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PROCESS FOR REDUCING THE HYDROGEN CONTENT IN CHLORINE GAS PRODUCED BY ALKALI-METAL CHLORIDE ELECTROLYSIS

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ABSTRACT OF THE DISCLOSURE

There is disclosed a process for the reduction or prevention of hydrogen development at the mercury cathode during the amalgam process of alkali metal chloride electrolysis. The process comprises incorporating into the mercury from 0.001 to 0.5 mole percent of a metal capable of forming an intermetallic mercury-soluble compound with the metals giving rise to this phenomena. The invention lies in the finding that copper, zinc, tin, lead or indium are capable of forming an intermetallic compound with the so-called troublesome metals, i.e., chromium, germanium, tungsten, nickel, cobalt, etc., the intermetallic compound being soluble in mercury, unlike the troublesome metal, thereby preventing their concentration at the mercury cathode surface and thus reducing or eliminating the evolution of hydrogen.

This invention relates to a process for reducing the hydrogen content in chlorine gas produced by alkali metal chloride electrolysis.

More particularly this invention relates to a process for reducing or eliminating evolution of hydrogen at the mercury cathode in the amalgam process of alkali metal chloride electrolysis.

It is known that the presence of even extremely small amounts of certain metals in the crude salts employed in alkali-metal chloride electrolysis causes the overvoltage at the mercury cathode in the amalgam process to be greatly reduced. The precipitation of such metals, as for example, chromium, molybdenum, tungsten, nickel, cobalt, or germanium, on the mercury cathode causes a strong evolution of hydrogen, which gives rise to difficulty inasmuch as the hydrogen forms an explosive gas mixture with the chlorine gas.

The salt brines that are used in the electrolysis procedure are first subjected to a preliminary purification, which consists of a precipitation treatment with alkali carbonate and barium carbonate. In this manner the calcium and sulfate ions are removed from the brine. The precipitation of the calcium ions is necessary because in their presence iron exhibits a troublesome effect. The fine barium sulfate that precipitates not only removes the sulfate ions which are generally considered responsible for the oxidative ablation of the anodes, but also most of the above-mentioned troublesome metals. However, small amounts of troublesome metals still remain in the brine and are the cause of the evolution of hydrogen at the mercury cathode.

Attempts have already been made to eliminate or reduce the above-mentioned difficulties by the addition of silicates or phosphates to the brine. These methods, however, have but a relatively slight effect, if any, on eliminating the difficulties.

In accordance with the invention, it has now been found that hydrogen evolution at the mercury cathode in the amalgam process of alkali-metal chloride electrolysis can be reduced or substantially eliminated by adding a metal to the mercury which is capable of forming with the troublesome metals an intermetallic compound that is soluble in mercury, the metal being added in an amount of 0.001 to 0.5 mole percent.

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The metals which are suitable for use in accordance with the invention for forming the intermetallic compounds can also be added in the form of their soluble salts, e.g., as chlorides, to the alkali brine.

The metals which can be used for formation of mercury-soluble intermetallic compounds include copper, zinc, tin, lead and indium.

It has surprisingly been found that when the process of the invention is carried out, the evolution of hydrogen at the mercury cathode is greatly reduced or even entirely eliminated. The action of the added metals is based on the fact that they are capable of forming an intermetallic compound with the troublesome metals, this compound being easily soluble in mercury. The troublesome metals, however, are poorly soluble in mercury by themselves. As a result of the addition of the metals according to the invention, an amalgamation of the troublesome metals is brought about, thereby preventing the metals from concentrating at the mercury cathode surface.

The removal of the troublesome metals from the mercury cathode surface takes place according to the following equations:

$$Me_1^{(n+)}+e^- \rightarrow Me_1 \qquad (1)$$

$$Me_1+Me_2+Hg \rightleftharpoons [Me_1 \cdot Me_2]Hg_x \qquad (2)$$

or

$$Me_1+[Me_2]Hg_x \rightleftharpoons [Me_1 \cdot Me_2]Hg_x \qquad (2a)$$

In the above equations, Me_1 represents a troublesome metal that is reduced to the metal at the mercury cathode. Me_2 represents a metal that is easily soluble in mercury. It is apparent that the speed of reactions 2 and 2*a* determines the amount of hydrogen evolution. That is to say, if the speed of the reactions 2 and 2*a* are greater than that of reaction 1, the troublesome metal is immediately dissolved in the mercury as a binary compound and exerts no effect on the evolution of hydrogen. If the speed of the reactions 2 and 2*a* is less than that of reaction 1, the troublesome metal, depending on how much of it is in the brine, can concentrate at the mercury surface and thus give rise to the formation of hydrogen.

The following examples are given for the purpose of illustrating the invention and are in no wise to be construed in limitation thereof.

EXAMPLE 1

When the concentration of chromium in the form of a chromium salt in the brine of an alkali-metal chloride electrolysis exceeds 10^{-8} mole per liter, the evolution of hydrogen must be expected. On addition of 0.01 mole percent of zinc to the cathode mercury, the concentration of the chromium salt can be raised as much as a thousandfold without any evolution of hydrogen taking place.

EXAMPLE 2

Example 1 was modified to the extent that copper amalgam was used instead of zinc amalgam. In this case, also, no hydrogen gas was developed when chromium salts were added to the brine in excess of the concentration mentioned in Example 1.

EXAMPLE 3

No hydrogen gas was developed when chromium salts were added to the brine as set out in Examples 1 and 2 when an indium amalgam (indium content 0.01 mole-percent) was used instead of zinc or copper amalgam.

EXAMPLE 4

The troublesome metal germanium was added in the form of a soluble salt to a 3× molar KCl brine. Even at a concentration of 2×10^{-7} moles of germanium per liter of brine, hydrogen gas evolution takes place. When zinc or copper amalgam was added in the same amounts as described in Example 1, hydrogen evolution does not take place, until the germanium concentration amounts to 5×10^{-4} moles of germanium per liter of brine.

The process is further explained with the aid of Examples 5 to 19 set out in the following table:

Example	Troublesome metal in the brine	Minimum troublesome metal concentration in the brine at which hydrogen gas production could still be detected: With pure Hg cathode, mg./l.	With cathode of amalgam containing 0.001 wt. percent of Zn, Cu, Sn, Pb and In, mg./l.	Improvement factor
5	W	0.01	10	1,000
6	Ni	1.0	110	100
7	Co	0.06	1.2	20
8	Mo	0.01	0.1	10
9	V	0.01	0.1	10
10	As	0.75	7.5	10
11	Sb	0.6	6.0	10
12	Be	3.0	9.0	3
13	Mg	1.0	2.4	2
14	Ti	1.9	2.4	1
15	Zr	9.0	9.1	1
16	Ca	(1)	(1)	----------
17	Ba	(1)	(1)	----------
18	Al	4.0	2.7	0.7
19	Fe	(1)	30	----------

1 Unknown, because no effect on the H_2 evolution was measurable.

I claim:

1. Process for the reduction or elimination of hydrogen development at the mercury cathode in the amalgam process of alkali-metal chloride electrolysis which takes place due to the presence in the alkali brine of at least one metal impurity which comprises incorporating at least one metal selected from the group consisting of copper, zinc, tin, lead and indium capable of forming an intermetallic mercury-soluble compound with said metal impurity into the mercury in an amount of 0.001 to 0.5 mole-percent.

2. Process according to claim 1 wherein said metal which is incorporated is incorporated into the alkali brine in the form of its soluble salt.

3. Process according to claim 1 wherein said metal which is incorporated is copper.

4. Process according to claim 1 wherein said metal which is incorporated is tin.

5. Process according to claim 1 wherein said metal which is incorporated is indium.

6. Process according to claim 1 wherein said metal which is incorporated is lead.

7. Process according to claim 1 wherein said metal which is incorporated is zinc.

8. In the amalgam process of alkali metal chloride electrolysis the step for reducing or eliminating hydrogen development at the mercury cathode due to the presence of at least one metal impurity in the alkali brine, which comprises incorporating into the mercury at least one metal selected from the group consisting of copper, zinc, tin, lead and indium capable of forming an intermetallic mercury-soluble compound with the metal impurity in an amount of 0.001 to 0.5 mole-percent.

9. A mercury cathode for use in the amalgam process of alkali metal chloride electrolysis having incorporated therein 0.001 to 0.5 mole-percent of a metal selected from the group consisting of copper, zinc, tin, lead and indium capable of forming an intermetallic mercury-soluble compound with a metal selected from the group consisting of tungsten, nickel, cobalt, molybdenum, vanadium, arsenic, antimony, beryllium, magnesium, titanium, zirconium, calcium, barium, aluminum, iron, chromium, and germanium.

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