolysis is carried out as a batch operation, the electrolyte, prepared as above described, being circulated through a cell, as above described, and back to a run-down tank where make-up water, to replace water lost by electrolysis and evaporation and perchloric acid to maintain the desired pH, are continuously or periodically added. As above mentioned, very little, if any, perchloric acid will be needed during the latter third of the run. Circulation of the electrolyte and operation of the cell is preferably continued until the sodium chlorate concentration has dropped to only a few grams per liter.

The optimum pH for operation in accordance with my preferred process is within the range of about 6 to 6.8. However, operation within the pH range of about 5 to about 7 represents good operation, and my process is operative outside these limits, i. e., up to about 9 on the one side, and below 5 on the other, as some of the examples illustrate.

The cell may be operated at ambient or other convenient temperature but is preferably operated at a temperature of 100–120° F., cooling usually being needed during the run to maintain this temperature. Under the conditions above described, the average current efficiency over a period of operation that reduces the sodium chlorate content of the electrolyte to about 3 grams per liter will generaly be about 80%. The electrolyte, now containing around 750 grams per liter of sodium perchlorate, may be processed in the usual way for recovery or utilization of its perchlorate content.

The following examples are further illustrative of the process of my invention:

Example 1

A run was carried out as a batch operation in a cell to produce sodium perchlorate. At the beginning of the run, the electrolyte was composed of approximately 650 grams per liter of sodium chlorate, 1.0 gram per liter of sodium dichromate and 0.5 gram per liter of calcium chloride. Electrolysis and recirculation, replenishment of water and perchloric acid were continued until a sodium chlorate content of about 3 grams per liter was reached. A total of 725 pounds of sodium chlorate was used. The perchloric acid requirement (employed as a 50% solution) amounted to 9.6 pounds of perchloric acid (100%) per ton of sodium perchlorate produced, to main-

tain the pH in a range of 5.5 to 6.3 during electrolysis. No perchloric acid was added during the final third of the run.

Example 2

In another run, under essentially the same conditions as described in Example 1, an equivalent of 13 pounds of perchloric acid for each ton of sodium perchlorate produced was required, maintaining the pH of the electrolyte during the operation in the range of 2.0 to 6.0.

Example 3

In another run, an equivalent of 8.7 pounds of perchloric acid was required for each ton of sodium perchlorate produced to maintain the acidity of the electrolyte between 4.8 and 6.5 pH during electrolysis.

The same principle of acidification by means of perchloric acid is applicable in the electrolytic production of perchlorates other than sodium perchlorate. It may be employed, for example, in the production of alkali metal perchlorates generally, such as potassium, lithium, rubidium, and cesium perchlorates, and other similar perchlorates such as perchlorates of the alkaline earth metals, such as barium, calcium, and strontium perchlorates, from their corresponding chlorates.

The above description of the process of my invention is intended to be illustrative only and my invention is not to be limited thereby.

I claim:

1. In a process for the production of a perchlorate by the electrolysis of an aqueous acid solution of the corresponding chlorate in a non-diaphragm electrolytic cell in which without acid addition the electrolyte becomes alkaline during the course of electrolysis, the improvement comprising the addition of perchloric acid to maintain the electrolyte at a pH below 7.

2. A process for the production of an alkali metal perchlorate by electrolysis of an aqueous acid solution of the corresponding alkali metal chlorate in a non-diaphragm electrolytic cell, in which without acid addition the electrolyte becomes alkaline during the course of electrolysis, the improvement comprising the addition of perchloric acid to maintain the electrolyte at a pH below 7.

3. A process for the production of sodium perchlorate by electrolysis of a concentrated aqueous acid solution of sodium chlorate in a non-diaphragm electrolytic cell, said solution also containing small amounts of a dichromate and a soluble salt of an element selected from the group consisting of calcium and magnesium, in which without acid addition the electrolyte becomes alkaline during the course of electrolysis, the improvement comprising the addition of perchloric acid to maintain the electrolyte within the pH range of 1 to about 7.

4. A process for the production of sodium perchlorate by electrolysis of an aqueous acid solution of sodium chlorate in a non-diaphragm type electrolytic cell, said solution also containing small amounts of a dichromate and a soluble salt of an element selected from the group consisting of calcium and magnesium, in which without acid addition the electrolyte becomes alkaline during the course of electrolysis, the improvement comprising the addition of perchloric acid to maintain the pH within the range of 5 to 7 during the course of electrolysis.

5. A process for the production of sodium perchlorate by electrolysis of an aqueous acid solution of sodium chlorate in a non-diaphragm type electrolytic cell, said solution also containing small amounts of a dichromate and a soluble salt of an element selected from the group consisting of calcium and magnesium, in which without acid addition the electrolyte becomes alkaline during the course of electrolysis, the improvement comprising the addition of perchloric acid to maintain the pH within the range of 6 to 6.8 during the course of electrolysis.

References Cited in the file of this patent

UNITED STATES PATENTS

693,035	Lederlin	Feb. 11, 1902
1,279,593	Schoch	Sept. 24, 1918
2,512,973	Schumacher	June 27, 1950

OTHER REFERENCES

Schumacher: Transaction of the Electrochemical Society, vol. 92, 1947, pp. 45 to 53.