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PEROXIDATION PROCESS

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This invention relates to electrolytic peroxidation processes which require platinum anodes such as the production of perchloric acid, perchlorates, persulfates, periodates, perborates, perbromates, and various organic oxidations such as the preparation of anthraquinone, and para-aminophenol. The invention will be particularly set forth as it has been applied to the production of sodium perchlorate, but it is not limited to this.

Sodium perchlorate is one of the starting raw materials for the production of ammonium perchlorate which is used for the manufacture of jet assisted take off units and other rocket applications. However, the large scale use of ammonium perchlorate has been limited by the method of manufacture of sodium perchlorate.

Perchlorates have been customarily produced by electrolysis of sodium chlorate solution utilizing a platinum anode and a steel cathode. The high cost of platinum, its unavailability, and the fact that it erodes away in use and cannot be recovered has resulted in a process with substantial limitations. Moreover, to utilize steel as a cathode and cell material it has been necessary to add chromates or dichromates as inhibitors. These inhibitors are frequently carried over into the end product as a contaminant which is difficult to remove, and which makes the end product less desirable.

Production of perchlorates by electrolysis using a lead dioxide anode in various geometric shapes along with a solid nickel or a stainless steel cathode has been proposed by a number of investigators. This substitution of solid nickel or stainless steel has been an improvement; nevertheless, there still remains the disadvantage that solid nickel and stainless steel are expensive, and are difficult to fabricate into large commercial cells. Furthermore, existing steel cells used in commercial production, representing a considerable investment, cannot be converted to use with lead dioxide anodes. Moreover, many investigators, who have proposed nickel and stainless steel as cathode materials with lead dioxide anodes, have concluded that they were unsatisfactory. These prior art processes have in truth been misleading for they have, in some instances, either deliberately or unintentionally added dichromates as impurities to their electrolyte. In most chlorate processes the chromate is added as an inhibitor and appears as an impurity in the feed to the perchlorate cells. If the anode in this cell is of platinum and the cathode is steel, the dichromate is beneficial. However, we have found that dichromate is detrimental to a process using a lead dioxide anode and either nickel or stainless steel as a cathode.

We have discovered that chemically-plated nickel-on-steel as a cathode material in conjunction with lead dioxide as an anode can be used advantageously to convert sodium chlorate to sodium perchlorate. Using these electrodes, we have been able to convert chlorates to perchlorates at cumulative current efficiencies equal to those obtained with platinum and steel electrodes. Also, the energy requirement for cells made in accordance with

our invention is lower than that for the platinum-steel combination. A further advantage is that with the chemically-plated nickel-on-steel cathode, it is not necessary to control the pH of the electrolyte, since the pH appears to reach an equilibrium in the desirable range of 5–5.7. In contrast, present commercial practice with platinum-steel electrodes requires the continued addition of acid to maintain the pH on the acid side. Still another advantage of our process was discovered in the course of our investigation when chemically-plated nickel was compared with electrolytically-plated nickel, for we found that the corrosion resistance of chemically-plated nickel to the cell solution is greater than that of electrolytically-plated nickel. Finally, electrolytically-plated nickel cannot be applied easily to complicated shapes required for commercial cells because some type of metal flashing must be effected prior to electrolytically depositing the nickel plate.

The actual chemical plating of nickel on steel or other metals is well known in the art and constitutes no part of this invention herein described and claimed. Instead of steel one can use any other metal consistent with the electrolyte and the conditions of use such as copper and aluminum.

We have also discovered that the addition of sodium fluoride or other alkali metal fluoride increases the cumulative current efficiency when incorporated into an electrolyte which is electrolyzed with a lead dioxide anode and chemically-plated nickel-on-steel as a cathode. An added advantage of the fluoride as an additive is that the required concentration is extremely low and has no detrimental effect on the end product when present as an impurity. The sodium fluoride may be used in a concentration range of 0.5–2.0 g./l.; however, we do not wish to be limited thereto, but prefer to use the lower value of 0.5 g./l. The addition of sodium fluoride increases the current efficiency when compared to the electrolysis of a system not containing it. Moreover, its concentration is low enough so that it does not contaminate the end product.

An anode current density in the range of from 0.5–1.5 amps./sq. in. is satisfactory, but we prefer a current density of 1.0 amp./sq. in. which appears to give the best current efficiency. Cathode current densities from 0.25 to 1.50 amps./sq. in. can be employed, but we prefer, but do not wish to be limited thereto, 0.5 amp./sq. in. since this also gives the highest cumulative current efficiency. The preferred densities are 0.5 amp./sq. in. on the cathode and simultaneously 1.0 amp./sq. in. on the anode.

The voltage and amperage for cell operation depend to some extent on cell design and electrolyte circulation. The voltage for cell operation is lower for the lead dioxide chemically-plated nickel-on-steel combination than for any known to us. We have found that the electrolysis proceeds in a potential range of 4.75–5.2 volts.

Finally, we have found that the cumulative current efficiency is a function of the sodium chlorate concentration in the cell electrolyte. The economic cut-off point is a function of the end application. If the sodium perchlorate is to be converted to ammonium perchlorate, the chlorate concentration must be low; hence, it is desirable to have a high cumulative current efficiency even down to low sodium chlorate concentrations. The lead dioxide-chemically-plated nickel on steel combination does this.

To illustrate the practice of this invention, in perchlorate production, an electrolyte containing from about 400 to about 700 g./l. of sodium chlorate, which has been free of sodium chromate or dichromate, and containing 0–2.0 g./l. of NaF was fed to an electrolytic cell similar

in design to that described in U. S. Patent 2,475,157, with the exception that the anode was a rough-surfaced, rod-shaped, lead dioxide electrode, $1\frac{3}{16}$" dia. x 14" in length. The cathode consisted of carbon steel with a chemical-nickel plate 2–2.5 mils thick. The temperature was maintained in the range of 30–45° C., the production proceeding in an efficient and smooth manner.

Residence Time (hrs.)	Concentration (g./l.)			Cumulative Current Efficiency, Percent
	NaCl	$NaClO_3$	$NaClO_4$	
0	0	516.9	0	0
2	0.10	488.6	27.2	91.6
10	0.10	388.1	141.6	95.6
14	0.10	338.7	195.3	96.0
18	0.10	276.4	247.0	92.4
26	0.18	211.1	343.6	89.0
38	0.44	90.0	471.8	83.6
46	0.50	51.2	513.7	75.2

Temperature—41° C.
pH—5.7.
Voltage—5.2 volts.
NaF concentration—0.5 g./l.
Cathode current density—1.38 amps./sq. in.

Although the data are presented for a batch cell for purposes of illustration, the actual operation can readily be carried out on a continuous basis.

The sodium perchlorate prepared by this method was later converted to ammonium perchlorate of very high purity, meeting the rigorous requirements for rocketry. There was no contamination of nickel or lead in the product. Although sodium perchlorate is used as an example, we do not wish to be limited thereto, since this combination of lead dioxide anode and chemically-plated nickel cathode can be used in other electrolytic peroxidation processes, as we have mentioned.

We claim:

1. In a process for the electrolytic production of sodium perchlorate, the step of passing a current through a sodium chlorate electrolyte between a lead dioxide anode and a cathode consisting essentially of nickel plated chemically on a metal base, said electrolyte being substantially freed of sodium chromate and dichromate.

2. In a process for the electrolytic production of sodium perchlorate, the step of passing a current through a sodium chlorate electrolyte between a lead dioxide anode and a cathode consisting essentially of nickel plated chemically on a steel base, said electrolyte being substantially freed of sodium chromate and dichromate.

3. In a process for the electrolytic production of sodium perchlorate, the step of passing a current through a sodium chlorate electrolyte between a lead dioxide anode and a cathode consisting essentially of nickel plated chemically on a metal base, the metal being selected from the group consisting of steel, copper and aluminum, said electrolyte being substantially freed of sodium chromate and dichromate.

4. In a process for the electrolytic production of sodium perchlorate, the step of passing a current through a sodium chlorate electrolyte between a lead dioxide anode and a cathode consisting essentially of nickel plated chemically on a metal base, the electrolyte also containing a small amount of an alkali metal fluoride, said electrolyte being substantially freed of sodium chromate and dichromate.

5. In a process for producing sodium perchlorate, the step of passing a current through an electrolyte between a lead dioxide anode and a cathode consisting essentially of nickel chemically plated on a metal base, the electrolyte consisting essentially of from about 400–700 grams per liter of sodium chlorate containing from about 0.5 to about 2.0 grams per liter of an alkali metal fluoride, the anode current density being from about 0.5 to about 1.5 amperes per square inch under a potential of from about 4.75 to about 5.2 volts, said electrolyte being substantially freed of sodium chromate and dichromate.

6. In a process for producing sodium perchlorate, the step of passing a current through an electrolyte between a lead dioxide anode and a cathode consisting essentially of nickel chemically plated on a metal base, the electrolyte consisting essentially of from about 400–700 grams per liter of sodium chlorate, the anode current density being from about 0.5 to about 1.5 amperes per square inch under a potential of from about 4.75 to about 5.2 volts, said electrolyte being substantially freed of sodium chromate and dichromate.

7. In a process for producing sodium perchlorate, the step of passing a current through an electrolyte between a lead dioxide anode and a cathode consisting essentially of nickel chemically plated on a metal base, the electrolyte consisting essentially of from about 400–700 grams per liter of sodium chlorate, the anode current density being substantially 1.0 ampere per square inch and the cathode current density being substantially 0.5 ampere per square inch.

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