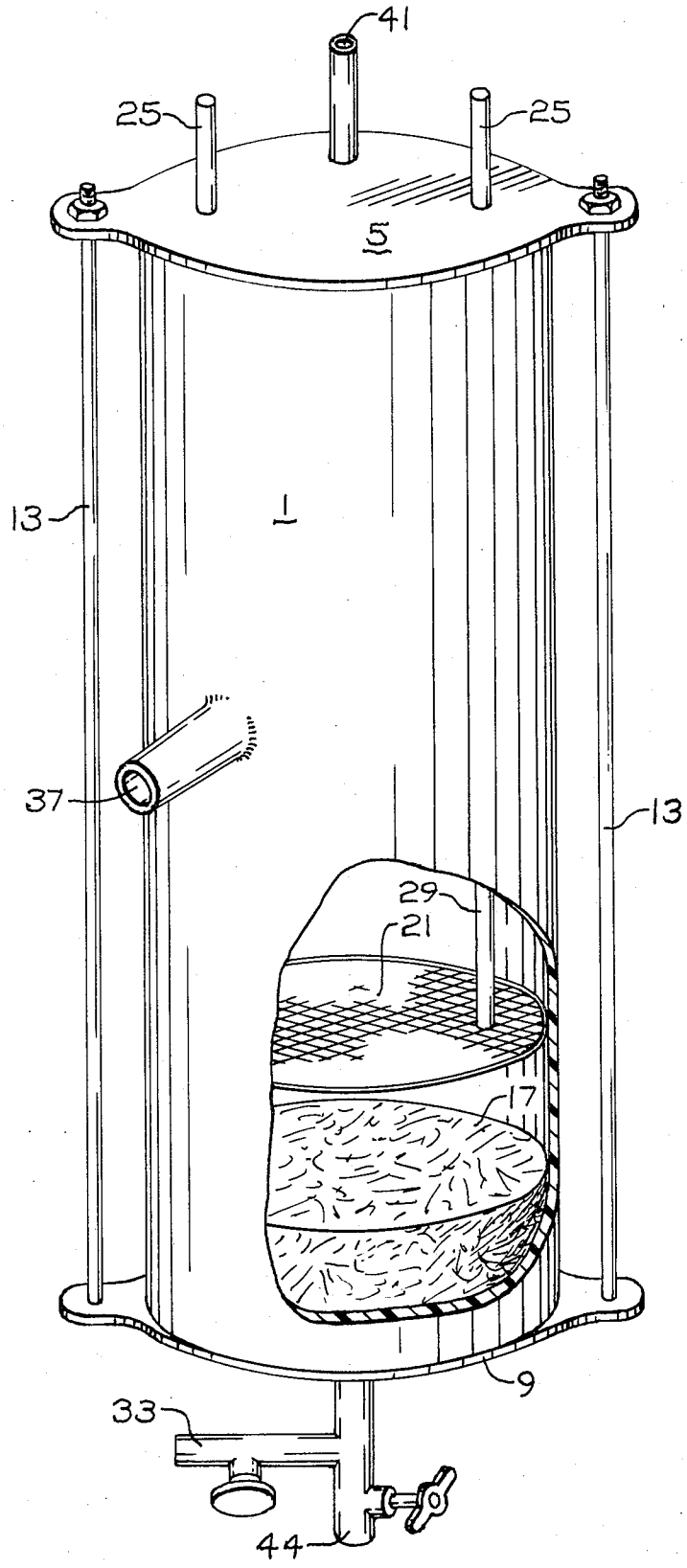
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METHOD FOR REDUCING THE ORGANO LEAD COMPOUND CONTENT OF AQUEOUS SOLUTIONS BY ELECTROLYSIS IN AN ELECTROLYTE PERMEABLE METALLIC CATHODE ELECTROLYTIC CELL

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METHOD FOR REDUCING THE ORGANO LEAD COMPOUND CONTENT OF AQUEOUS SOLUTIONS BY ELECTROLYSIS IN AN ELECTROLYTE PERMEABLE METALLIC CATHODE ELECTROLYTIC CELL

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ABSTRACT OF THE DISCLOSURE

A method and apparatus for reducing the lead content of dilute aqueous solutions is disclosed. The lead is present as organo-lead compounds from the manufacture of automotive anti-knock compounds most frequently as triethyl lead chloride. The organo-lead compound-containing solution is passed through an electrolytic cell having an electrolyte permeable cathode fabricated from a metal having hydrogen over voltage in excess of 1.6 volts. The lead is deposited on the cathode.

BACKGROUND OF THE INVENTION

In the production of alkyl lead compounds, especially tetraethyl lead anti-knock compound, a sodium lead alloy and ethyl chloride are reacted in an autoclave. The resulting product is a complex mixture of solids, liquids, gases, and vapors, containing inter alia, sodium chloride, ethane, ethane chloride, various chlorinated hydrocarbons, various alkyl leads, alkyl lead complexes, and the like. This mixture is fed to a steam still. In the steam still, considerable quantities of water and steam are added to the mixture, and the gases are separated from the liquids and solids. While the solid fraction yields tetraethyl lead and other automotive anti-knock compounds, the liquid and gaseous fractions are rich in lead compounds, e.g., triethyl lead chloride.

Furthermore, in the various stages of the tetraethyl lead production process, the reactants, intermediates, and products, are frequently contacted with large quantities of water. This water, containing small amounts of organo-lead compounds as well as the by-products from the steam still presents a serious lead disposal and control problem. In the past, it has been the practice to store these lead and organo-lead containing streams in a clarifier tank or settling lagoon, and allow the lead to settle out. Typically, the water in the clarifier tank and in the settling lagoon contains about 1 to about 20 parts per million of lead.

Attempts to electrolytically remove the organo-lead compounds from the various aqueous streams in the tetraethyl lead production process have generally resulted in the dimerization and trimerization of the organo-lead compounds. For this reason, most attempts at removing these trace quantities of water soluble organo-lead compounds, have involved the use of complexing agents and sequestrants.

SUMMARY OF THE INVENTION

It has now surprisingly been found that when aqueous solutions of water soluble organo-lead compounds are electrolyzed at a metal cathode having a hydrogen over voltage in excess of 1.6 volts, dimerization and trimerization do not occur. Instead, the lead is reduced to metallic lead. It has further been found that when the cathode is porous and electrolyte permeable and the organo-lead solution is passed through the cathode during electrolysis, the metallic lead liberated at the cathode is deposited on the cathode.

According to this invention, an aqueous solution of organo-lead compounds, containing from about 1 to about 200 parts per million generally from 1 to about 100 parts per million, and most frequently from about 5 to about 20 parts per million of lead as organo-lead compounds is fed to an electrolytic cell. The electrolytic cell has an anode and a porous, electrolyte permeable cathode containing a material having a hydrogen over voltage in excess of 1.6 volts. The aqueous solution passes through this porous, electrolyte permeable cathode, and the lead is electrolytically reduced to metallic lead and deposited on the cathode. The solution is recovered from the cell, considerably reduced in lead content, for example, containing from about 0.01 to about 1.0 part per million of lead while the metallic lead itself is recovered from the cathode.

In one exemplification of this invention, the anode is located upstream of the electrolyte permeable cathode. In this configuration, hypochlorite ion is formed at the anode, and passes through the cathode. The presence of hypochlorite ion results in a slightly better rate of lead removal than is encountered in the absence of hypochlorite ion in the electrolyte feed to the cathode.

DETAILED DESCRIPTION OF THE INVENTION

In the method of this invention, an aqueous solution containing from about 1 part per million to about 200 parts per million generally from about 1 to about 100 parts per million, and most frequently from about 5 to about 20 parts per million of water-soluble organo-lead compounds is fed to an electrolytic cell. The electrolytic cell has an anode and an electrolyte permeable, porous cathode. The cathode has as its active surface metal having a hydrogen over voltage in excess of 1.6 volts. The solution is caused to pass through the electrolyte permeable porous cathode. Within the electrolyte permeable cathode, metallic lead is deposited on the cathode.

The solution fed to the cell for lead removal is an aqueous solution of water-soluble organo lead compounds. Such a solution is normally formed during the various reaction steps and separation steps in the production of the automative anti-knock compounds. The water-soluble organo lead compounds are formed by the reaction of a sodium lead alloy with ethyl chloride in an autoclave, the subsequent separation steps involving the use of large quantities of water anl the treatment and handling of the solids, sludges and the gases formed at various stages of the automotive anti-knock compound manufacturing process.

The organo lead compounds normally present in such waste water streams will typically be of the form

$$PbR_nCl_{4-n}$$

where n is the stoichiometry of the compound and may vary between 0 and 4, and R is the organic constituent of the organo-lead compound. R may be an alkyl having from 1 to 5 or 8 or more carbon atoms, for example, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl radicals. Alternatively, R may be an aryl radical such as a benzyl, tolyol, or the like radical. Most frequently, R will be a methyl, ethyl, or propyl group. Most commonly, the water-soluble organo lead compounds present in the waste water stream will be a mixture of triethyllead chloride, diethyllead dichloride, trimethyllead chloride, and dimethyllead dichloride. In a process where the feed stream is ethyl chloride, the most common organo-lead compounds in the waste water stream will be diethyllead dichloride and triethyllead chloride. Additionally, small amounts of dimers and trimers may be present.

The use of large quantities of water in the automative anti-knock comvound manufacturing process forms large amounts of aqueous solutions of water soluble organo lead compounds. Most of the streams of these aqueous

solutions of organo lead compounds are ultimately collected at a single point, e.g., a clarifier pond or settling lagoon. This collected aqueous solution of organo lead compounds, or any of the constituent feeds thereto, may be reduced of its lead content by the method of this invention.

Aqueous solutions of water soluble organo lead compounds which may be purified according to the method of this invention contain from about 1 part per million to about 100 parts per million and most frequently from about 1 to about 20 parts per million of lead calculated as total lead. Higher concentrations of water soluble organo lead compounds may be encountered and are included within the scope of this invention, for example, as high as 500 parts per million or even 1000 parts per million. However, because of the nature of the separation processes utilized in the production of anti-knock compounds, especially chemical processes such as pH control, and the use of precipitants, such high concentrations will not normally be encountered in the waste-water streams from automotive anti-knock compound production units. Additionally, while less concentrated solutions, for example, as low as 0.1 part per million or even as low as 0.01 part per million of lead calculated as metallic lead may be encountered such streams are not usually present as waste water streams from automotive anti-knock compound production units because of the expense of reducing lead content to such low levels by conventional chemical means. However, such concentrations may be encountered when the feed to the electrolytic cell is the effluent from a prior cell in a series of electrolytic cells in cascade relationship.

According to this process, a feed stream containing from about 1 part per million to about 20 parts per million of lead calculated as metallic lead is reduced in lead content to an effluent stream having from about 0.001 part per million to about 1.0 part per million of lead calculated as metallic lead.

The solution is caused to pass through an electrolyte permeable porous cathode. The cathode contains an electrolytically active surface of a metal having a hydrogen over voltage of 1.6 volts or greater. The metal may be present as the surface of the cathode, or it may be the entire cathode. Suitable cathode materials include lead, lead-mercury amalgam, nickel, aluminum, zinc, bismuth, copper, tin, and cadmium.

The cathode itself may be in the shape of a single porous mass. Alternatively, it may be in the form of small members with void volumes therebetween such as spheres, saddles, rings, helixes, and other shapes frequently used in liquid-liquid mass transfer operations. Or, the cathode may be powders or sludge of the cathode metal.

Most frequently, as the material being recovered is lead, the cathode will be in the form of a lead packing such as lead shot, lead sludge, lead powders, lead scrap, or lead shavings. Lead shot is preferred over other forms of lead because of its easier handling ability, and more reproducible packing characteristics. However, other forms of lead may be used interchangeably therewith. Where a lead shot cathode is used, the cathode bed will have a porosity of from about 0.35 to about 0.40, depending on the uniformity of the lead shot, and most frequently about 0.38. Preferably, the lead shot will be in the range of 0.09 inch to 0.25 inch diameter. Lead shot larger than about 0.25 inch diameter will cause the size of the individual void volumes to be increased and electrolytically less efficient lead removal will result although the feed rate may be increased thereby. Alternatively, lead shot smaller than about 0.09 inch in diameter will cause the void volumes to be too small and the packing to be too tight so that high hydrostatic pressures will be necessary to maintain an economical feed rate. However, more electrolytically efficient lead removal may occur thereby.

According to this invention, the aqueous solution of water-soluble organo lead salts is fed to the cell and caused to pass through the electrolyte permeable metal cathode. An electromotive force is then imposed across the cell causing an electrical current to pass from an anode of the cell through the cathode, decomposing the organo lead compounds and plating the lead onto the cathode.

The feed solution is recovered from the cell as a product significantly reduced in lead content, e.g., from a feed content of about 13 parts per million of lead to a product containing less than about 1 part per million of lead, e.g., about 0.5 part per million of lead.

The residence time of the solution in the cathode may be from about 1 to about 100 minutes and is generally from about 7 minutes to about 14 minutes. Residence times in the cathode significantly greater than about 14 minutes may be used resulting in a product stream containing from about 0.1 to about 0.3 part per million of lead for a feed containing about 9 to about 13 parts per million of lead. Residence times of less than about 7 minutes may be utilized although with a reduction in the amount of lead removed. The residence time, as used herein, is the void volume of the cathode and liquor between the cathode and anode divided by the volumetric flow rate of the solution to the cathode and is in units of time.

The current density is from about 75 amperes per square foot of cathode surface to about 185 amperes per square foot of cathode surface. Cathode surface as used in defining current density is the planar area of the cathode in a direction normal to the electrolyte flow. The cell voltage is from about 3.7 volts to about 6 volts. Lower voltages as discussed hereinbefore result in the dimerization and trimerization of the organo-lead salts. Higher voltages, for example, in excess of about 6.5 volts or more do not result in any significant increase in lead removal.

Generally, the pH of the feed to the cell should be above about 7, and from about 7 to about 10 to maintain the cell voltage in the desired range. Preferably, the pH of the feed should be between 8 and 9, with particularly satisfactory results being obtained in the range of 8.3 to 8.5.

The anode may be upstream from the cathode, downstream from the cathode, or there may be two anodes, one upstream from the cathode and one downstream from the cathode. In the anode upstream geometry, the solution passes from the anode to the cathode. In this geometry, where the feed is a chloride salt of an organic lead compound, small amounts of chlorine most likely as OCl^- ion, are present in the feed stream to the cathode. Only small amounts of this ion are present, for example, only about 0.1 to about 6.0 grams per liter, and preferably from about 2 to about 4 grams per liter. This small amount of hypochlorite ion present in the solution results in increased removal of lead at a constant residence time or in a constant removal of lead at a reduced residence time. Alternatively, the geometry of the electrodes may be such that the solution passes from the cathode to the anode. In the anode downstream geometry, smaller amounts of hypochlorite ion are present in the cathode.

The lead removed from the solution and recovered on the cathode may be removed from the cathode by various methods well known in the art. For example, the lead may be solubilized by various acids such as hydrochloric acid. Thereafter, the lead may be recycled to form the lead sodium alloy utilized in the original production of tetraalkyl lead automotive anti-knock compounds. In a preferred exemplification of this invention, when a lead cathode is used, the lead cathode and the electroplated lead thereon may be recycled to the automotive lead anti-knock compound production process, or another lead consuming process.

An electrolytic cell particularly useful in carrying out the method of this invention is shown in the figure. The electrolytic cell has a cylindrical cell body **1** with a cell top **5** and a cell bottom **9**. The cell top **5** and cell bottom **9** are held in compression against the cell body **1** by connecting rods **13**. The connecting rods may be fabricated of an electrically insulating material, or they may be metal rods having an electrically insulating portion therein between the cell top **5** and the cell bottom **9**. Alternatively, when the cell top is fabricated of an electrically insulating material, such as polytrifluoroethylene, polyvinylchloride, or polyvinylidene chloride, the connecting rods **13** may be fabricated of a metal. The cathode packing **17** rests on the cell bottom **9**. The cell bottom **9** also serves as a cathode connector and is fabricated of an electrolyte-resistant electroconductive metal, for example, iron, steel, or stainless steel. In the exemplification of this invention wherein the anode is downstream of the cathode, the anode **21** may be a mesh anode connected to the anode current connectors **25** by anode connector rods **29**. The cell has a feed inlet **33** and an effluent discharge **37**. Additionally, because of the generation of gases within the cell, the cell has a cell gas vent and air purge **41**. The feed inlet may also contain a drain **44**. A particularly satisfactory lead cathode electrolytic cell, useful in the practice of this invention, is provided by a cylindrical tank 12 feet in diameter and 10 feet high. This cell has a lead shot particulate cathode consisting of approximately 48 inches of lead shot. This cell is useful at flow rates up to about 200 to 500 gallons per minute reducing the concentration of lead therein from approximately 15 parts per million to less than 1 part per million.

For smaller amounts of feed, a particularly satisfactory electrolytic cell is as shown in the figure.

The following examples are illustrative.

EXAMPLE I

An aqueous feed containing approximately 8 to 12 parts per million of lead as triethyllead chloride, and 3 weight percent sodium chloride was fed to an electrolytic cell having a lead shot cathode, and an effluent was recovered therefrom containing approximately 1 part per million of lead.

The electrolytic cell was constructed as shown in the figure. The electrolytic cell body was a 2 inch inside diameter Plexiglas tube 6 inches long.

The cathode consisted of a 3-inch deep bed of No. 8 lead shot. At a feed rate to the cell of 8 grams per minute, a residence time of 24 minutes, and a current density of 125 amperes per square foot, the effluent contained 1.0 part per million of lead.

EXAMPLE II

Example I was repeated with a one-half inch deep No. 8 lead shot cathode, at a residence time of 19 minutes and a current density of 115 amperes per square minute. The effluent contained approximately 1.0 part per million of lead.

EXAMPLE III

Example II was repeated at a residence time of 28 minutes and a current density of 126 amperes per square foot. The effluent contained 0.4 parts per million of lead.

EXAMPLE IV

An aqueous feed, having a pH of 8.3 to 9 and containing approximately 8 to 12 parts per million of lead as triethyllead chloride was fed to a particulate cathode electrolytic cell of the type described in Example I except that the cathode consisted of copper-coated steel shot to a depth of 2¼ inches. Two runs were conducted at a current density of 69 amperes per square foot. The first run was at a residence time of 36 minutes. The effluent contained 1.0 part per million of lead. The second run was at a residence time of 15 minutes. The effluent contained 2.0 parts per million of lead.

EXAMPLE V

Example IV was repeated with a residence time of 46 minutes and a current density of 46 amperes per square foot. The filtered effluent contained 1.0 part per million of lead.

EXAMPLE VI

Exampe IV was repeated with two runs at residence time of 15 minutes. The first run was at an anode current density of 69 amperes per square foot and the filtered effluent contained 2.0 parts per million of lead. The second run was at a current density of 184 amperes per square foot and the filtered effluent contained 1.0 parts per million of lead.

EXAMPLE VII

An aqueous feed having a pH of 8.5 and containing approximately 6 parts per million of lead, as triethyllead chloride was fed to a particulate lead cathode electrolytic cell.

The electrolytic cell had a 5½ inch outside diameter by 10 inch high cell body. A feed line entered the cell through the bottom beneath the cathode packing. The cathode packing was a ⅝ inch deep bed of ¼ inch by ¼ inch lead slugs. The anode was an Englehart "Type N" platinized titanium expanded wire mesh anode positioned ¾ of an inch above the top of the cathode packing.

Run A

The feed rate to the cell was 25 milliliters per minute, providing a residence time of 62 minutes. At a current density of 150 amperes per square foot, the filtered cell product was 1.4 parts per million of lead.

Run B

The feed rate to the cell was 50 milliliters per minute providing a residence time of 31 minutes. At a current density of 150 amperes per minute, the filtered cell effluent contained 2.8 parts per million of lead.

Run C

The feed rate to the cell was 50 milliliters per minute providing a residence time of 31 minutes. At a current density of 75 amperes per square minute, the filtered cell product contained 3.5 parts per million of lead.

Run D

The feed rate to the cell was 50 milliliters per minute providing a residence time of 31 minutes. Electrolysis was conducted at a current density of 37.5 amperes per square minute and the filtered cell product contained 2.6 parts per million of lead.

Run E

The feed was fed to the cell at a rate of 50 milliliters per minute providing a residence time of 31 minutes. Electrolysis was conducted at 150 amperes per square foot and the filtered cell product contained 7.0 parts per million of lead.

EXAMPLE VIII

Example VII was repeated except that the particulate cathode was a ⅝ inch deep layer of 0.09 inch diameter lead shot.

Run A

Electrolysis was conducted with a current density of 150 amperes per minute and a feed rate of 50 milliliters per minute providing a residence time of 7.8 minutes. The filtered cell product contained approximately 0.5 part per million of lead.

Run B

Electrolysis was conducted at a current density of 150 amperes per square foot, and a feed rate of 25 milliliters per minute providing a residence time of 15.6 minutes. The filtered cell product contained approximately 0.15 part per million of lead.

Run C

Electrolysis was conducted at a current density of 75 amperes per square foot, and a feed rate of 50 milliliters per minute providing a residence time of 7.8 minutes. The filtered cell product contained 0.51 to 0.6 part per million of lead.

Run D

Electrolysis was conducted at a current density of 75 amperes per square foot, a feed rate of 25 milliliters per minute which gave the residence time of 15.6 minutes. The filtered cell effluent contained between 0.25 and 0.28 part per million of lead.

It is to be understod that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

I claim:

1. A method for reducing the lead concentration of aqueous solutions of triethyl lead chloride comprising:

feeding an aqueous solution having a pH of from 7 to 10 and containing from about 1 part per million to about 100 parts per million of triethyl lead chloride to an electrolytic cell having an anode and an electrolyte permeable lead cathode;

causing said solution to pass through said cathode with a residence time of from 1 to 100 minutes;

causing an electrical current to pass from said anode to said cathode at a current density of from about 75 to about 185 amperes per square foot of planar cathode area normal to the flow of electrolyte; and

recovering from said cell an effluent solution containing from about 0.1 to about 1.0 part per million of lead.

2. A method of reducing the lead concentration of aqueous solutions of organo-lead compounds comprising:

feeding an aqueous solution having a pH of from about 7 to about 10 and containing from about 1 to about 100 parts per million, elemental basis, of lead, said lead being present as an organo lead compound chosen from the group consisting of triethyl lead chloride, diethyl lead chloride, trimethyl lead chloride, and dimethyl lead chloride, and mixtures thereof, to an electrolytic cell having an anode, and a cathode comprising a metal having a hydrogen overvoltage in excess of 1.6 volts chosen from the group consisting of lead, lead-mercury amalgam, nickel, aluminum, zinc, bismuth, tin, copper, and cadmium;

causing said solution to pass through said cathode;

causing an electrical current to pass from said anode to said cathode at a current density of from about 75 to about 185 amperes per square foot of planar cathode area normal to the flow of electrolyte; and

recovering an effluent solution containing less than 1.0 part per million of lead, elemental basis.

3. The method of claim 2 wherein the cathode comprises lead.

4. The method of claim 2 wherein the metal is in the form of particles chosen from the group consisting of spheres, rings, saddles, slugs, shot, and sludge.

5. The method of claim 2 wherein the solution has a residence time within the cathode of from 1 to 100 minutes.

6. The method of claim 2 wherein the effluent solution contains from 0.01 to 1 part per million of lead.

7. The method of claim 2 wherein the solution in the cell contains from about 0.1 to about 6.0 grams per liter of hypochlorite ion.

8. The method of claim 2 wherein the cathode is lead, and the lead cathode and electroplated lead thereon are removed from the cell and recycled to a lead consuming process.

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