PROCESS FOR THE ELECTROLYSIS OF ALKALI CHLORIDE SOLUTION

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References Cited
UNITED STATES PATENTS
3,630,863 12/1971 Jeffery et al. 204/98

Primary Examiner—R. L. Andrews
Attorney, Agent, or Firm—Stevens, Davis, Miller & Mosher

ABSTRACT
The anodic overvoltage and the decomposition of the amalgam during the electrolysis of alkaline chloride solutions in electrolytic cells are reduced by adding to the electrolyte small quantities of one or more compounds selected from the group consisting of the ethers of alcohols or phenols with polyoxyethylene and of the esters of carboxylic acids with polyoxyethylenes.

12 Claims, No Drawings
PROCESS FOR THE ELECTROLYSIS OF ALKALI CHLORIDE SOLUTION

This is a continuation, of application Ser. No. 130,472, filed Apr. 1, 1971 and now abandoned which in turn was a continuation-in-part of application Ser. No. 796,190, filed Feb. 3, 1969, and now abandoned.

This invention relates to a process for the electrolysis of solutions of alkaline chlorides. More particularly, this invention has for its object a process for reducing the anodic overvoltage during the electrolysis of solutions of alkaline chlorides in cells having a mercury cathode and in diaphragm cells for reducing the decomposition of the amalgam during the electrolysis of said solutions in cells having a mercury cathode.

It is well known that the voltage that must be applied in practice to said cells is definitely in excess of the sum of the electromotive force of the electrolysis reaction and of the voltage drops due to the resistance of the electrolyte, of the electrodes and of the electrical connections. One of the main reasons for this voltage excess lies in the insurmountable barrier arising from the formation on the anode surface of relatively large chlorine bubbles which reduce the active surface of the anode itself.

Another drawback in the operation of cells having a mercury cathode arises from the development of hydrog en caused prevalingly by the presence of impurities in the brine, which impurities act on the surface of the amalgam as active centers for the decomposition of the amalgam itself.

This decomposition, although of relatively little extent, causes however a useless consumption of current and leads to a contamination of the chlorine produced in the cell, with consequential complications arising in the liquefaction plant for the produced chlorine.

Furthermore, if the development of hydrogen reaches values exceeding about 7 percent by volume, explosive mixtures may form.

Thus, one object of this invention is that of reducing the anodic overvoltage during the electrolysis of solutions of alkaline chlorides in electrolytic cells having a mercury cathode and in diaphragm cells.

Still another object of this invention is that of reducing the decomposition of the amalgam in electrolytic cells having a mercury cathode.

A further object is that of attaining all the objects specified before also in the electrolysis operations when carried out under high temperatures, that is, at temperatures between 70° and 90°C.

All these objects, as well as many others, are attained by the process of this invention, according to which the anodic overvoltage (in cells having a mercury cathode and in diaphragm cells) and the decomposition of the amalgam (in cells having a mercury cathode) during the electrolysis of solutions of alkaline chlorides are reduced by adding to the electrolyte from 2 to 200 ppm of at least one compound selected from a group consisting of alcohol ethers or phenol ethers with polyoxyethylene and of esters of carboxylic acids with polyoxyethylene.

In the case of ethers of alcohols with polyoxyethylene, the alcohols used are generally aliphatic or aromatic alcohols of which the alkyl radical contains from 2 to 20 carbon atoms. The aliphatic chain linked to the alcoholic group may be linear or variously branched. The alcohols may contain one or more additional functional groups, and more particularly: —OH, —Cl, —Br, —F, —SO₂H, —SO₃Me wherein Me is an alkali metal, —COOR wherein R is an alkyl radical containing from one to four carbon atoms, and

\[
R_1 \left(\text{O—CH—CH}_2\right)\text{O—H}
\]

wherein R₁ and R₂ are hydrogen or alkyl radicals containing from 1 to 12 carbon atoms. Preferably, the alcohols contain from 8 to 20 carbon atoms. Particularly suitable are the aliphatic alcohols containing from 12 to 18 carbon atoms.

Some specific examples of suitable alcohols are, for instance, lauryl alcohol, oleyl alcohol, stearyl alcohol and phenylethyl alcohol.

The ethers derived from the condensation of such alcohols with ethylene oxide contain, in general, from 2 to 150 molecules of ethylene oxide for each molecule of alcohol. Preferably they contain from 10 to 120 molecules of ethylene oxide for each alcohol molecule.

The degree of ethoxylation that gives the best results depends in part on the nature of the R-radical. Amongst the alcohol ethers with polyoxyethylene which have yielded the best results may be listed the monolauryl ethers of polyethyleneglycols containing from 10 to 30 ethoxy groups and the monooleylethers of polyethyleneglycols containing from 60 to 120 ethoxy groups.

The ethers of phenols with polyoxyethylene suited for the purposes of this invention may be represented by the general formula:

\[
R \left(\text{O—CH—CH}_2\right)\text{O—H}
\]

wherein:

R is an alkyl or aralkyl radical having from 1 to 20 carbon atoms and n is between 2 and 40, inclusive.

The alkyl radical R (or the alkyl part of the radical) may be linear or variously branched.

The radical may contain one or more additional functional groups, in particular those already specified for the alcohol condensates with ethylene oxide.

Preferably, the R radical contains from 8 to 20 carbon atoms. Particularly suitable are the compounds in which R contains from 8 to 13 carbon atoms. If R is an alkyl radical, it may for instance be an octyl, nonyl, decyl or tridecyl group. If it is an aralkyl radical it may, for instance, be a cumyl or methylcumyl group. The radical may be in an ortho-, para- or meta-position with respect to the polyethoxy chain.

Because of the method of their preparation these compounds are generally mixtures of numerous isomers and homologues, both as far as the alkyl chain is concerned, which may be variously branched, as well as with regard to the position of the R radical with respect to the ethoxy group.

Although good results are obtained when all the compounds have a degree of ethoxylation between 2 and 40, in general those are preferred which have a degree of ethoxylation between 5 and 30. Here again, the de-
3,849,266

The feature of being able to use the additives at high temperatures (e.g., 70°-90°C) represents a considerable advantage because said high temperatures correspond to high current densities and therefore to a greater potentiality of the cells.

The process of this invention may be applied with excellent results to all types of mercury cathode cells, that is, both to the horizontal cathode types and to the vertical cathode types and to all types of diaphragm cells as well as to all the types of anodes, that is both to the graphite anodes and to the metal anodes, for instance titanium anodes.

When the present process is applied to diaphragm cells, one does not see, obviously, the particular advantage due to the reduction of the decomposition of the amalgam.

The additives have proved to be equally efficacious throughout the range of current densities that are used in the electrolytic cells, that is in the range from about 20 to about 100 amp/dm² when working with graphite anodes and from about 20 to about 200 amp/dm² when working with metal anodes. The current density is not a critical feature of the process of the invention but depends solely upon the characteristics of the cells employed.

The additive, which at room temperature may be solid or liquid, may be added as such to the brine before the introduction thereof into the cell or as solution in water or in the brine.

The solutions used for the purposes of the present invention have in general a concentration between 0.1 to 10 percent by weight. During the admixture of the additive to the brine, one must ensure an effective mixing in order to bring about a homogeneous distribution of the additive in the brine.

The following detailed working examples are given for the purpose of still better illustrating the inventive idea:

EXAMPLE 1

The tests were carried out in small experimental cells having Plexiglass walls, into which were placed in a horizontal position one or two graphite anodes at an adjustable distance from the level of the mercury that flowed on the bottom of the cell.

The anodic surface amounts to about 2.0 dm². The concentration in NaCl of the brine fed into the cell amounts to 310 gr/lt (grams per liter); its pH is between 3 and 4. Its NaCl concentration at the outlet equals 260-270 gr/lt. Its content in impurities is the following:

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity</td>
<td>&lt;10 ppm</td>
</tr>
<tr>
<td>CaO</td>
<td>0.01-0.04 gr/lt</td>
</tr>
<tr>
<td>MgO</td>
<td>&lt;0.005 gr/lt</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>&lt;0.001 gr/lt</td>
</tr>
<tr>
<td>Other metal cations</td>
<td>&lt;0.01 ppm</td>
</tr>
<tr>
<td>Sulphate anions, expressed as SO₃</td>
<td>2-5</td>
</tr>
</tbody>
</table>

A current density of 70 amp/dm² was applied. The temperature of the brine at the outlet of the cell was 76°C.

The tests were carried out with different infraeletrode distances, with the following additives:

1. mono(para-alpha-cumylphenyl) ether of heptaethylene glycol (PCF-7);
2. mono(3-methylcubylalkyl) ether of eicosanethylene glycol (PCF-20);
3. nonylphenylethers of 26-ethyleneglycol (NF-26).
The mixture contained about 90 percent of para isomers and 10 percent of ortho isomers;
4. mono-laurylether of eicosane-ethyleneglycol (AL-20);
5. mono-oleylether of 100-ethyleneglycol (AO-100).

For comparative purposes, each test was also repeated without the additives.
30 minutes after the starting of the cells, their voltage was measured and the concentration of the hydrogen in the electrolysis gas, which contains about 99.0 percent of chlorine by volume, was checked.
These measures were repeated every 15 minutes throughout the test, which lasted 3 hours. The conditions, as recorded below in Table 1, were maintained practically constant throughout the test.

TABLE 1

<table>
<thead>
<tr>
<th>Additive</th>
<th>Concentration in ppm</th>
<th>Infraelectrode distance in mm</th>
<th>Tension in volts without additive</th>
<th>Tension in volts with additive</th>
<th>Percentages by volume of H$_2$ in the electrolysis gas without additive</th>
<th>Percentages by volume of H$_2$ in the electrolysis gas with additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCF-7</td>
<td>10</td>
<td>2.5</td>
<td>4.36</td>
<td>4.12</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>PCF-7</td>
<td>10</td>
<td>4.0</td>
<td>4.55</td>
<td>4.32</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>PCF-20</td>
<td>10</td>
<td>2.5</td>
<td>4.35</td>
<td>4.15</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>NF-26</td>
<td>10</td>
<td>2.0</td>
<td>4.56</td>
<td>4.36</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>AL-20</td>
<td>10</td>
<td>2.0</td>
<td>4.32</td>
<td>4.15</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>AO-100</td>
<td>10</td>
<td>2.0</td>
<td>4.35</td>
<td>4.15</td>
<td>0.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

From Table 1 it can be seen that with additives there is a decrease of anodic potential of about 0.20 - 0.25 volt.
In those cells where an additive was used, there was observed a better distribution and uniformity in the development of gaseous bubbles on the anodes and inside the solution.
The development of hydrogen was reduced, on the average, by about 15 percent.
It may be noted that the conditions which obtain in the small experimental cells do not fully reflect, so far of test no. 2, the cell was very dirty. Test no. 3 was carried out with new anodes.
30 minutes after starting to feed the cells with the brine containing the additive, the voltage of each cell and the concentration in hydrogen of the electrolysis gas were measured, the electrolysis gas containing about 96% by volume of Cl$_2$.
The measurements were repeated every 15 minutes for a total duration of 8 hours. The resulting values are recorded below in Table 2 and remained practically constant throughout the respective tests.

TABLE 2

<table>
<thead>
<tr>
<th>Number of Test</th>
<th>Additive</th>
<th>Concentration in ppm</th>
<th>Tension in volts without additive</th>
<th>Tension in volts with additive</th>
<th>Percentages by volume of H$_2$ in the electrolysis gas without additive</th>
<th>Percentages by volume of H$_2$ in the electrolysis gas with additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PCF-7</td>
<td>20</td>
<td>4.58</td>
<td>4.42</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>PCF-7</td>
<td>10</td>
<td>4.70</td>
<td>4.40</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>NF-30</td>
<td>10</td>
<td>4.65</td>
<td>4.40</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td>4</td>
<td>I5-10</td>
<td>10</td>
<td>4.85</td>
<td>4.45</td>
<td>0.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

From the examination of the preceding Table 2, it will be seen that also in this case there was a considerable drop in anodic potential which drop reached 0.30 volt in test no. 2 and test no. 4.
The development of hydrogen was reduced, on the average, by about 25 percent.
Tests nos. 3 and 4 were carried out for 12 days; during their whole duration a reduction in the voltage and in the development of hydrogen was recorded having a value at all times substantially equal to those which appear in the table.

EXAMPLE 2
These experiments were conducted on an industrial scale in commercial De Nora cells having the following operational characteristics:
distance between electrodes: about 3 mm;
The cells that operated with additive were maintained in a condition of greater cleanliness.

EXAMPLE 3

The tests of this example were carried out in pilot scale De Nora cells fitted out with dimensionally stable anodes manufactured by Permelec. These anodes are made of titanium coated with metallic oxides such as ruthenium, iridium, tantalum and titanium oxides (for a description of said kind of anodes, see, for instance, Dutch Patent Application No. 68/179577). The exact composition of the coating is not specified by the manufacturer.

The whole anodic surface amounted to about 54.0 dm².

The operational characteristics were:

- distance between anodes and cathode: about 3 mm;
- average temperature of the brine at the cell outlet: 85°C;
- current density: 125 (test 1) and 150 (test 2) amp/dm².

The brine used was identical with that used in Example 1, its concentration in NaCl at the outlet of the cell being 290 gr/l.

The experiments were carried out with nonylphenylethers of 30-ethyleneglycol (NF-30), the mixture containing about 90 percent of para-isomers and 10 percent of ortho-isomers.

Thirty minutes after starting to feed the cells with brine containing the additives, the voltage of the cell and the concentration in hydrogen of the electrolysis gas were measured, the electrolysis gas containing about 97 percent by volume of Cl₂.

The measurements were repeated every 2 hours for a total period of 8 days.

The resulting values are recorded in Table 3. They remained practically constant throughout the respective tests.

| Table 3 |
|---|---|---|---|---|---|
| Number of Test | Additive | Concentration in ppm | Current Density amp/dm² | Tension in volts without additive | Tension in volts with additive | Percentages by volume of H₂ in the electrolysis gas without additive | Percentages by volume of H₂ in the electrolysis gas with additive |
| 1 | NF-30 | 10 | 125 | 3.90 | 3.74 | 0.9 | 0.6 |
| 2 | NF-30 | 10 | 150 | 4.03 | 3.85 | 0.9 | 0.6 |

From an examination of Table 3, it can be seen that also in this case there was a considerable drop (0.16 – 0.18 volt) in anodic potential. It can also be seen that the effectiveness of the additives is not lowered by an increase in the current density as a higher drop (0.18 volt) has been reached with the higher density (150 amp/dm²).

The development of hydrogen was reduced, on the average, by about 33 percent.

What is claimed is:

1. In a process for the electrolysis of alkaline chloride solutions in mercury cathode cells and diaphragm cells, the improvement comprising reducing the anodic overvoltage in both kinds of cells and the decomposition of the amalgam in mercury cathode cells during the electrolysis by adding to the electrolyte from 2 to 200 ppm of at least one compound selected from the group consisting of,

- the ethers of alcohols with poloxylethelnes which
  - a. are derived from alcohols selected between aliphatic and aromatic ones and having from 8 to 20 carbon atoms, and
  - b. contain from 2 to 150 molecules of ethylene oxide for each molecule of alcohol,
- the ethers of phenols with poloxylethelnes having the following formula:

```
R     \( \textOCHCH_nOH \)
```

wherein
- a. R is a radical selected between alkyl and aralkyl and has from 1 to 20 carbon atoms, and
- b. n is between 2 and 40, inclusive,
- iii. the esters of carboxylic acids with poloxylethelnes which
  - a. are derived from acids selected between aliphatic and aromatic ones and having from 6 to 20 carbon atoms, and
  - b. contain from 200 to 6000 ethylene oxide molecules for each molecule of acid.

2. The process of claim 1, wherein the ethers of alcohols with poloxylethelnes contain from 10 to 120 molecules of ethylene oxide for each molecule of alcohol.

3. The process of claim 2, wherein the ethers of alcohols with poloxylethelnes are derived from alcohols having from 12 to 18 carbon atoms.

4. The process of claim 3, wherein the alcohol is selected from the group consisting of lauryl alcohol, oleyl alcohol, stearyl alcohol and phenylethyl alcohol.

5. The process of claim 1, wherein the R radical of the ethers of phenols with poloxylethelnes contains from 8 to 20 carbon atoms and n is between 5 and 30, inclusive.

6. The process of claim 5, wherein R contains from 8 to 13 carbon atoms.

7. The process of claim 6, wherein R is selected from the group consisting of octyl, nonyl, dodecyl, tridecyl, cumyl and methylcumyl.

8. The process of claim 1, wherein the carboxylic acids are aliphatic acids having from 12 to 18 carbon atoms.

9. The process of claim 8, wherein the acid is selected from the groups consisting of lauric, oleic, stearic and palmitic acid.

10. The process of claim 1, wherein the aliphatic or aromatic alcohol and acid moieties contain one or
9. more additional -OH, -Cl, -Br, -F, -SO₄H, -SO₄Me, -COOR and

10. -SO₄Me groups in which Me is an alkali radical containing from one to four carbon atoms, and

groups in which Me is an alkaline metal, R is an alkyl radical containing from 1 to 4 carbon atoms, and R₁ and R₂ are hydrogen or alkyl radicals containing from 1 to 12 carbon atoms.

11. The process of claim 1, wherein the R radical contains one or more -OH, -Cl, -F, -Br, -SO₄H, -SO₄Me groups in which R₁ and R₂ are hydrogen or alkyl radicals containing from 1 to 12 carbon atoms.

12. The process of claim 1, wherein from 5 to 20 ppm by weight of additive is employed.

* * * * *