

[54] **CATHODIC PROCESS FOR THE
PREPARATION OF TETRAALKYL
LEAD COMPOUNDS**

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[58] Field of Search **204/72, 73; 260/657**

[56] **References Cited**

UNITED STATES PATENTS

1,567,159	12/1925	Mead.....	204/72
3,392,093	7/1968	Smeltz	204/72
3,432,409	3/1969	Schuler et al.	204/72

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[57]

ABSTRACT

The present invention relates to a process for the preparation of tetraalkyl lead compounds wherein the anolyte comprises a solution of tetrabutyl ammonium bromide or tetrabutyl phosphonium bromide in water. In this process bromine is produced at the anode and forms a precipitate with the tetrabutyl ammonium or phosphonium bromide present. This bromine can be recovered by treating the anolyte solution with hydrogen sulfide to convert the bromide present to hydrogen bromide, sulfur and the tetrabutyl ammonium or phosphonium bromide. The sulfur is removed from the solution and the solution is then treated with ethanol to form ethyl bromide by reaction with the hydrogen bromide present in the solution. The ethyl bromide is separated from the solution and returned to the cathode compartment of the electrolytic cell whereby it is subsequently converted to tetraethyl lead. The quaternary bromide salt such as tetrabutyl ammonium or phosphonium bromide is recovered from the solution as an aqueous salt and is returned to the anode compartment of the electrolytic cell where it then becomes part of the anolyte.

4 Claims, No Drawings

CATHODIC PROCESS FOR THE PREPARATION OF TETRAALKYL LEAD COMPOUNDS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to a cathodic process for the preparation of tetraalkyl lead compounds but more particularly to a process wherein the bromine generated at the anode is subsequently recovered as ethyl bromide and returned to the cathode compartment of the electrolytic cell for production of additional tetraalkyl lead compounds.

2. Description of the Prior Art

Cathodic processes for the production of alkyl leads are known. For example, Calingaert (U.S. Pat. No. 1,539,297) and Mead (U.S. Pat. No. 1,567,159) disclose tetraalkyl lead formation at a lead cathode by electrolyzing a catholyte consisting of an alkyl iodide in either alcoholic caustic or aqueous caustic containing casein. Also Silversmith et al. (U.S. Pat. No. 3,197,392) disclose a process for preparing tetraalkyl lead compounds by electrolyzing at a lead cathode a solution of an alkyl halide in a normally liquid nonhydroxylic cathodic solvent. In addition, a recent disclosure in this field is a patent to Smeltz (U.S. Pat. No. 3,392,093) which discloses a process for producing tetraalkyl lead compounds at a lead cathode in an electrolytic cell having a catholyte containing acetonitrile as a solvent, alkyl halide as an alkylating agent, a tetraalkyl ammonium monohalide as a current carrier and from about 1 to about 20 moles of water per mole of said current carrier added as a side product suppressor. It is also known to utilize a quaternary salt such as tetrabutyl ammonium bromide or tetrabutyl phosphonium bromide as a salt for use in the anolyte of a cathodic tetraalkyl lead process. These tetrabutyl ammonium and phosphonium bromides have been used to overcome the problem created by using a salt such as ammonium bromide whereby the ammonium ion was transferred from the anolyte compartment into the catholyte compartment and interfering with the cathodic reaction. This problem is avoided by using the tetrabutyl ammonium and phosphonium bromides because the size of the molecule retards its transference through the membrane into the cathode compartment. Even if a small amount of the tetrabutyl ammonium or phosphonium bromide salt happens to enter the cathode compartment from the anode compartment, it would not interfere with the cathodic reaction because this is the same salt which is used as a current carrier in the catholyte. There was a problem, however, with the use of these tetrabutyl ammonium and phosphonium bromides in that the bromine formed at the anode would form a precipitate with the tetrabutyl ammonium and phosphonium bromides and would result in a loss of bromine. The present invention provides a method of recovering the bromine which forms a precipitate with the tetrabutyl ammonium and phosphonium bromides.

SUMMARY OF THE INVENTION

The present invention relates to a method for recovering the bromine which is precipitated in the anode compartment of the electrolytic cell while utilizing a tetrabutyl ammonium or tetrabutyl phosphonium bromide as a component of the anolyte. The bromine which is produced at the anode forms a precipitate with the tetrabutyl ammonium or phosphonium bromide salts. The formation of this precipitate creates the problem of loss of anolyte salt and in addition a waste of valuable bromine. In this invention the quaternary salt-bromide precipitate is reacted as an aqueous solution with hydrogen sulfide whereby the bromine is converted to hydrogen bromide and this hydrogen bromide is subsequently reacted with ethanol to produce ethyl bromide. This ethyl bromide is then returned to the cathode compartment wherein it is converted to additional tetraethyl lead. The quaternary salt is recovered as an aqueous solution of tetrabutyl ammonium or phosphonium bromide which is then returned to the anode compartment of the electrolytic cell for use in recovering the bromine again produced at the anode. It is therefore a general object of the

present invention to provide a method for recovering bromine from the anode and returning this bromine as ethyl bromide to the cathode compartment wherein the ethyl bromide is subsequently converted to tetraethyl lead.

5 A further object of the invention is to provide a method for recovering the tetrabutyl ammonium bromide or tetrabutyl phosphonium bromide for subsequent use as a component of the anolyte of said electrolytic cell. Other and further objects will become apparent from the following detailed description of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Broadly described, the method of the present invention comprises the addition of hydrogen sulfide to a precipitate containing bromine and a quaternary salt such as tetrabutyl ammonium bromide or tetrabutyl phosphonium bromide. This quaternary salt-bromide precipitate is formed by the reaction of bromine on the tetrabutyl ammonium or phosphonium bromide in the anolyte of the electrolytic cell.

We have found experimentally when hydrogen sulfide is bubbled through an aqueous suspension of the quaternary salt-bromine precipitate such as tetrabutyl ammonium bromide salt-bromine precipitate and tetrabutyl phosphonium bromide salt-bromine precipitate the precipitate dissolves forming free sulfur and a clear aqueous solution of the quaternary salt plus hydrogen bromide, plus a possible trace amount of sulfuric acid. The sulfur is filtered from the anolyte, the anolyte is then contacted with ethanol to form ethyl bromide that is separated from the anolyte. This ethyl bromide can be subsequently returned to the cathode compartment of the electrolytic cell whereby the ethylbromide is converted to tetraethyl lead at the cathode by a cathodic process which is well known in the art. The anolyte is then treated with lime to precipitate any sulfuric acid which may be present. The precipitate formed by this addition of lime is calcium sulfate which can then be removed. This leaves the anolyte solution of water plus tetrabutyl ammonium or tetrabutyl phosphonium bromide salt. This salt can then be returned to the anode compartment of the electrolytic cell for further use in recovering the bromine values. As previously stated, this process solves problems which were created by the use of tetrabutyl ammonium and phosphonium bromides as salts for use in the anolyte. It was found that when aqueous solutions of ammonium bromide or alkali bromide were used as the anolyte a significant fraction of the current was carried by the ammonium ions and the alkali metal ions through the semipermeable ion exchange organic membrane separating the anode and cathode compartments. This means a substantial waste to these cations and a loss of electricity because these ions are either reacted at the cathode or interfere with the cathodic reduction of tetraethyl lead. In an ideal process all the current would be carried by bromine ion migrating through the semipermeable membrane from the cathode to the anode compartment. It was also found that a quaternary salt such as tetrabutyl ammonium bromide or tetrabutyl phosphonium bromide could be used to alleviate the problems of the migrating ions present when ammonium bromide or alkali bromides are used. It was also found, however, that the quaternary salts formed a precipitate with the bromine which was liberated at the anode. This precipitate appeared to be an insoluble precipitate which resulted in the loss of bromine from the process and resulted in an economic waste. This invention then provides a means whereby the bromine can be recovered and subsequently converted to a useable product such as ethyl bromide which becomes a part of the catholyte and is converted to the desired tetraethyl lead compound.

70 Principle advantages of this process are (1) the large cation present in the anolyte does not pass freely through the semipermeable membrane into the cathode compartment, as do other cations, such as ammonium and the alkali metal cation, where they interfere with the cathodic production of tetraalkyl lead compounds, (2) the hydrogen sulfide used to

convert the bromine to hydrogen bromide yields principally sulfur rather than sulfuric acid. Sulfur is more valuable than sulfuric acid and (3) the bromine liberated at the anode is immediately tied up by the tetrabutyl ammonium or tetrabutyl phosphonium bromide salts and therefore is not free to contact and damage the semipermeable organic membrane used to separate the cathode and anode compartments. (4) the hydrogen bromide formed by the reaction is easily converted to ethyl bromide which is a starting material used in the cathodic process, and (5) the quaternary salt such as tetrabutyl ammonium bromide or tetrabutyl phosphonium bromide is recovered as an aqueous solution and can be returned to the anode compartment for further use as a current carrier in the anolyte. The invention can be better understood by the following examples.

EXAMPLE 1

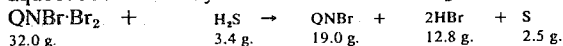
A pyrex cell was divided into cathode and anode compartments by using an anion selective membrane. The cathode was lead and had an effective area of about 3 cm². The anode was a carbon rod (10 cm.²). The catholyte composition was 51 grams H₂O, 24 grams acetone, 5 grams tetrabutyl ammonium bromide, and 20 grams of ethyl bromide. The anolyte was 10 grams of tetrabutyl ammonium bromide and 90 grams of water. The electrolysis of the stirred solution was conducted at 200 ma. for 4 hours and gave the following results:

Lead loss efficiency	97.1%
TEL efficiency	83.8%
Lead converted	86.3%

A precipitate formed in the anolyte which was analyzed and found to be a tetrabutyl ammonium bromide-bromine adduct (QNBr-Br₂).

EXAMPLE 2

The tetrabutylammonium bromide-bromine adduct formed in Example 1 was combined as an aqueous slurry with additional adduct formed from several runs of Example 1. The aqueous adduct slurry was then reacted with H₂S as follows:



The sulfur was removed by filtering and the HBr-QNBr solution was reacted with ethanol to yield ethyl bromide as follows:

EXAMPLE 3

The QNBr-HBr solution recovered from Example 2 was reacted with ethanol and a product of ethyl bromide was recovered.



5 The ethyl bromide was recovered by using a separatory funnel and returned to the catholyte of Example 1. The QNBr+H₂O solution was returned to the anolyte of Example 1.

10 Although certain specific embodiments of the invention have been described as exemplary of its practice these examples are not intended to limit the invention in any way. Other process parameters and materials may be used in accordance with the broad principles outlined herein and when so used are deemed to be circumscribed by the spirit and scope of the invention except as necessarily limited by the appended claims and reasonable equivalents thereof.

15 What is claimed is:

1. In a cathodic process for the preparation of tetraalkyl lead compounds at a lead cathode in an electrolytic cell having a lead cathode, an anode, and a current-permeable partition separating the catholyte from the anolyte and where the catholyte comprises an alkyl bromide and a current carrier selected from the group consisting of tetrabutyl ammonium bromide and tetrabutyl phosphonium bromide, and the anolyte comprises an aqueous solution of a quaternary bromide salt selected from the group consisting of tetrabutyl ammonium bromide and tetrabutyl phosphonium bromide, the improvement comprising:

a. treating the anolyte solution with H₂S to convert any quaternary salt-bromine precipitate, which has formed by the reaction of bromine and said quaternary salt, to sulfur, HBr and quaternary salt;

b. removing the sulfur from said solution of step (a);

c. contacting said solution from step (b) WITH ETHANOL TO FORM ETHYL BROMIDE;

d. separating ethyl bromide from the solution of step (c) and returning said ethyl bromide to the cathode compartment of said electrolytic cell;

e. treating the solution remaining from step (d) with lime to precipitate any sulfuric acid present, which may have been formed in step (a), as calcium sulfate;

f. removing the calcium sulfate from step (e);

g. recovering the anolyte solution as an aqueous solution of said quaternary bromide salt; and

h. returning said anolyte solution of step (g) to the anode compartment of the electrolytic cell.

2. The process of claim 1 wherein the sulfur removal in step (b) is accomplished by filtration.

3. The process of claim 1 wherein the calcium sulfate removal in step (f) is accomplished by filtration.

4. The process of claim 1 wherein the H₂S treating in step (a) is accomplished by bubbling H₂S through an aqueous suspension of said quaternary salt-bromine precipitate.

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