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# ELECTROLYTIC PROCESS

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The present invention is concerned with an electrolytic process, particularly one for the production of organolead compounds employing organoboron complexes as the electrolyte.

There are many procedures disclosed in the art for the production of organolead compounds, particularly the commercial product, tetraethyllead. These procedures have all suffered particular disadvantages, among which are the cost and the yield of the organolead product produced. For example, the commercial process used today involves the reaction of ethyl chloride with a sodium lead alloy. While this process is very efficient, it still suffers certain inherent disadvantages which desirably are to be overcome. In particular, the maximum conversion of lead possible is one-fourth of the lead employed as reactant with the other three-fourths necessarily being recovered and re-processed.

There have been attempts to provide organolead compounds by electrolytic procedures. For example, Hein et al., Z. Anorg Allgem. Chemie, 141, 161–227 (1924) describes an electrolysis wherein a current is passed through a lead anode into an electrolyte comprising ethyl sodium dissolved in diethylzinc. This procedure operates rather efficiently, but has never been used on a commercial scale for various reasons. For example, inherent in the procedure is the necessity of the difficult preparation of the diethylzinc and ethyl sodium. Further, a disadvantage of the process is that the electrolyte is a highly reactive mixture which is difficult to handle, requiring considerable precaution. Additionally, the conductivity of this system still leaves much to be desired.

More recently, an electrolytic procedure has been discovered for producing organolead compounds wherein the electrolyte comprises an organoaluminum compound complexed with certain metal salts, especially sodium fluoride. This procedure has certain advantages in its use of the more easily prepared organoaluminum compound and the cheaper metal halide. However, it, like the Hein process, still suffers the disadvantages of a highly reactive electrolyte requiring safety measures which desirably are to be overcome.

Both of the above electrolytic procedures also have a further important disadvantage in that the metal of the solvating organometallic compound, i.e. aluminum or zinc, are plated out during the electrolysis upon the cathode in various forms. It is therefore necessary, for economical operation, to recover this metal and reuse it, usually in regenerating the organoaluminum or zinc compound. This operation is conducted with difficulty.

There are also some disclosures in the literature to electrolytic procedures involving certain other organometallic compounds and certain other metal anodes to produce an organometallic compound corresponding to the metal anodes. For example, the Grignard reagent, ethyl magnesium bromide, has been electrolyzed using a zinc anode to form, presumably, diethylzinc. Similar electrolytic procedures are described in an article by Jones et al., Chem. Reviews, 54, 844–845. All of these prior procedures have been primarily of academic interest because of the above and other disadvantages.

Accordingly, it is desirable to provide an improved method for the preparation of organometallic compounds,



particularly organolead compounds, which overcomes the above and other disadvantages of the prior art.

Therefore, an object of this invention is to provide a new and novel electrolytic procedure for the production of organometallic compounds, particularly the organolead compounds. Another object is to provide a more efficient and economical process for the production of organolead compounds. A still further object is to provide an electrolytic procedure for the production of organolead compounds whereby an anionic metal component of the electrolyte is not plated out at the cathode. An additional object of the invention is to provide a more efficient and novel electrolytic procedure wherein the electrolyte is readily regenerated, thereby conserving the electrolyte and re-using its components in a simplified manner. A still further object is to provide a method for electrolytically producing tetraethyllead more efficiently and economically than possible heretofore in a less hazardous manner. These and other objects of the invention will be more completely understood from the discussion which follows.

The above and other objects of this invention are accomplished by electrolyzing an organoboron complex using a lead anode. Thus, an electric current is passed through the lead anode which is immersed in the electrolyte, then through the electrolyte to a cathode. The organoboron complex is, in general, a compound which contains anionic boron having 4 chemical groups attached thereto, at least one of which groups is attached to boron via a carbon atom of an organic radical, and sufficient associated cations to compensate the anionic charges of the boron anion. The organoboron complexes in which the anionic portion comprises a boron bonded only to organic radicals, preferably hydrocarbon, through carbon and at least one of such radicals is a lower alkyl radical having up to about 8 carbon atoms, especially the ethyl radical, and wherein the cation portion of the complex comprises an alkali metal, especially sodium, are particularly preferred. The electrolysis can be performed at various temperatures up to the decomposition temperature of the electrolyte and products. Under certain conditions of performing the electrolysis, the electrolyte employed would ordinarily be a solid. In these and other instances, it is advantageous to employ a solvent for the electrolyte. For this purpose, the lower alkyl ethers of ethylene glycol and diethylene glycol, particularly the dimethyl ether of diethylene glycol, and tetrahydrofuran are preferred. In other instances wherein the electrolyte would ordinarily be solid under the conditions of electrolysis, water or aqueous solvents are employable to particular advantage. While the electrolyte employed in the present process has an excellent conductivity, it is sometimes desirable to improve its conductivity by adding certain ionizable salts. The preferred ionizable salts that are added are the halides of sodium or potassium. Accordingly, one embodiment of the present invention comprises passing an electric current through a lead anode and an organoboron complex to a cathode wherein the organoboron complex comprises an anionic boron atom having 4 lower alkyl groups bonded thereto, at least one of which is an ethyl group, and sodium as the cationic constituent with the electrolyte being dissolved in a lower alkyl ether of diethylene glycol, particularly the dimethyl ether of diethylene glycol. In other embodiments of the invention, the electrolysis is integrated with a regeneration of the electrolyte either in situ or by removing the consumed electrolyte from the electrolytic cell, and then treating it as is more fully described hereinafter. The other various embodiments of the invention will be evident as the discussion proceeds.

The process of this invention has many advantages

over the prior art processes. For example, organolead product is produced in high yield and purity using a minimum of current. A particular advantage of the process is that the electrolyte is not readily flammable nor is it reactive to moisture as are the prior art electrolytes. Indeed, if desired, water can even be employed as a solvent to form an even more conductive system. Another outstanding advantage of the process is that boron metal is not plated out upon the cathode as does aluminum and zinc when electrolytes containing the alkyl zinc or alkyl aluminum compounds are employed. Therefore, the present process overcomes the need for a difficult separation of any boron on the cathode and the attendant problems of attempting to reclaim and reuse this boron in forming the electrolyte or for other uses. Another advantage of the present process is that more simplified and economical methods for regenerating the electrolyte are available, some of which are described in detail hereinafter. A still further advantage of the present process is that greater efficiencies at higher conductivities for producing organolead compounds are now possible. Other advantages will be evident as the discussion proceeds.

The present invention is based primarily upon unique electrolytes which can generally be termed "organoboron complexes" as distinguished from the simple organoboron compounds, such as the trialkylboranes. The organoboron complexes are those which conduct an electric current. Therefore, the organoboron complexes are compounds which contain anionic boron having 4 chemical groups attached to the boron, at least one of which is an organic group, preferably hydrocarbon, attached to the boron atom via a carbon atom, and such associated cations to compensate the anionic charges of the boron anion. To further describe the anionic boron portion of the complex it will contain groups attached to boron wherein at least one of such groups is an organic radical, preferably hydrocarbon, having up to about 30 carbon atoms for practical purposes attached via a carbon atom; and the other groups can be the same or different from the aforementioned organic radical, or the other groups can be halogen; hydrogen; alcohol residues (—OR) wherein the hydrocarbon portions contain up to about 18 carbon atoms; pseudohalides, e.g., cyanide, cyanate, thiocyanate, amide, mercaptide, azide, and the like; organic acid anions wherein the hydrocarbon portions have up to about 18 carbon atoms, or inorganic acid anions, e.g. sulfate, nitrate, borate, phosphate, arsonate, and the like. The cationic portion of the organoboron complex is generally an alkali or alkaline earth metal, the substituted ($R_4N^+$) or unsubstituted ($NH_4^+$) ammonium cationic moieties, the substituted phosphonium ($R_4P^+$) and substituted arsonium cations ($R_4As^+$)—the "R" groups being organic radicals as described above—or the pyridinium cation. The organic boron complexes can be depicted by the following empirical formula:

$$M(BR^1R^2R^3R^4)_y$$

wherein the R groups are the groups described hereinabove in relation to the anionic boron portion of the complex, M corresponds to the cationic portion of the complex described hereinbefore, and $y$ is equal to 1 or 2. Such complexes are generally prepared by reacting a $BR^1R^2R^3$ compound with an $M(R^4)_x$ compound wherein the R groups are those described above in relation to the anionic boron groupings, M is the cationic material described above, and $x$ is equal to the valence of M.

Accordingly, typical examples of the organoboron complexes constituting the basic electrolyte employed in the present process include: sodium tetramethylboron, sodium tetraethylboron, sodium tetraisopropylboron, sodium tetraoctylboron, sodium tetraoctadecylboron, sodium tetraeicosylboron, sodium tetravinylboron, sodium tetra-2-butenylboron, sodium 1-hexynyltriethylboron, sodium tetraethynylboron, sodium tetracyclohexylboron, sodium tetraphenylboron, sodium tetrabenzylboron, sodium tetranaphthylboron, sodium tetracyclohexenylboron, sodium tetrabutadienylboron; sodium ethyltributylboron, sodium ethyltrioctylboron, sodium ethyltrioctadecylboron, sodium ethyltricyclohexylboron, sodium ethyltriphenylboron, sodium ethyltri(2-phenylethyl)boron, sodium ethyltriisopropylboron, sodium diethyldiisopropylboron, sodium diethyldiphenylboron, sodium diethyldioctadecylboron, sodium octyltrioctadecylboron; sodium ethylborontrichloride, trifluoride, tribromide, or triiodide; sodium triethylboron hydride, sodium trioctylboron hydride; sodium ethyltrimethoxyboron, sodium triethylethoxyboron, sodium trioctylboron octanoate, sodium triethylboron cyanide, sodium triphenylboron cyanide, sodium triethylboron cyanate and thiocyanate; sodium triethylboron amide, sodium triethylboron hydroxide, sodium triethylboron mercaptide, sodium triethylboron azide, sodium triethylboron acetate, sodium triethylboron octanoate, sodium triethylboron phenolate; sodium triethylboron sulfate, nitrate, nitrite, sulfite, phosphate, phosphite, arsonate, or chlorate; and the like complex organoboron compounds wherein the cationic groups described hereinbefore are substituted for sodium including, for example, potassium tetraethylboron, lithium tetraethylboron, calcium bis-tetraethylboron, magnesium bis-tetraethylboron, strontium bis-tetraethylboron, tetraethyl ammonium tetraethylboron, ammonium tetraethylboron, pyridinium tetraethylboron, tetraethyl phosphonium tetraethylboron, tetratethyl arsonium tetraethylboron, potassium ethyltriphenylboron, potassium triethylboron cyanide, potassium triethylboron chloride, potassium triethylboron cyanate, potassium triethyloboron sulfate, and the like. It is to be understood that the hydrocarbon portions of the above and other complex organoboron compounds can be further substituted with organic groups which do not interfere with the electrolysis as, for example, the halogens, acid groups—both organic an inorganic—and the like.

It is preferable that the anionic portion of the organoboron complex have only organo groups, especially hydrocarbon, bonded to boron through carbon and that one of said organo groups be a lower alkyl hydrocarbon radical having up to and including about 8 carbon atoms with the other organo groups being the same or different but identical with each other. In some cases, advantage is obtained when one of the organo groups in this preferred embodiment is a lower alkyl hydrocarbon group having up to 8 carbon atoms and the other 3 groups are of a greater chain length up to even about 30 carbon atoms, since such results in a lower melting electrolyte and an easier separation of the by-product organoboron compound from the organolead product produced at the anode. A similar effect is achieved when the other 3 groups are branched chain alkyl groups, e.g. isopropyl, isobutyl, and the like. Likewise, in the preferred embodiment, the alkali metals are employed as the cationic material. Sodium is especially preferred. Typical examples of this embodiment comprise sodium ethyltrioctylboron, sodium ethyltricyclohexylboron, sodium ethyltributylboron, sodium ethyl triisopropylboron, sodium ethyltriphenylboron, and sodium ethyltrioctadecylboron.

It is also to be understood that mixtures of the aforementioned organoboron complexes are employable as, for example, a mixture of sodium tetraethylboron and potassium tetraethylboron with the latter being present in varying proportions from about 0.01 to as high as 99 percent by weight. Other mixtures include, for example, sodium ethyltriphenylboron in admixture with potassium tetraethylboron, sodium ethyltriphenylboron in admixture with potassium ethyltriphenylboron, and other such combinations which are readily evident from the above representative examples of the organoboron complexes. All that is basically required in formulating these mixtures is that the 2 or more complexes be miscible with each

other. Frequently, this results in the formation of new and improved complexes of the type defined above.

It is also advantageous, although not required, to add an ionizable salt to the above organoboron complexes. The employment of such salts will, in general, lower the melting point of the electrolyte and further increase its conductivity. The principal criteria of such ionizable salts are that they go into solution with the organoboron complex under the conditions of the electrolysis or react with the organoboron complex to form a complex or mixture of complexes of the types decribed above. The inorganic alkali and alkaline earth halides and pseudohalides, as described hereinbefore, are particularly well suited for this purpose. Typical examples of such include the chlorides, bromides, iodides, and fluorides of sodium, potassium, lithium, rubidium, cesium, magnesium, calcium, strontium, barium, and the cyanates, cyanides, thiocyanates, amides, hydroxides, mercaptides, and azides of these metals. The alkali metal halides, especially those of sodium and potassium, are particularly preferred for this purpose.

One feature of the present process is that a number of the electrolytes described herein are liquid and no solvent is required. While the electrolysis can be performed at various temperatures, in certain instances the electrolyte is solid at the chosen temperature of electrolysis. In some instances the electrolyte is solid even at temperatures above about 100° C. Of course, the electrolyte employed must be liquid and form an essentially homogeneous liquid system under the reaction conditions. When the electrolyte chosen would ordinarily be solid under the reaction conditions employed, one can use solvents to provide a liquid system. The general criteria of such solvents are that they be liquid under the reaction conditions and dissolve the electrolyte to form the essentially homogeneous liquid system. For this purpose, various solvents are available including the organic solvents such as the hydrocarbons, ethers, amines, lactones, and carbonates. While the solvents should be essentially inert in the system, they can form complexes with the electrolyte since such complexes will not hinder the electrolysis. Typical examples of suitable solvents are ethers, such as dimethyl ether, diethyl ether, methylethyl ether, methylisopropyl ether, methyl-n-propyl ether, and mixtures thereof. Suitable polyethers are ethylene and diethylene glycol diethers, such as dimethyl, methylethyl, diethyl, methylbutyl, ethylbutyl, dibutyl, and butyllauryl; trimethylene glycol ethers, such as dimethyl, diethyl, methylethyl, etc.; glycerol ethers, such as trimethyl, dimethylethyl, diethylmethyl, etc.; and cyclic ethers, such as dioxane, and tetrahydrofuran. Typical amines suitable for this invention include aliphatic and aromatic amines and heterocyclic nitrogen compounds. The preferred amines are tertiary amines such as trimethylamine, dimethylethylamine, triethylamine, dimethyl aniline, pyridine, tetraethylethylenediamine, N-methylmorpholine, and the like. Primary and secondary amines can also be used such as methylamine, dimethylamine, acetonitrile, etc. Alcohols can also be employed as solvents, viz., ethyl, methyl, isopropyl, etc. Other suitable solvents include hydrocarbons such as the aromatics as toluene, xylene, etc.; cyclic compounds such as cyclohexane, etc. The lactones are also employable as, for example, gamma-butyrolactone, gamma-valero-lactone, gamma-caprolactone, delta-valerolactone, and delta-caprolactone. Typical examples of the organic carbonates include ethylene, propylene, butylene, and the like carbonates. Likewise, water can also be employed as a solvent.

The solvents which are particularly preferred are tetrahydrofuran, water, and the lower alkyl ethers in which the alkyl groups have up to about 4 carbon atoms of the polyethers, particularly ethylene glycol and diethylene glycol. Of the polyethers, the dimethyl ether of diethylene glycol comprises an especially preferred embodiment.

The proportions of the aforementioned constituents of the electrolyte are, in general, subject to considerable latitude. In those instances wherein an ionizable salt is added to the organoboron complex, such can be added in minor amount as about 0.01 to not over 50 mol percent. The solvent, if employed, is generally added in amount at least sufficient to dissolve the electrolyte up to about 5 times that amount. When a solvent is employed, it is preferable that it be used in amount between about 45 percent to 90 percent of the saturation point of the solution.

The electrolysis is subject to varied manipulative operations, but generally only involves the provision of an electrolytic cell having one or more lead anodes and a corresponding number of appropriate cathodes to which is added the electrolyte or its solution. The cell is then heated to the desired operating temperature, e.g. above the melting point of the electrolyte when no solvent is employed, and then a current is applied. During the electrolysis, additional electrolyte can be added as make-up and the product, organolead compound, is withdrawn from the anode portions of the cell. Should the anolyte be a mixture of the organolead product with by-products and/or solvent, it is readily recovered by the usual physical separation techniques. In many instances, the product organolead compound is withdrawn from the cell in essentially pure form being immiscible in the system. Other modifications of the electrolytic procedure involve, for example, regeneration of the electrolyte which will be described in more detail hereinafter.

The electrolytic operation of the present invention will be more completely understood from a consideration of the following examples wherein all parts are by weight unless otherwise specified.

## EXAMPLE I

An equimolar complex of triethylborane with potassium cyanide is formed by mixing these materials. This mixture is then added under a nitrogen atmosphere to an electrolytic cell having a lead anode and a copper cathode. The cell is then closed and externally heated to 65° C. The cell is operated at a current density of 5 milliamps./cm.$^2$ and these conditions maintained for 2 hours. Tetraethyllead is produced.

## EXAMPLE II

In this run, the cell of Example I was employed. To the cell was added 0.7 part of triethylborane, 12 parts of dry toluene and 0.35 part of 1-hexynyl sodium suspended in 1 part of toluene. The cell was closed and a current of 1.08 milliamps. was applied to the cell at room temperature. The conditions were maintained for 4 hours and 56 minutes. The contents of the reactor were filtered at the end of this period and the liquid portion analyzed for organolead content. Tetraethyllead was obtained in good yield.

## *EXAMPLE III*

Employing the procedure of Example II, 1 part of the dietherate of the dimethylether of diethylene glycol with sodium tetraethylboron dissolved in 5 parts of this ether were added to the cell and a current of 10 milliamps. was applied for 150 minutes at room temperature. The current efficiency was 100 percent. The tetraethyllead product is readily recovered by extraction with an aliphatic hydrocarbon, e.g. hexane.

When this run is repeated substituting sodium tetramethylboron and sodium tetraoctylboron, tetramethyllead and tetraoctyllead are obtained in high yield, respectively.

## *EXAMPLE IV*

Employing the cell of Example I, there was added to the cell 40 parts of dimethyl ether of diethylene glycol, 2 parts of methylcyclopentadienyl sodium and 5 parts of triethylborane. Then a current of 10 milliamps. was applied to the cell at room temperature and these conditions maintained for 424 minutes. Di-(methylcyclo-

pentadienyl) lead was produced in a high current efficiency.

*EXAMPLE V*

In this run, sufficient diethyl ether is added to 10 parts of the dietherate of dimethyl ether of diethylene glycol with sodium tetraethylboron until two phases first appear. The lower phase, which has a specific resistance of 63 ohm-centimeters at 25° C., is added to the cell of Example I and electrolyzed at 25° C. for one hour at 40 milliamps. Tetraethyllead is produced at a current efficiency of essentially 100 percent.

*EXAMPLE VI*

Employing the cell of Example I, the diethyl etherate of sodium tetraethylboron, 0.432 part as $NaBEt_4$, was added to the cell along with 40 parts of water. The cell was closed and a current of 0.01 amp. was applied for a total of 233 minutes. During the electrolysis, tetraethyllead formed and collected at the bottom of the cell for ready withdrawal therefrom. At the end of this period, a 100 percent yield of tetraethyllead was recovered.

When the above example is repeated employing sodium tetraethylboron, free of ether, equally satisfactory results are obtained.

*EXAMPLE VII*

When the above run was repeated with exception that the dietherate of the dimethyl ether of diethylene glycol with sodium tetraethylboron was substituted for the diethyl etherate and a minor amount of caustic was added to bring the pH of the water solution to 12 with the electrolysis being conducted at room temperature for 180 minutes, the yield of tetraethyllead obtained was 88.2 percent.

Larger amounts of alkali metal hydroxide, up to about 40 percent by weight of the water present, can be added in the above example, and other examples where water is employed as solvent, in order to further improve the conductivity.

*EXAMPLE VIII*

Employing the procedure of Example II, sodium ethyl tributylboron, 2 parts, dissolved in 10 parts of tetrahydrofuran are electrolyzed at 60° C. with a potential of 3 volts applied to the cell for 2 hours. Tetraethyllead is recovered in high yield.

*EXAMPLE IX*

When sodium ethyltriphenylboron, as an essentially saturated solution in diethyl ether of diethylene glycol, is added to the cell of Example I and electrolyzed at 100° C. with an applied potential of 4 volts for 2½ hours, a mixture of tetraethyllead and triphenylborane is produced at the anode and readily recovered from the system. The tetraethyllead-triphenylborane mixture is readily separable. During the course of the electrolysis, liquid sodium metal is withdrawn from the cathode.

*EXAMPLE X*

When an essentially saturated solution of sodium ethyl trioctadecylboron in the dimethyl ether of diethylene glycol is electrolyzed at 110° C. with an applied potential of 10 volts, tetraethyllead and trioctadecylborane are withdrawn from the anode and liquid sodium from the cathode in high yield. The tetraethyllead-trioctadecylborane mixture is readily separable for recovery of the tetraethyllead.

*EXAMPLE XI*

In this run, the electrolyte employed comprises a solution of sodium tetraethylboron to which has been added an equivalent amount of potassium tetraethylboron in the dimethyl ether of diethylene glycol in order to have an electrolyte with sodium tetraethylboron containing a potassium ion. The electrolysis is conducted at 100° C. employing a potential of 3 volts for 4 hours. A mixture of tetraethyllead and triethylborane is recovered from the anode, during the electrolysis, in high yield and liquid sodium metal is also withdrawn from the cell at the cathode.

*EXAMPLE XII*

Employing the cell of Example I, a solution of sodium tetraethylboron in the ethylmethyl ether of diethylene glycol to which has been added 1 percent by weight of potassium iodide is electrolyzed at 30° C. for 3 hours with an applied potential of 5 volts. Tetraethyllead is produced at a high current efficiency.

When sodium bromide, sodium iodide, potassium bromide, or potassium cyanide are substituted for the potassium iodide in the above example, in amounts between 0.01 up to the saturation point but preferably not over 10 mol percent, equally satisfactory results are obtained.

*EXAMPLE XIII*

When 1 part of potassium tetracyclohexylboron dissolved in 20 parts of benzene are added to the cell of Example I, and a potential of 4 volts applied to the cell at a temperature of 75° C. for 3 hours, tetracyclohexyllead is produced in high yield.

*EXAMPLE XIV*

Sodium tetraphenylboron dissolved in dioxane is employed as an electrolyte using a lead anode at 70° C. and a potential of 10 volts for 5 hours. Phenyllead product is obtained in high yield.

*EXAMPLE XV*

Employing the procedure of Example II, a solution of sodium ethylboron trifluoride dissolved in tetrahydrofuran is electrolyzed at 50° for 2 hours. Tetraethyllead is produced at the anode in high yield.

*EXAMPLE XVI*

When lithium tetraethylboron, dissolved in amyl ether, is employed as the electrolyte in Example II, tetraethyllead is again formed in high yield.

*EXAMPLE XVII*

A solution of tetraethyl ammonium tetraethylborane in triethylamine is employed as the electrolyte in the procedure of Example II resulting in an essentially quantitative yield of tetraethyllead.

*EXAMPLE XVIII*

When magnesium tetraethylboron is substituted for sodium tetraethylboron in Example III, equally satisfactory results are obtained.

EXAMPLE XIX

A complex is formed by adding sodium amide to triethylborane. The complex is then dissolved in pyridine and placed in a cell as in Example II. The cell bath is heated to 70° C., and then a potential of 10 volts is applied. When these conditions are maintained for a period of 3 hours, tetraethyllead is produced at a high current efficiency.

The above examples are presented by way of illustration and it is not intended to be in any way limited thereto. It will be evident that complexes of the type described hereinbefore can be substituted as well as other solvents and other ionizable salts in order to produce similar results. For example, in any of the above examples, one can substitute tetraethyl arsonium tetraethylboron, potassium triethylboron cyanate, ethylpyridinium tetraethylboron, and sodium ethyltridodecylboron as the organoboron complex. Likewise, one can substitute in the above examples, solvents such as benzene, propylene carbonate, gamma-butyrolactone, tetralin, cycloheptane, dibutylether, ethyl alcohol, octanol, octadecanol, and the like solvents described hereinbefore.

As stated above, the temperature at which the electrolysis is conducted is subject to considerable latitude,

the only limitation being that it be below the decomposition temperature of the electrolyte or product. The temperature is ordinarily also such that the electrolyte is liquid. Since the organolead products tend to decompose at temperatures above about 120° C., it is preferable to maintain the temperature below this level. In a preferred operation, electrolysis is conducted at temperatures between about 70 to 110° C. since the conductivities are higher at these conditions. There is no need to employ pressure in the system unless one operates above the boiling point of the constituents of the electrolyte or the product. Autogeneous pressure is generally applicable, particularly when one does not combine the electrolysis with an integrated in situ regeneration of the electrolyte as described hereinafter.

The potential which is applied to the cell is generally up to about 50 volts, but preferably below about 10 volts. The current density is usually above 0.01 amp./cm.$^2$ for practical reasons and preferably maintained below 1 amp./cm.$^2$ in order to avoid excessive localized heating and shorting.

While direct current is generally employed in the electrolysis, it is frequently advantageous to superimpose an alternating current over the direct current. Such results in better current efficiencies. During the course of the electrolysis, it is also possible to occasionally reverse the current momentarily. This is advantageous in cleaning the electrodes.

Advantage is achieved when the electrolyte is circulated in order to obtain a more uniform distribution. This results in a greater efficiency of the system. It is, likewise, frequently advantageous to employ compartmented cells as, for example, the use of a porous diaphragm between the anode and the cathode as is frequently done in electrolytic procedures.

The cathode can be constructed of any conducting material which is essentially inert to the electrolyte employed. For example, in addition to the copper electrodes used in the above examples, one can substitute platinum, nickel, tungsten, nickelcarbon alloys, and the like. The cathode can also be lead metal itself and this is particularly useful when the current is occasionally reversed in order to clean the electrodes. Other examples of cathodes will be evident to those skilled in the art.

The basic electrolytic step described above is well suited for combination in an integrated manner with a regeneration of the electrolyte in various manners. While regeneration in the manner described herein is possible with all cationic materials described above, it is particularly advantageous when the organoboron complex is one in which the cationic portion is an alkali or alkaline earth metal, preferably the alkali metals, especially sodium and potassium, and the anionic portion is one wherein during the electrolysis a radical, which is analogous to an olefinic material, is removed to form the organolead product. One such method of regenerating the electrolyte comprises an in situ regeneration wherein hydrogen and an appropriate olefin are maintained as an atmosphere in the cell or more preferably fed to the cell into the electrolyte around the cathode. The hydrogen and olefin can be fed simultaneously or sequentially, that is, first feeding hydrogen for a period of time until no more is taken up as evidenced by the pressure drop, then feeding olefin until essentially no more is taken up as evidenced by the pressure drop and repeating this cycle during the electrolysis. In a sequential feeding, the unique reverse feeding is possible, that is, first feeding the olefin, and then the hydrogen as described above. Thus, in this embodiment, the process will comprise passing an electric current through the lead metal and the organoboron complex to a cathode while simultaneously feeding the hydrogen and/or olefin around the cathode in the above manner.

In conducting this operation in situ, the conditions described above with regard to the simple electrolysis are employed. However, in the initial electrolyte there is added, in amount between about 1/20 to 1 mol ratio of boron compound, $BR^1R^2R^3$, wherein the R groups have the meaning described hereinbefore and which compounds are preferably analogous to the boron compound co-produced with the organolead product at the anode per mol of organoboron complex. Thus, if a boron halide is co-produced with the organolead at the anode, this material will be a boron halide. Likewise, in the electrolysis of sodium tetraethylboron, triethylborane is initially added to the electrolyte.

It is not necessary to employ a pressure cell for this regenerative operation. Although the autogeneous pressure of the reaction system is quite suitable, pressure will result in faster regeneration of the electrolyte. For this purpose, pressures up to about 200 p.s.i. can be employed.

The olefins that are used will, of course, be analogous to the hydrocarbon radical consumed during the electrolysis in forming the organolead product. For example, if tetraethyllead is produced, ethylene is the olefin employed. Typical examples of the olefins which can be employed include ethylene, propylene, butylene, hexene-1, hexene-2, 1-octene, butadiene, cyclohexene, octadecylene-1, styrene, and the like olefins having up to about 18 carbon atoms. The terminal unsaturated olefins, that is, those wherein the double bond is in the alpha position of straight chain hydrocarbon olefins having up to about 8 carbon atoms, are particularly preferred because of their greater availability and applicability to the regenerative procedure.

The regenerative procedure is, of course, not applicable when the electrolysis step per se is conducted in water or an aqueous medium. It is, however, applicable in all other instances, that is, when the electrolysis involves dry electrolyte or conducting the operation in the presence of the organic solvents described hereinbefore. It is particularly effective when the organic solvents are the polyethers and tetrahydrofuran which are preferred organic solvents even in the electrolysis step as described above.

This embodiment of the present invention will be more completely understood from a consideration of the following examples.

### *EXAMPLE XX*

The procedure of Example III is repeated with exception that incorporated into the electrolyte prior to electrolysis is 1 mol of triethylborane per mol of the sodium tetraethylboron present. During the electrolysis, ethylene and hydrogen are simultaneously fed into the electrolyte around the cathode and maintained at 10 atmospheres pressure. In this manner, tetraethyllead is produced with an equally high current efficiency and the electrolyte is consistently regenerated.

### *EXAMPLE XXI*

The procedure of Example XX is repeated with exception that during electrolysis, ethylene is passed into the electrolyte around the cathode for a period of 30 minutes, then stopped; then hydrogen is fed into the electrolyte around the cathode for a period of 30 minutes, then stopped and this cycle repeated during the production of the tetraethyllead, and the electrolysis is conducted at 100° C. Tetraethyllead is produced in an equally efficient manner and the electrolyte is constantly regenerated.

### *EXAMPLE XXII*

The procedure of Example VIII is repeated with exception that ½ mol of tributylborane per mol of sodium ethyl tributylboron are initially added to the electrolyte prior to the electrolysis and during the electrolysis, ethylene and hydrogen are sequentially fed over periods of 20 minutes, respectively, to the electrolyte around the cathode to maintain a pressure of 175 p.s.i. Tetraethyl-

lead is produced in a high current efficiency and readily withdrawn from the anode side of the cell and the electrolyte is continuously regenerated.

*EXAMPLE XXIII*

The electrolysis of Example IX is repeated with exception that prior to the electrolysis 1 mole of triphenylborane per mole of sodium ethyl triphenylboron are added to the electrolyte and during electrolysis ethylene and hydrogen are fed into the electrolyte at the cathode as described in Example XXII. Tetraethyllead is continuously withdrawn from the anode space and produced at an essentially quantitative current efficiency while the electrolyte is regenerated.

*EXAMPLE XXIV*

Example X is repeated except that 0.75 mol of trioctadecylborane per mol of sodium ethyl octadecylboron are added to the electrolyte prior to the electrolysis and ethylene and hydrogen are fed into the electrolyte at the cathode in the manner described in Example XXII to regenerate the electrolyte during the electrolysis and produce tetraethyllead in a high current efficiency.

*EXAMPLE XXV*

Example XIII is repeated with exception that 0.5 mol of tricyclohexylborane per mol of potassium tetracyclohexylboron are added to the electrolyte prior to electrolysis and during the electrolysis sufficient cyclohexene is incorporated as solvent and reactant to replace that consumed in forming the organolead product and hydrogen is continuously fed into the electrolyte around the cathode at a pressure of 200 p.s.i. Tetracyclohexyllead is produced in high yield while the electrolyte is regenerated simultaneously.

The above examples are presented by way of illustration of the in situ regeneration embodiment of the present invention and it is not intended to be limited thereby. It will be evident that other combinations of in situ regeneration and electrolysis are possible. For example, Example I can be repeated by first incorporating 0.75 mol of triethylborane per mol of potassium triethylboron cyanide in the electrolyte and then feeding ethylene and hydrogen into the electrolyte during the electrolysis sequentially at pressures of 150 p.s.i. Example XV can be repeated by first incorporating 0.5 mol of boron trifluoride per mol of sodium ethylboron trifluoride employed into the electrolyte and again feeding ethylene and hydrogen sequentially during the electrolysis at pressures of about 175 p.s.i.

The above regeneration operation can more advantageously be conducted when the cathode is a gas electrode. The gas electrodes are hollow electrodes having capillary or porous passages and the hydrogen and olefin can be passed internally through the gas electrode to make contact with the electrolyte and thereby bring about the regeneration. Further improvement is also obtained when the gas electrode is impregnated with typical hydrogenating catalysts as, for example, nickel, silver, platinum, palladium, and the like. The impregnation of these catalysts in the electrode is readily accomplished by immersing a carbon gas electrode into a saturated solution of a salt of the metal, then drying the electrode and heating it to a sufficient temperature for in situ reduction, thereby plating the metal upon the surfaces of the electrode. Other methods of plating and impregnating the metal will be evident. Additionally, the gas electrode can be made non-wetting by treating it with anti-wetting agents such as "Teflon" to provide a very thin coating of these materials. Therefore, in any of the Examples XX through XXV and other regeneration operations of the type described therein, further improvement is obtained by substituting for the cathodes employed therein a gas electrode impregnated with nickel, silver, platinum, or palladium, and which have been treated with anti-wetting agents such as "Teflon" and others well known in the art.

It has also been found that certain materials will catalyze the regeneration reactions homogeneously. For this purpose, compounds of the transition metals, both organic and inorganic, are applicable, the transition metals including Groups IB, IVB, VB, VIB, VIIB and VIII of the periodic chart of the elements. The only criteria of such compounds is that they be soluble in the electrolyte and not react destructively with the electrolyte. Typical examples of such compounds are those wherein the metal is an aforementioned transition series metal which is bonded to organic and inorganic radicals of the type described above in relation to the complex organoboron compounds. Illustrative examples of these compounds include, copper, nickel, cobalt, iron, titanium, maganese, and chromium halides, alkyls, alkynyls, cycloalkyls, aromatics, cycloalkenyls, sulfates, phosphates, chlorates, carbonyls, and nitrosyls, and the like. Such are generally employed in amounts up to about 10 percent by weight of the electrolyte and preferably between about 0.01 to 1 percent by weight.

The following examples will illustrate the regeneration operation employing typical catalysts of this type.

*EXAMPLE XXVI*

In this run, a cell like that of Example I is employed. An electrolyte is made up by mixing together 12 parts of the dimethyl ether of diethylene glycol, 1.5 parts of triethylborane and 0.74 part of 1-hexynyl sodium. This mixture is then electrolyzed first with a copper anode at 75° C. and 50 milliamps. for 84 minutes to anodically incorporate copper into the electrolyte. The electrolyte is then transferred to a cell having a lead anode. This cell is run at 25° C. and 4 milliamps. of current with hydrogen and ethylene sequentially fed into the electrolyte around the cathode at atmospheric pressure. Hydrogen and ethylene are taken up at a rate essentially equivalent to the current applied during the electrolysis with tetraethyllead being produced at a high current efficiency.

*EXAMPLE XXVII*

Employing an electrolytic cell analogous to that of Example I, but with a means for adding hydrogen and olefin around the cathode, there was added to the cell 40 parts of the dimethyl ether of diethylene glycol, 3.5 parts of triethylborane, 1.86 parts of sodium tetraethylboron, and 0.1 part of titanium tetrachloride. The electrolysis was conduced at room temperature and 10 milliamps current with ethylene fed around the cathode during the first 4½ hours of operation as fast as it was taken up. Then, the atmosphere was changed to hydrogen and the electrolysis continued for 6 hours. Tetraethyllead was continuously produced at a high current efficiency.

Other examples of the catalysis will be evident by substituting other transition metal compounds in the above examples and Examples XX through XXV, such as, for example, dicyclopentadienylmanganese, cuprous chloride, zirconium fluoride, dibenzene chromium, methylcyclopentadienyl manganese tricarbonyl, the dimer of methylcyclopentadienyl iron dicarbonyl, and the like.

In another embodiment of the present invention, the regeneration of the electrolyte is readily accomplished by continuously withdrawing the catholyte from the cell and treating it as above with hydrogen and ethylene. This procedure is particularly advantageous when the rate of consumption of the electrolyte in forming the organolead compound greatly exceeds the rate of regeneration of the electrolyte. Withdrawing the catholyte from the cell and then conducting a regeneration reaction with hydrogen and olefin as described above permits the use of higher temperatures and pressures as up to about 250° C. and 10,000 p.s.i. in order to achieve a faster reaction rate. Likewise, this type of operation can be continuously conducted so that the catholyte after regenerative treatment is

recirculated into the cell thereby providing a continuous electrolytic operation. As in the in situ regeneration, one adds additional $BR^1R^2R^3$ compound to the catholyte during or prior to the electrolysis operation in the same amounts.

A still further embodiment of this invention exists wherein the above described electrolysis is well suited to another type of integrated process for regeneration of the electrolyte, particularly when the cationic portion of the organoboron complex is an alkali or alkaline earth metal, especially sodium and the by-product boron compound is an organoboron compound. In this embodiment the electrolysis can be conducted under reaction conditions wherein the cationic alkali or alkaline earth metal is produced as a solid at the cathode and recovered therefrom for the regeneration operations. It is preferable in this type of regeneration that the cationic portion of the electrolyte be an alkali metal, especially sodium, and the electrolysis is preferably conducted above the melting point of the alkali metal so that it can be readily withdrawn from the cell at the cathode as a liquid while simultaneously a mixture of the organolead and by-product boron compound is withdrawn at the anode. In any case, in this regeneration embodiment, there is no need to add any excess boron compound, $BR^1R^2R^3$, to the electrolyte prior to or during the electrolysis. The metal withdrawn at the cathode is hydrogenated by techniques well known in the art. Then, the metal hydride so-formed is added, if desired, with heating up to the decomposition temperature of the reactants and products but preferably below about 120° C, to the mixture of the organolead product and by-product boron compound produced at the anode whereby a complex of the metal hydride with the by-product boron compound forms which is immiscible in the organolead product and readily recovered therefrom. Alternatively, the mixture of organolead product and by-product boron compound recovered at the anode can be first subjected to conventional separation techniques such as decantation, fractional crystallization, or distillation, and the like and then the by-product boron compound is reacted with the metal hydride. This latter technique is usually preferred, especially when the metal hydride is reactive or partially destructive of the organolead product. Then the metal hydride-by-product boron compound complex which is formed is reacted with an appropriate olefin thereby producing the starting organoboron complex employed as an electrolyte. The olefins described previously are, of course, employable in this type of operation and the operation is generally performed at between about 0 to 250° C., but below the decomposition temperature of the reactions or the product and pressures up to about 10,000 p.s.i. when the olefins are gaseous under the reaction conditions.

The following examples will typify this type of regeneration in combination with the electrolysis per se.

*EXAMPLE XXVIII*

Example III is repeated with exception that the electrolysis is conducted at 100° C. During the electrolysis, the liquid sodium formed at the cathode is withdrawn and reacted with hydrogen at 200° C. and 10 atmospheres of hydrogen while suspended in mineral oil with vigorous agitation. The sodium hydride suspension is cooled to room temperature and filtered from the mineral oil. The sodium hydride is then continuously added to the mixture of triethylborane and tetraethyllead which is continuously withdrawn from the electrolytic cell at the anode whereby two phases form, one being the sodium triethylboron hydride and the other being the tetraethyllead phase. The tetraethyllead is decanted from the sodium triethylboron hydride phase and the latter is then reacted with ethylene while dissolved in the dimethyl ether of diethylene glycol at 80° C. and 10 atmospheres. The resulting solution is continuously fed to the electrolytic cell as required to make up the electrolyte.

This run is readily duplicated when the anode product mixture of tetraethyllead and triethylborane is first subjected to fractional distillation and the recovered triethylborane then reacted with the sodium hydride in the presence or absence of the solvent employed in the electrolyte and then proceeding as described.

The above procedures are readily duplicated by employing the appropriate olefin in Examples VIII, IX, X, XI, XIII, and XV and in other similar procedures.

The organolead products produced according to the invention are of well known utility. A major use, particularly for tetraethyllead, is as an additive to motor fuels in order to enhance the octane rating. For example, when a minor amount of tetraethyllead is added to a base gasoline stock, the octane number of the gasoline is increased. Other uses of the organolead products produced are well known.

While the above discussion has been in relation to the electrolytic preparation of organolead compounds and the various embodiments of the invention are especially applicable to the preparation of the lead compounds, the invention is also applicable for preparing other organometallic compounds. To prepare such other organometallic compounds, the appropriate metal is substituted for lead as the anode in the above description and examples. By way of illustration when magnesium, cadmium, mercury, aluminum, rare earth metals, zinc, tin, bismuth, arsenic, and antimony are substituted for the lead anode the corresponding organometallics are obtained. Of course, with some of the other metals aqueous systems are not applicable because the product is reactive to water, e.g. when a magnesium, zinc, or aluminum anode is employed.

Having thus described the process of this invention, it is not intended that it be limited except as set forth in the following claims.

I claim:

1. A process for the production of an organolead product comprising passing an electric current through a cathode, an electrolyte and a lead anode, the electrolyte consisting essentially of a liquid organoboron complex component, forming thereby an organolead product at the lead anode and a cationic product at the cathode essentially free of elemental boron, and withdrawing the organolead product from the electrolyte.

2. A process for the production of an organolead product comprising passing an electric current through a cathode, an electrolyte system and a lead anode, said electrolyte system consisting essentially of a solution of an organoboron complex component in a liquid medium selected from the class consisting of ethers, aqueous liquids, amines, and aromatic hydrocarbons, forming thereby an organolead product at the lead anode and a cationic product at the cathode essentially free of elemental boron, and withdrawing the organolead product from the electrolyte system.

3. A process for the production of an alkyllead product and concurrent regeneration of the electrolyte employed therein which comprises passing an electric current through a cathode, an electrolyte system, and an anode, said electrolyte system consisting essentially of a solution of an organoboron complex component in a liquid medium selected from the class consisting of ethers, amines, and aromatic hydrocarbons, the organoboron complex being further defined in that the cationic proportion is selected from the group consisting of alkali and alkaline earth metals and the anionic portion has at least one alkyl group whereby an alkyllead product is formed at the lead anode and a product consisting essentially of the said cationic metal is formed at the cathode, and concurrently feeding an olefin and hydrogen into the electrolyte around the cathode, said olefin corresponding to the alkyl groups consumed in forming the said alkyllead product.

4. A process for the production of tetraethyllead comprising passing an electric current through a cathode, an

electrolyte system and a lead anode, said electrolyte system consisting essentially of a solution of sodium tetraethyl boron in the dimethyl ether of diethylene glycol, forming thereby tetraethyllead at the anode while simultaneously feeding ethylene and hydrogen into the electrolyte system at the cathode in amount sufficient to regenerate the electrolyte consumed in forming the tetraethyllead.

5. A process for the production of an alkyllead product comprising passing an electric current through a cathode, an electrolyte system and a lead anode, said electrolyte system consisting essentially of a solution of an organoboron complex component in an anhydrous liquid medium selected from the class consisting of ethers, amines, and aromatic hydrocarbons, the cationic portion of the organoboron complex component being selected from the group consisting of alkali and alkaline earth metals and the anionic portion having at least one alkyl group, forming thereby an alkyllead product at the lead anode and a cationic metal product at the cathode essentially free of elemental boron and withdrawing the cationic metal and the by-product boron compound and the organolead from the electrolytic zone, hydriding the cationic metal and forming the hydride thereof, and reacting the recovered by-product boron compound with the hydride of the cationic metal to form a complex, and reacting said complex with an olefin corresponding to the alkyl groups in said alkyllead product and recycling to the electrolytic zone.

6. The process of claim 2 wherein the electrolyte is an alkali metal tetraalkylboron compound dissolved in an ether.

7. The process of claim 2 wherein the electrolyte is sodium tetraethylboron dissolved in the dimethyl ether of diethylene glycol.

8. The process of claim 2 wherein the electrolyte is sodium tetraethylboron dissolved in water.

9. The process of claim 5 wherein the electrolyte is sodium tetraethylboron dissolved in an ether and said olefin is ethylene.

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