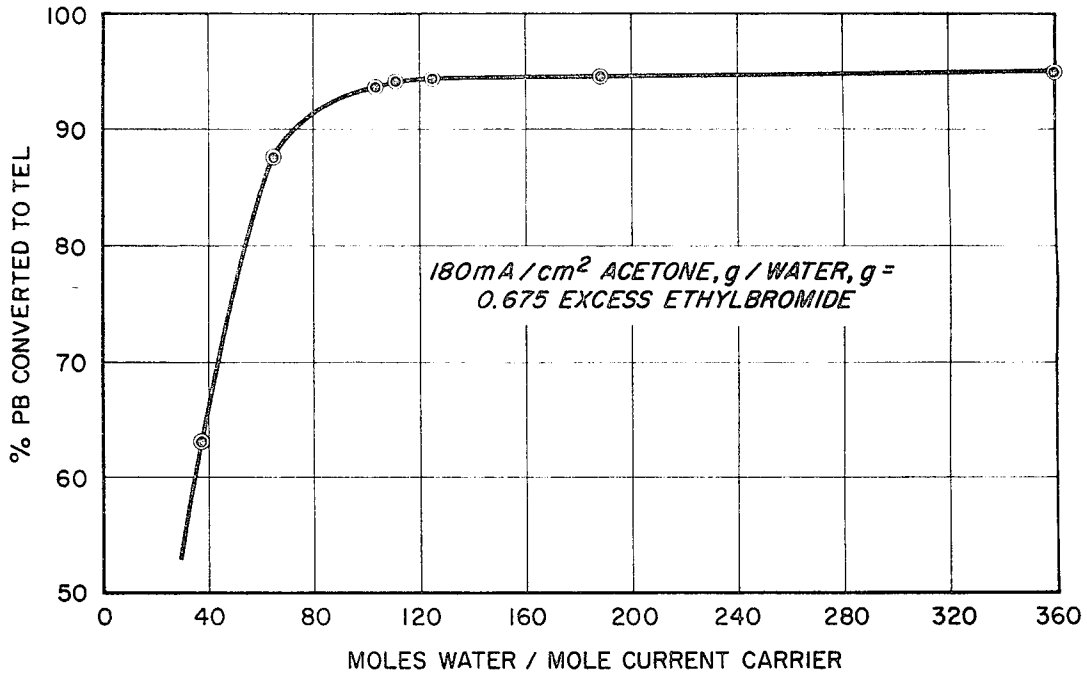


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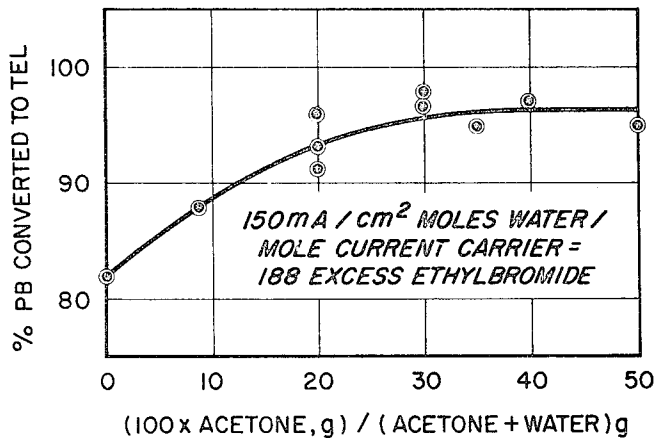
KANG YANG ET AL  
CATHODIC PROCESS FOR THE PREPARATION  
OF TETRAALKYL LEAD COMPOUNDS  
Filed Oct. 2, 1969

3,649,482



DEPENDENCE OF TEL YIELD ON THE MOLES  
WATER PER MOLE OF CURRENT CARRIER

FIG. 1



DEPENDENCE OF TEL YIELD ON ACETONE CONCENTRATION

FIG. 2

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1

3,649,482

## CATHODIC PROCESS FOR THE PREPARATION OF TETRAALKYL LEAD COMPOUNDS

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Continuation-in-part of application Ser. No. 773,321, Nov. 4, 1968. This application Oct. 2, 1969, Ser. No. 863,096

Int. Cl. C07b 29/06; C07f 7/26

U.S. Cl. 204—72

14 Claims

2

### ABSTRACT OF THE DISCLOSURE

A process for cathodically producing tetraalkyl lead compounds wherein the cathode is lead and the catholyte contains an alkyl halide, a tetrabutyl ammonium halide, or a tetrabutyl phosphonium halide, water, and an alkylating agent solubilizer, such as acetone or tetrahydrofuran (THF).

### CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application for United States Letters Patent Ser. No. 773,321 filed Nov. 4, 1968.

This invention relates to a process for producing tetraalkyl lead compounds and more particularly to an electrolytic process wherein an alkyl halide or mixture of alkyl halides is reduced at a lead cathode to form tetraalkyl lead compounds.

Cathodic processes for the production of alkyl leads are known. For example, Calingaert and Mead disclosed tetraalkyl lead formation at a lead cathode by electrolyzing a catholyte consisting of an alkyl iodide in either alcoholic caustic (Calingaert in U.S. Pat. No. 1,539,297)<sup>1</sup> or aqueous caustic containing casein (Mead in U.S. Pat. No. 1,567,159).<sup>2</sup> Also, Silversmith et al. disclosed 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 (Silversmith in U.S. Pat. No. 3,197,392).<sup>3</sup> The most recent disclosure in this field appears to be a patent to Smeltz 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, an 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 (Smeltz in U.S. Pat. No. 3,392,093).<sup>4</sup>

Electrolytic processes for the production of tetraalkyl lead compounds employing a lead cathode can be classified on the basis of the major solvent employed in the catholyte. This classification is as follows:

- (A) Processes using water
- (B) Processes using alcohols
- (C) Processes using aprotic solvents

In processes which are of the classification type (A), water has been used together with NaOH where the alkyl halide is C<sub>2</sub>H<sub>5</sub>I dispersed by using casein.<sup>2</sup> The yield from these processes is less than 10 percent; and, when C<sub>2</sub>H<sub>5</sub>Br is used, the yield is found to be negligible. This low yield together with the need to use expensive iodides is apparently a reason for lack of commercial interest in these processes.

In processes which are of the classification type (B), NaOH<sup>1</sup> and (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBr<sup>5</sup> have been used as the sup-

porting electrolytes; however, we found that the yield obtained with C<sub>2</sub>H<sub>5</sub>Br in the ethanol-NaOH system is nearly zero; and with C<sub>2</sub>H<sub>5</sub>Br in the (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBr system the yield is reported to be only about 35 percent.<sup>5</sup> Such a low yield process in which side reactions predominate is of no commercial interest.

In processes which are of the classification type (C), various shortcomings are inherent, such as (1) the aprotic solvent is lower conducting than aqueous systems, (2) materials needed for cell construction, particularly the cell membrane which separates the anolyte from the catholyte, are less stable in aprotic solvents than in aqueous systems, (3) halogens, generated at the anode tend to react the most aprotic solvents, and (4) aprotic solvents are more expensive than water. In some cases, a small amount of water has been added to an aprotic solvent to suppress side reactions; however, where the major solvent component is an aprotic solvent, these shortcomings cannot be remedied as long as the water remains a minor component.

It has now been unexpectedly discovered that water can be used as a catholyte solvent in an electrolytic process for the production of tetraalkyl lead compounds provided certain current carrying salts and certain solubilizing agents are included in the catholyte. When tetrabutyl ammonium bromide or tetrabutyl phosphonium bromide is used as a current carrier and acetone or a water soluble ether such as tetrahydrofuran is used as a solubilizing agent for the cathodic reduction to form tetraalkyl lead from a lead cathode and alkyl bromide, the presence of a major amount of water in said system results in a yield of tetraalkyl lead which approaches 100 percent current efficiency. In systems such as this the anolyte is water with a current carrier therein, and it is therefore a simple matter to remove the bromine from the anolyte by distillation or other conventional means which are well known in the art. Some examples of suitable current carriers for the anolyte are NH<sub>4</sub>Br, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, NaBr, Na<sub>2</sub>CO<sub>3</sub>, MgBr, (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr, and a mixture of BrC<sub>2</sub>H<sub>4</sub>Br or C<sub>2</sub>H<sub>5</sub>Br and (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr.

While the previously known systems where water is a major component failed to give satisfactory yields, the present system gives a very high, nearly quantitative, yield of tetraalkyl lead.

FIG. 1 is a graph showing the effect of the ratio of water and current carrier on the production of alkyl lead compounds. This FIG. 1 is related to Example 5.

FIG. 2 is a graph showing the effect of acetone concentration on the production of alkyl lead compounds. This FIG. 2 is related to Example 6.

To more clearly describe this invention, the following examples are set forth:

### EXAMPLE 1

A Pyrex cell was divided into cathode and anode compartments by using an anion exchange membrane. The catholyte had the following composition:

Comps.	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> Br	(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> PBr	CH <sub>3</sub> COCH <sub>3</sub>
Moles.	27.7	0.138	0.0295	0.740

Lead cathode had an effective area of about 3 cm.<sup>2</sup>. Anolyte composition was: 55.5 moles water and 0.167 mole Na<sub>2</sub>CO<sub>3</sub>. A carbon rod was used as an anode. Before electrolysis, both catholyte and anolyte were degassed by bubbling through with ethylene. Two compartments were then blanketed with 5 p.s.i. ethylene. In the anode, ethylene was allowed to bubble through during electrolysis to scavenge free halogens. Electrolysis was carried out in a constant current mode using a potential controller. After electrolysis, excess water was added in the catholyte and TEL formed was extracted with hexane. The product was analyzed chromatographically. The peak was identified by trapping followed by mass-spectrometric analysis. Elec-

<sup>1</sup> U.S. Pat. No. 1,539,297.

<sup>2</sup> U.S. Pat. No. 1,567,159.

<sup>3</sup> U.S. Pat. No. 3,197,392.

<sup>4</sup> U.S. Pat. No. 3,392,093.

<sup>5</sup> Netherlands Patent application No.6508049 (1965).

3

trolisis for five hours at 150 ma. gave the following results:

Moles TEL formed= $7.00 \times 10^{-3}$   
 Grams Pb reacted=1.524  
 Percent current efficiency for TEL formation=100.1%  
 Percent current efficiency for Pb reaction=105.3%

#### EXAMPLE 2

The catholyte composition was:

Compds.	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> Br	(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> PBr	$\text{CH}_3\text{C}(\text{O})\text{CH}_3$
Moles.	13.9	0.184	0.0147	0.774

Electrolysis was carried out for 3 hours at 150 ma. Other details of experiment are the same as Example 1.

Moles TEL formed= $3.72 \times 10^{-3}$   
 Grams Pb reacted=0.8667  
 Percent current efficiency for TEL formation=88.6%  
 Percent current efficiency for Pb reacted=99.6%

#### EXAMPLE 3

The composition of catholyte was:

Compds.	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> Br	(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> PBr	Tetrahydrofuran (THF)
Moles.	1.39	0.184	0.0295	0.901

Electrolysis was carried out as described in Example 1 for 3.0 hours at 150 ma.

Percent current efficiency for TEL formation=85.7%  
 Percent current efficiency for Pb reacted=89.0%

#### EXAMPLE 4

The composition of catholyte was:

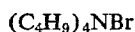
Compds.	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> Br	(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NBr	THF
Moles.	1.39	0.184	0.0310	0.485

Electrolysis was carried out as described in Example 1 for three hours at 150 ma.

Percent current efficiency for TEL formation=84.8%  
 Percent current efficiency for Pb reaction=91.5%

#### EXAMPLE 5

This example shows the dependence of TEL on a concentration ratio, [water]/[(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr]. Anolyte was 10 g. of BrC<sub>2</sub>H<sub>4</sub>Br together with 16 weight percent



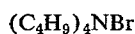
in water. Other electrolytic conditions are given in FIG. 1.

#### EXAMPLE 6

This example shows the effect of an addition of a solubilizer on TEL yield. The anolyte composition was the same as in Example 5. The cathodic conditions are given in FIG. 2.

#### EXAMPLE 7

Catholyte composition was: 14 g. of ethylbromide, and 60 g. of a solution having a composition of 10 g.



105 g. water, and 50 g. CH<sub>3</sub>CN.

Anolyte composition was 60 g. of a solution having a composition of 350 g. water, 14 g. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and 7 g. NH<sub>4</sub>Br.

After degassing with Ar, the electrolysis was carried out with a current density of 38 ma./cm.<sup>2</sup> to give a total current of  $(3.73 \times 10^{-3}) \times (4 \times 96500)$  coulombs. Results: current efficiency of lead loss=100; percent lead recovered as TEL=91 percent.

#### EXAMPLE 8

Catholyte composition was: 50 g. water, 10 g. C<sub>2</sub>H<sub>5</sub>CN, 3.60 g. (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr, and 14 g. of C<sub>2</sub>H<sub>5</sub>Br.

Anolyte composition: same as Example 7.

Electrolysis: same as Example 7.

Results: current efficiency of lead loss=96 percent; percent lead recovered as TEL=89 percent.

As shown in Example 5, the TEL yield in the present invention sharply increases with the increasing ratio of

4

water to a current carrier. A recent patent <sup>4</sup> teaches that, to obtain a good yield of alkyl leads, this ratio should not exceed 20. We find a complete opposite to this teaching: To obtain a commercially attractive yield, this ratio should exceed about 30. It is thus quite evident that whatever similarities may exist between the present invention and that disclosed in reference 4, they are only of superficial nature, and that there are fundamental differences between the two inventions.

As shown in Example 6, the addition of some acetone in the catholyte greatly improves the TEL yields. According to the teaching of an existing art, the electrochemical reduction of aqueous ketone at the lead cathode produces lead containing products which are not tetraalkyl leads.<sup>6</sup> The fact that we obtained nearly quantitative yields of TEL in the presence of acetone is contrary to this teaching and hence entirely unexpected.

There are various electrochemical processes which produce TEL with very high yield from ethyl bromides. All of these, however, belong to the classification (C) and hence employ some aprotic solvent as a major solvent component. Compared to these processes, our process described here has several very important advantages. First, water can be employed as an anodic solvent without complicating cathodic process loop. This is very important because bromine generated at the anode can be recovered readily by using various known methods.

The second advantage in the present process is that the catholyte is high conducting and hence power consumption is low. In addition both water and alkylating agent solubilizer are so cheap that appreciable decomposition of these compounds at the cathode, which may occur at some high current density, is not a serious problem. This is certainly not so in the system using aprotic solvents.

The concentration of ethyl bromide can be varied widely. In one extreme (Example 9), pure alkyl bromide together with the salts gave a reasonably good yield of TEL; while in the other extreme (Example 6), a small amount of ethyl bromide without any solubilizer is enough to give a decent yield of TEL. This is shown in the following example.

#### EXAMPLE 9

The catholyte composition was: 0.551 mole of C<sub>2</sub>H<sub>5</sub>Br and 0.0236 mole of (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>PBr. Electrolysis was carried out with cation membrane at 50 ma. for 1 hour, at 62 ma. for 1 hour and at 70 ma. for 2 hours.

Percent current efficiency for TEL formation=78%

While the concentration of the alkylating agent can be varied widely as shown above, it is preferable to use water and solubilizer to reduce power cost and to improve alkyl lead yields.

The nature of the solubilizer is also important in the present invention. Acetone and tetrahydrofuran can be employed with a good result as shown in previous examples, but ethyl alcohol is quite unsatisfactory, as shown below.

#### Example 10

The composition of catholyte was:

Compds.	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> Br	(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> PBr	CH <sub>3</sub> OH
Moles.	5.54	0.275	0.0295	4.06

Electrolysis was carried out for 3 hours at 150 ma. Other details are the same as in Example 1.

Moles TEL formed= $7.16 \times 10^{-4}$

Grams Pb reacted=0.3236

Percent current efficiency for TEL formation=17%

Percent current efficiency for Pb reaction=37%

Of prime importance in the present invention is a proper choice of supporting electrolyte. As mentioned earlier NaOH cannot be used. While tetrabutyl phosphonium bromide and tetrabutyl ammonium bromide

<sup>4</sup> See footnote (4), col. 1.

<sup>6</sup> Tafel, J., Ber., 39, 3626 (1906).

5

give an excellent result, tetraethyl ammonium bromide gives unacceptably low yield (Example 11). Existing art teaches that tetraethyl ammonium bromide is a good electrolyte in aprotic solvents; in addition, there is nowhere one can find any experimental result which indicates that other alkyl ammonium salts should be better than tetraethyl ammonium bromide in TEL production. Another salt, namely, LiBr, which, according to a past teaching, is a good electrolyte, gives only a low yield of TEL (Example 12).

#### Example 11

The composition of catholyte was:

Compds.	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> Br	(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NBr	Acetone
Moles.	2.77	0.138	0.477	1.55

Electrolysis was carried out as described in Example 1 at 150 ma. for 2.0 hours. There was appreciable gas formation at the cathode, and TEL yield was very low as indicated below:

Moles TEL formed= $2.80 \times 10^{-3}$

Percent current efficiency for TEL formation=22%

#### Example 12

The composition of catholyte was:

Compd.	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_3 \end{array}$	C <sub>2</sub> H <sub>5</sub> Br	LiBr
Moles.	0.861	0.459	0.0921

Electrolysis was carried out for 1.43 hours at 100 ma. using a cation exchange membrane.

Moles TEL formed= $5.54 \times 10^{-4}$

Percent current efficiency for TEL production=41%

In this experiment, there occurred a severe gas evolution at 150 ma. Even at 100 ma., there was some gas evolution, and undoubtedly this is one of the causes for the low yield. The addition of water in this system greatly reduces TEL yield.

In addition to TEL, the present process can also produce TML, TP(propyl)L, and Methyl-Ethyl Mixed Lead. These are demonstrated in the following examples.

#### Example 13

An H-type cell was divided into cathode and anode compartment by an anion exchange membrane. The catholyte composition was: 4.5 g. of (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr, 41.5 g. of water, 13 g. CH<sub>3</sub>COCH<sub>3</sub>, and 2004 cc. at 760 mm. (room temperature) of CH<sub>3</sub>Br. The anolyte composition was 8.0 g. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in 100 g. water. The cathode was a lead sheet with an effect surface area of about 3 cm.<sup>2</sup>, and the anode was a carbon rod. During electrolysis, the cell was cooled with cold air so that the vapor pressure of CH<sub>3</sub>Br in cathode remained below 5 p.s.i. After electrolyzing for 1 hour at 200 ma., we found 0.487 g. of TML and 0.3930 g. of lead loss. Hence, percent current efficiency for TML production=98%, and percent current efficiency for lead loss=101%.

#### Example 14

The cathode compartment contained 20 g. tetrabutylammonium bromide, 100 g. acetone, and 210 g. water. The anode compartment contained 36 g. ammonium carbonate dissolved in 450 ml. water. The anode was a carbon rod and the cathode was a lead sheet about 8 cm.<sup>2</sup> which was prepared and weighed before and after each reaction. The contents of both half-cells were vigorously stirred with magnetic stirrers.

The cathode was degassed first with argon, then with methyl bromide. The solution was electrolyzed for about 7 hours at 1 amp with slow bubbling of methylbromide through the cathode. Lead loss at the end of this electrolysis was 13.30 g. The organic layer was separated, washed with three 125 ml. portions of water. Yield, 10.60 g. product after separation, drying over sodium sulfate, and filtration. Gas chromatography showed only a trace

6

of methyl bromide, 99+ % TML. No other components were detected. This product was used in the preparation of motor mix for antiknock rating.

#### Example 15

The catholyte composition used in the preparation of TPL (tetrapropyl lead) was: 15.0 g. of C<sub>3</sub>H<sub>7</sub>Br (normal), and 75 cc. of a solution containing 100 g. water, 10 g. (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr, and 40 g. acetone. The anolyte composition was: 10 g. of BrC<sub>2</sub>H<sub>4</sub>Br and 70 g. of a solution containing 210 g. water and 40 g. (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NB. The cathode was a lead bar with an effective area of 5.26 cm.<sup>2</sup>. The electrolysis was carried out at 600 ma. to give a total current of  $7.46 \times 10^{-3} \times (4 \times 96500)$  coulombs. The product was extracted with n-hexane and was analyzed chromatographically.

Results:

Lead loss=1.3689 g.; 89% current efficiency

TPL formed=2.20 g.; 78% current efficiency

Percent lead converted to TPL=88%.

The major side product was (C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>PbPb(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>.

#### Example 16

Mixed lead was prepared under the following conditions:

Cathode: 14 g. C<sub>2</sub>H<sub>5</sub>Br, 0.665 g. CH<sub>3</sub>Br, and 75 cc. of a solution having a composition of 10 g. (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr, 100 g. H<sub>2</sub>O and 35 g. CH<sub>3</sub>COCH<sub>3</sub>.

Anode: 10 g. BrC<sub>2</sub>H<sub>4</sub>Br and 70 g. of a solution having a composition of 40 g. (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBr and 210 g. H<sub>2</sub>O.

Electrolysis: 114 ma./cm.<sup>2</sup> total current of

$$(4 \times 96500) \times 7.46 \times 10^{-3}$$

coulombs.

Results: Lead lost=1.44 g.

Lead recovered as mixed lead alkyls=1.45 g.

Composition of mixed lead alkyls (percent): (CH<sub>3</sub>)<sub>4</sub>Pb=8.85, (CH<sub>3</sub>)<sub>3</sub>Pb(C<sub>2</sub>H<sub>5</sub>)=10.30,

$$(\text{CH}_3)_2\text{Pb}(\text{C}_2\text{H}_5)_2=7.75$$

$$(\text{CH}_3)\text{Pb}(\text{C}_2\text{H}_5)_3=16.18, (\text{C}_2\text{H}_5)_4\text{Pb}=56.92.$$

#### Example 17

Mixed lead was prepared under the following conditions:

Cathode: 14 g. C<sub>2</sub>H<sub>5</sub>Br, 0.798 g. CH<sub>3</sub>Br, other components same as Example 16.

Anode: 20 g. BrC<sub>2</sub>H<sub>4</sub>Br, other components same as Example 15.

Electrolysis: Same as Example 16.

Results: Lead lost=1.44 g.

Lead recovered as mixed lead alkyls=1.44 g.

Composition of mixed lead alkyls (percent): (CH<sub>3</sub>)<sub>4</sub>Pb=16.70, (CH<sub>3</sub>)<sub>3</sub>Pb(CH<sub>2</sub>H<sub>5</sub>)=19.21,

$$(\text{CH}_3)_2\text{Pb}(\text{C}_2\text{H}_5)_2=11.83$$

$$(\text{CH}_3)\text{Pb}(\text{C}_2\text{H}_5)_3=18.72, (\text{C}_2\text{H}_5)_4\text{Pb}=33.54.$$

#### Example 18

The cathode compartment contained 20 g. tetrabutylammonium bromide, 100 g. acetone, and 210 g. water. The anode compartment contained 36 g. ammonium carbonate dissolved in 450 ml. water. The anode was a carbon rod and the cathode was a lead sheet about 8 cm.<sup>2</sup> which was prepared and weighed before and after each reaction.

To the cathode compartment was added 15 g. ethylbromide, and the solution was electrolyzed at about 1 amp for several hours at 5 p.s.i. methylbromide, with a cell temperature of 27° C. The product was shown by gas chromatography to be mostly TML, with only a trace of TEL, and other lead alkyls.

7  
Example 19

The cathode compartment contained 20 g. tetrabutylammonium bromide, 100 g. acetone, and 210 g. water. The anode compartment contained 36 g. ammonium carbonate dissolved in 450 ml. water. The anode was a carbon rod and the cathode was a lead sheet about 8 cm.<sup>2</sup>, which was prepared and weighed before and after each reaction.

To the cathode compartment was added 30 g. ethylbromide. The cathode solution was degassed first with argon, then with methylbromide. The solution was electrolyzed at a pressure of about ¾ p.s.i. methylbromide and about 1 amp for several hours. After electrolysis, the organic layer in the cathode compartment was separated, washed well with water, dried over sodium sulfate, and evacuated on a rotary evaporator at ambient temperature for a few minutes. Gas chromatography indicated the product was 98 percent TEL, about 1 percent methyltriethyl lead (PbMeEt<sub>3</sub>) and only a trace of TML. Lead loss was 9.63 g.

A variety of current-permeable membranes are known to the art and may be employed as cell partitions in this process. Suitable membrane materials are porous porcelain, asbestos, glass fiber paper, cellulosic substances such as porous cellophane and parchment, films of agar gel, and ion exchange resins.

Throughout the description of our invention, we emphasized the fact that in our process alkyl bromide can be employed in a water solvent system with or without an addition of a solubilizer. To be commercially successful, one must recover bromine generated at the anode almost quantitatively; in this connection, our system is ideally suited. When an anion exchange membrane is employed, the leakage of (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>P<sup>+</sup> or (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup> to the anode should be very small, and bromine loss due to the reaction with these ions becomes very low. Even if some leakage did occur, bromine can be recovered readily by reacting the complex between Br<sub>2</sub> and the leaked salt with ethylene. Resulting dibromoethane can be used in the motor mix.

Existing patents teach us that such ions as Li<sup>+</sup>, Na<sup>+</sup>, and (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup> are equally satisfactory current carriers. In our system, none of these ions are satisfactory. The fact that (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup> and (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>P<sup>+</sup> ions are much better current carriers is neither expected nor anticipated in any of the existing arts. In aprotic solvent systems, the use of (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup> gives a good yield of alkyl lead, and this result is at once generalized without any experimental support to mean that all alkyl quaternary salts work as well. In our system, we clearly demonstrated that the ion, (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup>, on which all the above generalization is based is indeed very bad, and that one must employ the tetraalkyl quaternary salt whose alkyl chain has carbon number 4. We thus claim that our choice of salts is not anticipated.

In our invention a proper choice of solubilizer is of prime importance. Acetone and tetrahydrofuran work very well, but alcohol is quite unsatisfactory. As far as we know, existing literature or patents do not contain experimental data indicating that in the electrochemical reductions of alkyl halides in water solvent, acetone and tetrahydrofuran should be better than alcohol. We thus feel that the use of acetones and water soluble ethers as alkyl bromide solubilizers in electrochemical reductions in water solvent is also unexpected. Some other solubilizers which may be used include: some ketones, C<sub>2</sub>H<sub>5</sub>CN and CH<sub>3</sub>CN.

Although the concept of the tetramethyl lead reaction evolved from work on electrochemical production of TEL, an entirely unexpected result of this work is the relative ease, and cleanness with which this reaction occurs, compared to the TEL process. Studies on the antiknock characteristics of the product from this reaction show that pure TML can be isolated directly from the cell with only water washing. In the case of TEL, the

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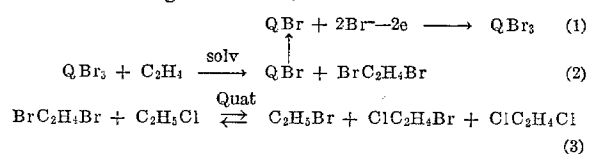
product which is isolated from the cell after washing with water still contains some ethyl bromide as well as some lead containing impurities, probably hexaethyldilead. Ethylbromide can easily be removed by vacuum distillation, but the dilead compound still remains. If the TEL is used in this form as motor mix, antiknock properties, per gram of lead added to gasoline, are significantly lower. This TEL can be easily purified by simple steam distillation. The yellow (dilead compound) disappears and the TEL tests as high as commercial TEL. However, steam distillation is an additional step in the process. Further, on large quantities of TEL, danger of human poisoning or explosion is greater.

Recently TML has been regarded as perhaps more beneficial in actual road octane rating than in the research or motor octane ratings usually performed at refineries. One drawback, of course, is the additional cost of TML over TEL. With the process of this invention, TML can be produced cheaper than TEL. Factors of cost include raw materials, electrical power, purification and product losses therefrom. In each of these factors, the TML process is superior to the TEL process.

In some cases, mixed lead alkyls are superior in antiknock properties to tetraethyl lead (TEL) and to tetramethyl lead (TML). These antiknock compounds have been more expensive, and more laborious to prepare than TEL or TML. We have developed a simple, inexpensive method of producing mixed lead alkyls (MLA). Further, the compositions of these MLA are significantly different from the usual MLA. By varying the temperature of the cell, and the pressure of methylbromide, the composition of our MLA can be varied.

An entirely unexpected advantage of this MLA process over the TEL process is the lack of unwanted side products. The product of this reaction is colorless to pale yellow contrasted with the bright yellow of the TEL product. The reasons are not understood, but there is much less dark sludge in the reaction than with TEL. Results of octane rating studies show that unpurified electrochemical MLA is as effective on a grams lead per gallon basis as its commercial analogues.

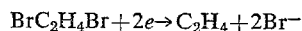
The bromine formed at the anode can be recovered, for example, by the bromine recycle method using QBr (tetrabutylammonium bromide) in the anode and is based on the following three reactions:



The oxidation of bromide ions at the anode yields a water-insoluble tribromide, QBr<sub>3</sub>. The tribromide tends to stick to the carbon anode. It can readily be removed from the cell, however, using a water-immiscible solvent. Either 1,2-dibromoethane or ethylbromide can be used for this purpose. Reaction (2) is essentially complete within about 10 min. at 100° C. and atmospheric pressure of ethylene.

The exchange reaction (3) is catalyzed by a phosphonium quat, (C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>PC<sub>18</sub>H<sub>37</sub><sup>+</sup>Br<sup>-</sup>. The exchange rate increases linearly with increasing quat concentration; it can also be increased sharply by increasing temperature. Preferably, reaction (3) is carried out at the outside of the anode loop. It is then sufficient to consider only reactions (1) and (2) in closing the anode loop.

When dibromoethane is used as a solvent in reaction (2), its leakage to the cathode must be minimized. Otherwise, current is wasted due to the reduction:



Ethylbromide does not suffer this fault. In addition, the solubility of tribromide in ethylbromide (exceeds 10 weight percent at room temperature) is much higher than that in dibromoethane (exceeds 5 weight percent at 40°

C.) These considerations might suggest the use of ethylbromide; but, then, reaction (2) must be carried out in a pressure vessel since the vapor pressure of ethylbromide at 100° C. is about 5.7 atmospheres. In addition, the whole solvent must be stripped off to recover the product, dibromoethane. When dibromoethane is used as solvent, reaction (2) can be carried out at atmospheric pressure, and the product recovery is greatly simplified. These pros and cons should be weighed carefully in selecting the solvent.

Having thus described the invention by providing specific examples thereof, it is to be understood that no undue limitations or restrictions are to be drawn by reason thereof and that many variations and modifications are within the scope of the invention.

What is claimed is:

1. In an electrolytic process for producing tetraalkyl lead compounds at a lead cathode in an electrolytic cell having a lead cathode, an anode of a material which is resistant to attack by bromine, and a current-permeable partition separating the catholyte from the anolyte which process comprises:

(A) passing an electrolyzing direct current through a liquid catholyte comprising (a) an alkyl bromide or a mixture of two alkyl bromides, in which the alkyl group has 1 to 3 carbon atoms, (b) a current carrier selected from the group consisting of tetraalkyl ammonium bromide and tetraalkyl phosphonium bromide, (c) water, and

(B) recovering tetraalkyl lead from the catholyte, the improvement which comprises carrying out said process wherein the alkyl group in the tetraalkyl ammonium bromide or tetraalkyl phosphonium bromide current carrier is tetrabutyl and wherein the molar ratio of water to said current carrier is from about 30:1 to about 1000:1.

2. A process as described in claim 1 in which a non-hydroxylic, alkyl bromide solubilizer is present in the catholyte.

3. A process as described in claim 2 wherein said non-hydroxylic solubilizer is acetone, THF, acetonitrile or propionitrile.

4. A process as described in claim 2 in which the con-

centration of solubilizer in the catholyte ranges from zero up to 80 weight percent.

5. A process described in claim 2 in which an excess amount of an alkyl bromide or alkyl bromides is added to make the initial catholyte a heterogeneous, two-phase system.

6. A process described in claim 5 in which the concentration of alkyl bromide or alkyl bromides in the water-rich phase exceeds 0.5 percent.

7. A process described in claim 2 in which the anolyte solvent is water, and the anolyte current carrier is  $\text{NH}_4\text{Br}$ , metal halides,  $(\text{C}_4\text{H}_9)_4\text{NBr}$  or  $(\text{C}_4\text{H}_9)_4\text{PBr}$ .

8. A process described in claim 2 in which the anolyte solvent is water, and the anolyte current carrier is  $(\text{C}_4\text{H}_9)_4\text{NBr}$  or  $(\text{C}_4\text{H}_9)_4\text{PBr}$ , and ethylbromide or  $\text{BrC}_2\text{H}_4\text{Br}$  is added to remove bromine-current carrier complex from the anode compartment.

9. A process described in claim 2 in which alkyl bromide is methylbromide and the product is TML.

10. A process described in claim 9 in which methylbromide is introduced in the catholyte continuously as a liquid or as a gas.

11. A process as described in claim 2 wherein alkyl bromide is ethylbromide and the product is TEL.

12. A process as described in claim 2 wherein alkyl bromide is propyl bromide and the product is TPL.

13. A process as described in claim 2 wherein the alkyl bromide is a mixture of methylbromide and ethyl bromide and the product is methyl-ethyl mixed lead.

14. A process described in claim 13 in which the mole ratio of  $\text{CH}_3\text{Br}$  to  $\text{C}_2\text{H}_5\text{Br}$ , when present together, does not exceed 1.

#### References Cited

##### UNITED STATES PATENTS

3,197,392	7/1965	Silversmith et al. --	204—590 M
3,392,093	7/1968	Smeltz -----	204—72
3,432,409	3/1969	Schuler et al. -----	204—72

##### OTHER REFERENCES

Fourilov et al., zh. Obshch. Khim. 35 (2) 391—3 (1965), C.A. 63 5238f, August 1965.

F. C. EDMUNDSON, Primary Examiner