United States Patent Office 3,028,323
Patented Apr. 3, 1962

3,028,323

MANUFACTURE OF ORGANOLEAD PRODUCTS

Paul Kobetz and Richard C. Pinkerton, Baton Rouge, La., assignors to Ethyl Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Filed Dec. 24, 1959, Ser. No. 861,757
10 Claims. (Cl. 204—62)

This invention relates to the manufacture of the organo compounds of lead. More particularly, the invention relates to the preparation of organo compounds of lead, such as tetraalkyllead materials, by a new and highly effective electrolytic process.

The organo compounds of lead, and in particular, tetraethyllead, have been known for quite some time. Of these, tetraethyllead is most extensively employed for antiknock use in the utilization of gasoline in internal combustion engines. The manufacture of the organolead compounds has hitherto been carried out by more or less classical methods. With respect to the commercially prominent example, tetraethyllead, this material is made by reacting a sodium lead alloy with ethyl chloride according to the following equation:

$$4NaPb+4C_2H_5Cl \rightarrow (C_2H_5)_4Pb+3Pb+4NaCl$$

It will be seen from the foregoing equation that the conventional method of manufacture of this product results, even with perfect reaction, in conversion of only one-fourth of the lead initially charged, as sodium lead alloy, into the desired product, tetraethyllead. Further, this type of process requires a substantial number of precursor operations, specifically, the formation of sodium metal by the electrolysis of fused salts, the synthesis of ethyl chloride to be used as an alkylating agent, the formation of the sodium lead alloy reused as a reagent in the principal reaction, and other features. Accordingly, in addition to the necessity and inconvenience and cost of recycling and recovering at least three-fourths of the lead metal originally present in the reactant, the economics of an over-all process are drastically effected by the preceding syntheses necessary, as outlined above.

It has heretofore been proposed that tetraorganolead compounds, particularly tetraethyllead could be synthesized by a process involving electrolytic operations. For example, see U.S. Patents 1,539,297 and 1,567,159. However, all attempts to devise a satisfactory electrolytic type process thus far advanced has exhibited certain serious deficiencies. For example, in the above cited patents, only one-half, at the most, of the lead product, is released as a tetraalkyl compound, the other half being deposited as a fine powder in the electrolysis chamber. In addition, these prior art processes use rather expensive sources of alkyl groups, such as ethyl iodide. More recently, certain improved processes have been advanced, but these yet exhibit certain inadequacies. For example, the electrical conductivity is not as high as desired, thus restricting production. In addition, the required degree of flexibility in operation is not attained in that in many instances, a solid metal cathodic product is necessarily produced. In addition, in many cases the lead organo product produced is necessarily accompanied by difficultly separable impurities.

It is, accordingly, a general object of the present invention to provide a new and significantly improved process for the manufacture of lead tetraorgano compounds, particularly lead tetraalkyl compounds, and especially tetraethyllead. A more specific object of the present invention is to provide a process of this character characterized by the electrolysis of an electrolyte of high conductivity, low melting point and high fluidity, with a high current efficiency and materials recovery. An additional object is to provide a process which vastly simplifies and avoids prior difficulties with respect to the removal of

the desired lead tetraorgano product, as such, from the process, and for recovering the material values of other components. A more specific object of certain embodiments of the invention is to provide an integrated process wherein a separation is accomplished concurrently with the electrolytic formation of the tetraalkyllead desired, allowing separate withdrawal of the lead compound product and an associated jointly formed material. Yet an additional object is to provide new and valuable anhydrous, low melting, fused salt-like electrolysis systems of electrolyte compositions exhibiting numerous important advantages contributing to the above objects.

The foregoing and additional objects of the invention are obtained by electrolyzing, in the presence of a lead anode, an anhydrous electrolyte which includes an alkali metal boron tetraorgano complex and a second or secondary component including a complex of an aluminum group metal, especially an organometallic complex including at least three organo radicals per mole. The desired lead tetraorgano product is released at the anode, on passage of the electric current, and concurrently a boron triorgano compound is released in this zone. In some cases, this joint product is an aluminum group triorgano product. An alkali metal cathode product is deposited or formed at the cathode of the apparatus employed. The lead tetraorgano product is withdrawn normally as a liquid, and is frequently suitable for further use as such, for example, as a constituent of antiknock compounds. The lead tetraorgano product is withdrawn as a relatively pure product in certain preferred embodiments wherein a boron triorgano product is concurrently released as a gaseous product, thus achieving a high degree of purification of the lead tetraorgano product concurrently with its formation. In other preferred embodiments, wherein a high melting lead tetraorgano product is formed, the product is released in solution in a jointly released boron triorgano liquid compound, or alternatively, in a specially added solvent for the lead compound. In the embodiments of the process presenting the highest benefits with respect to operation, in addition to separate withdrawal of the boron triorgano material, an alkali metal is withdrawn from the electrolysis zone in liquid phase, and is recombined, by operations described hereinafter, with the boron triorgano component mentioned above, to reform the alkali metal boron tetraorgano component of the electrolyte.

It will be apparent from the above that the electrolyte composition is a vital feature of the present process. The electropositive metal-boron tetraorgano complex component can be any of a large number of specific materials. Thus, illustrative types of complexes forming this component are sodium boron tetraalkyl compounds wherein the alkyl groups are the same or different, and other sodium boron tetrahydrocarbon compounds, for example, sodium boron tetraphenyl. Usually, but not necessarily, the alkali metal boron tetraorgano complex component should include as a substituent the hydrocarbon radical desired for the lead organo product to be manufactured.

The second essential component of the electrolyte of the invention is a complex of an electropositive metal with an aluminum group metal. By aluminum group metal is meant a member of the group aluminum, gallium, indium, and thallium, in group III of the periodic arrangement of the elements. These members of the aluminum group of metals, in compounds for the electrolyte system, generally all meet the requirements of the necessary second component and are highly effective. In most of the illustrations hereinafter aluminum metal is cited as the aluminum group metal, aluminum being preferred for practical and economic reasons. This secondary component, of an aluminum group metal, can be any of a large number of complexes or compounds. In

preferred systems, it is found that this component should contain at least three hydrocarbon radicals in the molecule. The organo radicals are preferably hydrocarbon, for example, alkyl, aryl, alkaryl, or aralkyl. Alkoxy or aroxy groups can be present in limited degree, that is, in the proportions of about one group per mole of the complex.

The aluminum group metal complexes, then, suitable for the electrolyte of the process, can be chosen from a large number of components. Various groups of such components have preferred properties or functions, such groups including, illustratively,

A mixture of the complexes of an alkali metal aluminum group metal tetramethyl complex with an alkali metal aluminum group metal tetrahydrocarbon radical complex, the hydrocarbon radicals of said latter complex being of a non-methyl type. An illustrative example of this category is an equimolar mixture of sodium aluminum tetramethyl and sodium aluminum tetraethyl,

An alkali metal aluminum group metal tetraorgano complex, the organic radicals thereof consisting of methyl and another hydrocarbon radical, and, further the radicals including at least one methyl and at least one of said other hydrocarbon radicals. An illustrative example of a component of this type is sodium aluminum dimethyl diethyl,

A mixture of alkali metal aluminum group metals tetrahydrocarbon complexes, including two different alkali metals. An illustrative illustration of this type of component is the mixture of sodium aluminum tetraethyl and potassium aluminum tetraethyl,

An alkali metal halide complex with an aluminum group metal organometallic compound. The radicals of said aluminum group organometallics being alkyl, aryl, alkaryl or aralkyl. An illustrative illustration of this type of second component is a sodium fluoride-aluminum triethyl complex, and

An alkali metal aluminum group tetraorgano complex, one of the organo radicals thereof being chosen from the group alkoxy and aroxy radicals.

It will be clear from the above definition, and from the detailed description hereinafter, that the total electrolyte compositions suitable for the purposes of the invention are very numerous and susceptible to considerable choice.

In carrying out the process generally, direct current is passed through the lead anode, the electrolyte, and to a cathode, which should be of material inert at the conditions of reaction and to the electrolyte composition. The passage of current is accompanied by the formation and release at the lead anode of a tetraorganolead compound which is, usually, immiscible with the electrolyte of the system and generally is collected as a more dense liquid phase below the non-aqueous electrolyte in the electrolysis zone. In addition, another organometallic compound, i.e., a boron trihydrocarbon compound is released. In the most preferred forms of the process of the invention, this jointly released product is discharged from the electrolysis zone as a gaseous phase, or, in other cases, as a liquid miscible with and actually a solvent for the tetraorganolead product. In addition, the electrolysis results in deposition at the cathode of an electropositive metal constituent from the electrolyte. Depending upon the conditions of operation and the particular identity of the alkali metals of the electrolyte, said cathodic deposit can be a solid but most desirably is a liquid at the temperatures of operation.

From the foregoing it will be clear that the process of the invention can be represented in short form by the following expression:

$$\text{Lead} + \text{Electrolyte (boron complex+aluminum group metal complex)} \xrightarrow{\text{Electrolysis}} \text{Lead tetrahydrocarbon} + \text{Boron trihydrocarbon} + \text{Alkali metal}$$

The radicals of the lead compound are hydrocarbon radicals, especially alkyl, and the radicals of the boron triorgano compound produced being the same or different hydrocarbon radicals. The alkali metal can be a single metal, or a low melting mixture.

The conditions of operation, such as the temperature employed, is subject to considerable latitude. Generally, the electrolysis of the process is carried out at temperatures below 200° C., and, in many cases, at about 100° C., and in certain cases, even below 100° C. A usually preferred range is from 50 to 150° C. Dependent upon the lead tetrahydrocarbon product to be made, and upon the conditions of operation chosen, it will frequently be desirable to provide to and mix with the organolead product a minor quantity of a thermal stabilizer for the organolead product, especially when temperatures of operation are above or in the neighborhood of 100° C.

The electropositive metal boron tetraorgano complex of the electrolyte can be one or more of an extensive number of materials, of which the following is an illustrative group. The organo complex is, in general, a compound which contains an anionic boron group having four organic radicals attached thereto, the organo radicals being, usually, hydrocarbon radicals, that is consisting of carbon and hydrogen. In the most common embodiments of the process, the radicals are alkyl radicals of up to about 16 carbon atoms, with the lower alkyl groups, i.e., up to and including four carbon atoms, most frequently employed. However, the organo groups can include other substituents such as substituted alkyl or alkaryl, for example benzyl radicals; or aryl groups such as phenyl, or aryl groups having alkyl substituents such as tolyl, or xylyl. The electropositive metal of the organo boron complex is as previously indicated, a strongly electropositive metal such as an alkali metal, including lithium, sodium, potassium, rubidium, or cesium. The preferred electropositive metal component is sodium metal because of its relative abundance and relatively low melting point of 97° C., potassium and lithium also being desirable.

Typical examples of the organo boron complexes constituting the boron component employed in the present invention include: sodium boron tetraethyl, sodium boron tetramethyl, sodium boron tetraisopropyl, sodium boron tetraoctyl, sodium boron tetraoctadecyl, sodium boron tetraeicosyl, sodium boron 1-hexynyl triethyl, sodium boron tetracyclohexyl, sodium boron tetraphenyl, sodium boron tetrabenzyl, sodium boron tetranaphthyl, sodium boron tetracyclohexynyl, sodium boron tetrabutadienyl, sodium boron ethyl tributyl, sodium boron ethyl trioctyl, sodium boron ethyl tridecyl, sodium boron ethyl tricyclohexyl, sodium boron ethyl triphenyl, sodium boron ethyl tri(2-phenylethyl), sodium boron ethyl triisopropyl, sodium boron diethyl diisopropyl, sodium boron diethyl diphenyl, sodium boron diethyl dioctadecyl, sodium boron octyl trioctadecyl; and other comparable organo-boron complexes wherein the cationic groups or elements can be other than the sodium illustrated above, thus potassium boron tetraethyl, lithium boron tetraethyl, calcium boron tetraethyl, magnesium boron tetraethyl, strontium boron tetraethyl, are suitable examples. It will be understood that, in the foregoing complexes of a bivalent alkaline metal, two of the boron tetraalkyl anionic groups are present. The cationic component can also be, instead of an alkali metal, an electropositive inorganic radical, particularly ammonium or amino type groups. Thus ammonium boron tetraethyl and pyridinium boron tetraethyl are suitable boron complexes.

A wide variety of components comprising a complex compound of an aluminum group metal and an electropositive metal can be employed. Illustrative examples of such components are sodium aluminum tetraethyl, sodium aluminum tetraisopropyl, sodium aluminum methyl triethyl, sodium aluminum tetrahexyl, sodium aluminum

diethyldioctyl, sodium fluoride complexed with aluminum triethyl, sodium aluminum triethyl bromide, and sodium aluminum triethyl ethoxide. The complex can contain a plurality of halogens, as in sodium aluminum tetrachloride and sodium aluminum ethyl trichloride. As already indicated, although sodium is a preferred electropositive metal constituent, corresponding complexes employing other alkaline metals can be employed as the aluminum group metal complex, for example, potassium aluminum tetraethyl, potassium aluminum tetraisopropyl, potassium aluminum methyl triethyl, potassium aluminum diethyldioctyl, and potassium aluminum triethyl bromide. Similarly, lithium aluminum group metal complexes are suitable, of which illustrative examples include lithium aluminum trimethyl ethyl, lithium gallium dimethyldiethyl, lithium aluminum triethyl ethoxide, lithium indium tetrahexyl, and lithium gallium triethyl fluoride. Strongly electropositive alkaline earth metal complexes can be present, but generally are avoided, because they contribute little to the conductance of the electrolyte and, further, the alkaline earth metals are relatively high melting. Thus, complexes such as, illustratively calcium aluminum tetraethyl should be avoided or be present in only minor concentrations for purposes of adjusting miscellaneous properties of the electrolyte, such as density.

From the earlier description herein it will be understood that the particular selection of aluminum group complex components of the electrolyte will be dictated by a variety of factors, one of the more important being the relative conductivity and the melting point and fluidity of the resultant total system. As already indicated, in instances in which the aluminum group component is a tetrahydrocarbon complex in which all of the organo radicals are identical, the most preferred situation then is to provide a plurality of such components in admixture, as it has been discovered that such a mixture provides a relatively low melting point, and thereby contributes greatly to the effectiveness of the process. Thus an illustrative mixture highly suitable as the aluminum group metal component is a stoichiometric or equimolar mixture of sodium aluminum tetraethyl and potassium aluminum tetraethyl. Although these individual components have melting points of 128 and 88° C., respectively, the mixture thereof has a melting point of only 80° C. In the presence of a desired electrolyte composition including, for example, sodium boron tetraethyl as a component, the melting point is decreased even further so that relatively low temperature operation is permissible. Another highly effective example of an aluminum group component is a mixed alkyl tetrahydrocarbon complex. Examples of such mixed alkyl complexes, with their melting points, are sodium aluminum ethyl tri-isobutyl, below 30° C.; sodium aluminum ethyl trioctyl, below 30° C.; sodium aluminum trimethyl ethyl, 218° C.; and sodium aluminum methyl triethyl. Yet another illustrative example of a suitable secondary component is the alkali metal fluoride complex of a trialkyl aluminum, for example, the complexes of sodium fluoride-triethyl aluminum. The aluminum group metal components can be one in which all the alkyl groups are identical, and, further, only one such component can be used. For example sodium aluminium tetraisobutyl is a satisfactory low melting constituent. However, when the non-boron components of the electrolyte is a compound of this character, the conductivity of the system is not as impressive as when using as the aluminum group metal components, one of the preferred compositions previously grouped herein.

As previously mentioned, the present process can be carried out over an exceedingly wide temperature range, as low as, in some instances of 0 up to about 200° C. The upper temperature at the anode is usually limited by the decomposition temperature of the tetraorganolead produced by the process. Typically, with tetraethyllead, it is preferred to maintain the temperature below about 100 to 110° C. without thermal stabilizers. However, with thermal stabilizers, the process can be carried out up to above 200° C., or up to the normal boiling point, without appreciable decomposition.

Typical examples of effective stabilizers are disclosed in United States Patents 2,660,591 through 2,660,596 inclusive. A representative group of thermal stabilizers which can be used in accordance with this invention are butadiene, di-amylene, di-pentene, heptene, trimethylethylene, styrene, divinylbenzene, cyclohexene, dicyclopentadiene, azobenzene, 2,2'-azonaphthalene, anthracene, chrysene, naphthalene, alpha-methyl naphthalene, tetrahydronaphthalene, indene, di-isobutylene, tetramethylene, semi-carbazide, stilbene, methyl styrene, o-ethylstyrene, and lepidine. These stabilizers are normally used in amounts varying from 0.01 to about 5 percent by weight of the tetraorganolead compound and greatly increase the stability of the lead compound at more elevated temperatures.

The process of the present invention is applicable to the production of numerous organolead products, specifically, the tetrahydrocarbonlead products, these compounds being those consisting of lead, carbon and hydrogen. The products, then, can consist of tetraalkyllead materials, tetraaryl lead materials, or lead organometallics of the nature specified wherein the hydrocarbon radicals are aryl, alkaryl, aralkyl, or alkyl. As previously indicated, the predominant example of commercially important products of this character is tetraethyllead which has wide and well known usage as antiknock material for internal combustion engine fuels. Illustrative products, then, which can be produced by the process of the present invention include lead tetraethyl, lead tetraisopropyl, lead tetra n-propyl, lead tetra n-butyl, lead tetraisobutyl, lead tetraamyl, lead tetraphenyl, lead tetrabenzyl, lead tetraorthomethylphenyl, lead diethyldiphenyl, lead triethylphenyl, lead triethyl n-butyl, lead dimethyl diethyl, lead triphenyl methyl, lead triphenyl ethyl, lead tetracetyl, lead tetraisobutyl, and numerous other products.

The details of the operation of the best mode of carrying out the process and the several embodiments thereof will be readily understood from the following working examples:

Example I

An electrolytic cell was provided having a central vertically positioned anode of lead metal, and a concentric cylindrical steel cathode surrounding the anode. The electrolysis zone was filled with an electrolyte composition as follows:

Sodium boron tetraethyl, $NaB(C_2H_5)_4$	10 wt. percent.
Sodium aluminum tetramethyl, $NaAl(CH_3)_4$	90 wt. percent in equimolal proportions.
Sodium aluminum tetraethyl, $NaAl(C_2H_5)_4$	

The electrolyte of this composition is very fluid at approximately 100° C., and has a melting point of about 80° C. The temperature of this system was maintained at approximately 100° C., and direct current was passed through the lead anode, the electrolyte and into the cathode at a rate corresponding to 300 milliamps. per square centimeter. Tetraethyllead was released at the anode and was collected at the bottom of the electrolysis zone below the anode and below the liquid electrolyte. Sodium metal was deposited at the cathode and was also collected, in the liquid phase, at the bottom of the electrolysis zone adjacent the cathode. The electrolyte composition was maintained at the indicated composition during the electrolysis.

The tetraethyllead was withdrawn as a clear, relatively pure liquid. Triethyl boron was concurrently released at the anode and was released as a gaseous concurrent product. A moderate vacuum was applied to the system to facilitate removal of the boron triethyl. A high current efficiency, approaching about 90 percent, was achieved.

Example II

The foregoing operation is repeated except that, in this instance, the electrolyte composition comprises approximately 20 weight percent sodium boron tetraethyl, and sodium aluminum tetraethyl and potassium aluminum tetraethyl, the latter components being in equimolar proportions. Again, passage of direct current through the electrolyte results in efficient formation of tetraethyllead, boron triethyl and a liquid cathodic product comprising sodium with minor amounts of potassium therein.

Example III

This example illustrates the embodiment of the invention wherein the aluminum group metal component of the electrolyte is a complex of a trialkyl aluminum group metal with a metal halide. In this instance, the electrolyte composition comprises approximately sodium boron tetraethyl, and a sodium fluoride-triethyl aluminum complex, $NaF.2Al(C_2H_5)_3$, in molal proportions of 1 to 2. This system has a melting point of only about 30° C., and provides a relatively highly conductive mixture. A good conversion or yield and high current efficiency is attained in producing tetraethyllead.

Other halogen containing aluminum group metal components can be substituted for a part or all of the sodium fluoride-aluminum triethyl complex in the foregoing example, and in the other examples herein, and similar results will be obtained. Such components include sodium aluminum tetrachloride and sodium aluminum ethyl trichloride.

As previously indicated a considerable latitude is available with respect to the the organo radicals involved in applicant's process, as illustrated in the following example.

Example IV

An electrolyte composition is prepared comprising approximately equimolar concentrations of sodium boron tetraphenyl, $NaB(C_6H_5)_4$; sodium aluminum tetraphenyl, $NaAl(C_6H_5)_4$ and potassium aluminum tetraphenyl, $KAl(C_6H_5)_4$ and sufficient naphthalene to provide a melting temperature of only about 150° C. Upon electrolysis of this system at a temperature of about 160 to 180° C., a good efficiency in release of tetraphenyl lead is achieved.

Example V

In this operation the electrolyte comprises the following mixture, sodium boron tetrabenzyl, 10 mole percent; sodium aluminum tetrabenzyl, 40 mole percent; and potassium aluminum tetrabenzyl, 40 mole percent. Electrolysis is conducted with a current density of the order of about 4 milliamps. per square centimeter, the anode product including a solution of lead tetrabenzyl dissolved in boron tribenzyl. The cathode product or joint product includes a low melting mixture of sodium and potassium, which is withdrawable as a liquid. The liquid product containing lead tetrabenzyl is collected in a collection zone at the bottom of the electrolysis zone, and a stabilizer comprising naphthalene or styrene is fed to this collection zone in the proportions of about one-half percent of the lead tetrabenzyl component.

As previously mentioned, in one of the forms of the invention, the aluminum sub-group metal component of the electrolyte has a variety of different alkyl substituents thereon. Components of this character are similar, with respect to conductivity and melting point contribution to the electrolyte, to true binary mixtures of the corresponding tetraalkyl components. This variation of the process is illustrated by the following example.

Example VI

The electrolyte in this operation is a 20 mole percent concentration of sodium boron tetraethyl in an aluminum complex component comprising sodium aluminum dimethyl diethyl. The operation is at a temperature of approximately 110° C., and a good yield of concentrated tetraethyllead liquid is produced adjacent to the anode and is collected and separately withdrawn. Desirably, a thermal stabilizing compound is fed to the tetraethyllead as it is collected. Concurrently, a vapor phase of boron triethyl is released and can be withdrawn as a vapor. The cathode product in this instance is metallic liquid sodium, which also is withdrawn as a liquid.

The following example illustrates an embodiment of the invention wherein one of the organo substituents of the aluminum group metal complex component of the electrolyte is an alkoxy radical.

Example VII

In this instance the electrolyte is a mixture of one mole of potassium boron tetraethyl with two moles of potassium aluminum triethyl ethoxide. Operating generally in the manner previously described, and at a temperature of about 110° C., a good production of tetraethyllead is produced from the anode portion of the apparatus, concurrently with release of boron triethyl, and with formation of liquid potassium metal at the cathode. A stabilizer comprising allo-ocimene is added to the tetraethyllead as it is collected.

Although the process is quite operable wherein the aluminum sub-group metal contains only one component in which one radical is an alkoxy group, frequently a second aluminum sub-group metal complex containing all alkyl groups is also provided, as in the following example.

Example VIII

The electrolyte in this operation is sodium boron tetraethyl, 20 mole percent; sodium aluminum triethyl ethoxide, 10 mole percent; and sodium aluminum tetraethyl, 70 mole percent. In carrying out electrolysis of this system, according to the method described heretofore, again a good yield of lead tetraethyl is produced and sodium metal is released at the cathode. The deposition or release at the anode includes boron triethyl, which is primarily removed as a vapor or gas phase.

Numerous other alkoxy, or aroxy, compounds can be employed in the manner described above. Thus, sodium aluminum triethyl butoxide, sodium aluminum tripropyl phenoxide, potassium aluminum diethyl decyloxide can be suitably substituted in the Example VII or VIII for the sodium aluminum triethyl ethoxide.

As previously mentioned the present invention is particularly efficient in that it lends itself to continuous operation, in that, in certain preferred forms, the lead tetrahydrocarbon product is released as an already purified, or partly purified product, concurrently with gaseous evolution of a boron trialkyl product. The integrated recovery and utilization of the conjointly produced boron alkyl is illustrated by the following example.

Example IX

The electrolyte of Example I is again used, that is, ten weight percent sodium boron tetraethyl, the remainder being an equimolal mixture of sodium aluminum tetramethyl and sodium aluminum tetraethyl. As in Example I, tetraethyllead is produced in good yield and is withdrawn as a liquid product. Boron triethyl is removed in the vapor phase, and sodium is withdrawn as a liquid from a collection zone adjacent the cathode.

The triethyl boron is liquefied and collected. The sodium metal is reacted with hydrogen, forming sodium hydride, which is combined, by mixing and heating, with the boron triethyl, forming sodium boron triethyl hydride. This complex is then reacted with ethylene gas under pressure, forming sodium boron tetraethyl, which is recirculated to the electrolysis zone to maintain a uniform composition.

The preceding examples have illustrated the production of lead tetrahydrocarbon products wherein the hydro-

carbon radicals are all the same group. The process, however, is fully adaptable to the generation of lead tetrahydrocarbon products having a plurality of different radical substituents as illustrated by the following example.

Example X

An electrolyte system is prepared comprising approximately 10 weight percent sodium boron tetraethyl, the balance or remainder of the electrolyte composition being in the proportions of about 1 mole of sodium aluminum tetraisopropyl to 4 moles of sodium aluminum tetraethyl. The system is maintained in the fluid state at about 90° C., and current is passed through a lead anode, the electrolyte, and a steel cathode, as in preceding examples. A liquid lead tetraalkyl product having both ethyl and isopropyl substituents is produced. The exact ratio of the isopropyl and ethyl radicals on the gross lead tetraalkyl product is a function of the relative total concentrations of the corresponding alkyl groups in the electrolyte. Generally, for formation of equal quantities of alkyl groups of different character, the concentration of the higher alkyl group, can be substantially lower, in the electrolyte system, than desired in the lead tetraalkyl product.

Similar principles control the production of lead tetrahydrocarbon products having both alkyl and aryl radical substituents, such as lead diethyldiphenyl, lead triethylphenyl, and others.

Although the preceding examples illustrate the invention employing, as the aluminum group metal component of the electrolyte, an aluminum complex compound, other metals in this category are suitable for this purpose. In some instances, the other metals, such as gallium, indium, or thallium, may be even more effective than a corresponding aluminum compound, since the aluminum group metal complex is not consumed in the process, and hence a high cost represents principally an inventory cost. An example of this alternative type of operation follows:

Example XI

The process of Examples I, II, and III are repeated, respectively, except that the corresponding gallium metal complex is employed. Similar results are obtained. Comparable substitution in Examples I–IV, and in the other examples, of the complexes of indium or thallium for the aluminum complex component specifically illustrated, also provides satisfactory results.

From the foregoing description and examples, it is seen that the present invention provides a highly effective and efficient electrolytic method for the production of tetrahydrocarbon compounds of lead. The reason for the effectiveness of the process is not fully understood. It is found that the conjoint presence of the alkaline metal boron complex and one or more of the aluminum group metal complexes provides significantly improved properties, over the corresponding composition in the absence of, or free of, the boron containing complex, with respect particularly to the melting point and fluidity. In some instances the electrical conductivity is greater with the boron complex present, whereas in other instances the conductivity is lower, particularly if a high concentration of the boron complex is employed. It is not exactly certain what the mechanism of the process is. Thus it is believed that the electrolysis can be actual electrolysis of either the boron component, or of both the boron component and the aluminum group metal complex component, or of the latter, dependent upon the specific compositions of the electrolyte. The aluminum group trihydrocarbon compounds are capable of reacting with the alkali metal boron tetrahydrocarbon compound, displacing a boron trihydrocarbon moiety as such. As already demonstrated, the embodiments of the process wherein the boron trihydrocarbon compound is a volatile material admits of the pronounced advantage of immediate removal from the electrolysis zone by vaporizing.

It will be apparent from the preceding description that the relative concentration of an alkali metal boron organocomplex in the electrolyte system is not highly critical. The usual concentration is of the order of at least about a percent to not over about 50 mole percent of the gross electrolyte, the preferred range being from about around 5 mole percent to about 25 mole percent. Concentrations significantly above this level become less desirable because of the, generally, higher melting points of the boron complexes relative to the corresponding aluminum group metal complexes, which introduces the problems of maintenance of temperature and avoidance of thermal decomposition of the organolead product. It will be understood that the electrolysis, in fact, is continually resulting in a change in composition of the electrolyte, unless, as mentioned in the preceding examples, a make-up is continually provided to compensate for the boron trihydrocarbon compound released concurrently at the anode, plus the alkali metal deposited at the cathode. In certain cases, some aluminum group metal trihydrocarbon product is also released by the process. In such instances, make-up of the corresponding constituent is also necessary.

In the preferred embodiments wherein the non-boron portion of the electrolyte is a mixture of at least two discrete aluminum group metal complexes, the relative proportions of said secondary components is not of great criticality. It is found that in all instances, the binary mixture will exhibit a particularly low melting or eutectic composition, usually involving compositions of approximately equimolar proportions. Frequently, this proportion is used, and in addition, the concentration of the boron complex component can be adjusted to correspond to a ternary eutectic. It is, however, unnecessary to delicately adjust the compositions to achieve precisely such a status, except in a very few instances. Examples of instances in which the non-boron portion of the electrolyte is a mixture of two components are Examples I, II, IV, and V.

As previously discussed, the usual temperatures of operation are in the neighborhood of 50 to 150° C., although the preferred range is from about 80 to 120° C. The actual temperature encountered during operation is a function of a number of factors, principally or most importantly, the melting point of the electrolyte system. Generally, the melting points are lowest for the ternary systems involved in the present invention, that is those systems wherein in addition to the alkali metal boron complex organometallic, the aluminum group metal is present as two additional components as in, for example, working Examples I, II, IV, V and VIII. The particular identity of the components is also of significance in effecting the temperature of operation, thus, components having larger alkyl radicals are lower melting than corresponding lower alkyl components. The alkali metal present in the complex is also of significance, although there is no inflexible or rigorous pattern for such effect. Ordinarily, the potassium compounds are lower melting than the corresponding sodium complexes, but in the case of tetramethyl complexes, it appears that the lithium alkali metal complex is lower melting than the sodium material. Another factor which affects the temperature of any explicit operation is the current density actually produced in the operation. The current density, it will be understood, is a function of the impressed voltage on the system, which can be as low as 4 volts with some installations successfully operating as high as 20 volts in a system such as in Example I. The higher voltages are employed when higher capacity, higher temperature, or higher production are to be gained. The higher current flow results in higher generation of heat within the system by normal resistance loss. Illustrative current densities can be from as low as 5 up to cover 300 milliamps. per square centimeter.

The operation of the present process can be conducted

at sub-atmospheric, atmospheric, or supra-atmospheric pressures. The pressure involved is not material to the electrolysis as such, but is of great significance with respect to recovery operations, particularly in those favored embodiments of the process wherein a conjoint separation of the lead tetraorgano product from the jointly released non-lead organometallic is desired. As previously described and illustrated by the examples, a highly preferred embodiment involves the removal from the electrolysis zone of a boron triorgano material as a vaporized component. This embodiment is particularly of value when the boron organometallic released is, for example, boron trimethyl or boron triethyl. These components being of substantially lower boiling point than the corresponding lead tetraalkyl compounds, can be removed by a simple vaporization, which requires an operating temperature equal to the boiling temperature of the boron trihydrocarbon compound at the operating pressure involved. Ordinarily, it will be satisfactory to utilize atmospheric pressure, but it is preferred to apply a moderate vacuum, of the order of, say 50 to 350 millimeters of mercury absolute pressure on the system. This allows a clean and rapid withdrawal of a vaporized boron trialkyl from the electrolyte zone.

Hydrocarbons are used frequently as components of the electrolyte. In those instances when the lead tetraorgano product is a high melting compound, as, for example, lead tetraphenyl or lead tetrabenzyl, the provision of a stable hydrocarbon solvent is helpful, to dissolve the lead organo product on its formation on the lead anode. When the solvent is an aliphatic hydrocarbon, a separate liquid phase containing the product is readily isolated and removed. Aromatics, on the other hand, tend to solubilize the lead organo product in the electrolyte bath. Certain of the electrolyte systems employed in the present invention are soluble in such aromatic hydrocarbon solvents, and, a stable solvent such as diphenyl, xylene, or toluene, is frequently highly desirable as an additive to high melting electrolyte systems. Sodium aluminum tetraethyl and other higher alkyl complexes of an alkali metal with an aluminum group metal are also soluble or partly soluble in such materials. Thus, anhydrous solvents are, then, frequently, helpful in improving the fluidity of a particular system and in lowering the melting point. However, the presence of an aromatic liquid of this character decreases the specific conductance of an electrolyte and thus has a disadvantage in this regard.

There is no particularly critical form of apparatus necessary to carry out the process of the present invention. Parallel plate electrodes, the anode being a lead plate, can be effectively used. Alternatively, in many cases, it will be desired to employ electrode pairs in which the cathode is a central electrode and the lead anode is a cylindrical shape concentric with the cathode. The lead anode is a reactant in the process and should provide a relatively high surface relative to the actual weight of the lead in the electrolysis zone. Hence, thin plates or thin walled cylinders are highly desirable configurations. In the most effective forms of the process, provision is made for continuously supplying a fresh anode material to the process.

Suitable collection zones for liquid products are incorporated in the electrolysis space. For example, a sump, or well, below the lead anode, is desirably provided for the tetrahydrocarbon lead products.

The electrical power for an installation can be supplied by any convenient source of direct current. Normally, a plurality of electrolysis cells are operated in series, because of the relatively low operating voltage required at each zone. The current supply is usually of a virtually non-pulsating type, but occasionally a pulsating source is found desirable.

Suitable materials of construction for the cathode can be carbon, or ferrous or non-ferrous metals. In those instances in which the process is maintained under partial pressures or pressures of below one atmosphere, the entire electrolysis zone is usually provided with an enclosing cover so that a volatile boron trialkyl can be readily withdrawn. It is not essential to isolate the application of negative pressures or vacuums to a zone adjacent the lead anode, because the components of the electrolyte, being salt-like materials, have virtually no vapor pressure. In addition, the materials deposited at the cathode are either liquid or solid metal materials and hence are not vaporized from the electrolysis zone.

Having fully described the method and compositions of the present invention, what is claimed is:

We claim:

1. A process for the manufacture of a lead tetrahydrocarbon comprising electrolyzing in the presence of a lead anode an anhydrous electrolyte consisting essentially of an alkali metal boron tetrahydrocarbon complex and an alkali metal aluminum group metal organometallic complex, said complex having at least three hydrocarbon radicals, and thereby forming a cathode product consisting essentially of an alkali metal, and anode products consisting essentially of a lead tetrahydrocarbon and a boron trihydrocarbon compound.

2. A process for the manufacture of a lead tetraalkyl comprising electrolyzing in the presence of a lead anode an anhydrous electrolyte consisting essentially of a sodium boron tetraalkyl, a sodium aluminum tetraalkyl and a potassium aluminum tetraalkyl, and thereby forming a cathode product consisting essentially of sodium and potassium, and anode products consisting essentially of tetraalkyllead and a boron trialkyl.

3. A process for the manufacture of a lead tetraalkyl comprising electrolyzing in the presence of a lead anode an anhydrous electrolyte consisting essentially of a sodium boron tetraalkyl and a sodium aluminum tetraalkyl, the alkyl radicals of the said aluminum compound being selected from the group consisting of methyl and ethyl and including at least a methyl and an ethyl radical, and forming thereby a cathode product consisting essentially of sodium, and anode products consisting essentially of a lead tetraalkyl and a boron trialkyl.

4. A process for the manufacture of a lead tetraalkyl comprising electrolyzing in the presence of a lead anode an anhydrous electrolyte consisting essentially of an alkali metal boron tetraalkyl and an alkali metal halide complex of an aluminum trialkyl, forming thereby a cathode product consisting essentially of alkali metal and anode products consisting essentially of a lead tetraalkyl and a boron trialkyl.

5. The process of claim 4 further defined in that the alkali metal halide complex with an aluminum trialkyl compound is a sodium fluoride complex with aluminum triethyl.

6. A process for the manufacture of a lead tetraalkyl comprising electrolyzing in the presence of a lead anode an anhydrous electrolyte consisting essentially of an alkali metal boron tetraalkyl and an alkali metal aluminum tetraorgano complex compound, the organo radicals thereof including one radical selected from the group consisting of alkoxy and aroxy, and the other radicals being alkyl radicals, forming thereby a cathode product consisting essentially of the alkali metal and anode products consisting essentially of a lead tetraalkyl and a boron trialkyl.

7. A process for the manufacture of lead tetraethyl comprising electrolyzing in the presence of a lead anode, an anhydrous electrolyte consisting essentially of sodium boron tetraethyl, sodium aluminum tetraethyl and sodium aluminum triethyl ethoxide, forming thereby a cathode product consisting of sodium, and anode products consisting essentially of lead tetraethyl and boron triethyl.

8. An electrolyte composition for manufacture of lead

tetraethyl consisting essentially of an anhydrous liquid mixture of sodium boron tetraethyl and sodium aluminum tetramethyl and sodium aluminum tetraethyl, the sodium boron tetraethyl being in the proportion of about 5 to 25 mole percent and the sodium aluminum tetramethyl and sodium aluminum tetraethyl being in approximately equimolal proportion.

9. An electrolyte composition for use in the production of lead tetraalkyl compounds consisting essentially of an alkali metal boron tetraalkyl complex and at least one additional alkali metal aluminum complex component, said aluminum component being selected from the group consisting of

(i) an alkali metal-aluminum group metal tetraalkyl complex, the hydrocarbon radicals thereof consisting of methyl and another alkyl radical, and including at least one methyl and at least one of said other alkyl radical,

(ii) a mixture of an alkali metal aluminum tetramethyl complex and an alkali metal aluminum nonmethyl tetraalkyl complex,

(iii) a mixture of two aluminum tetraalkyl complexes of different alkali metals,

(iv) an alkali metal halide aluminum trialkyl complex, and

(v) an alkali metal aluminum tetraorgano complex, the organo radicals including one radical selected from the group consisting of alkoxy and aroxy, and three alkyl radicals.

10. A process for the manufacture of lead tetraethyl comprising electrolyzing in the presence of a lead anode an electrolyte consisting essentially of sodium boron tetraethyl, sodium aluminum tetraethyl, and sodium aluminum tetramethyl, forming a cathode product consisting essentially of sodium and anode products consisting essentially of lead tetraethyl and boron triethyl, withdrawing separately the cathode product and the anode products, reacting the sodium with hydrogen and forming sodium hydride and then reacting the said sodium hydride with the boron triethyl to form a complex therewith, and reacting the said complex with ethylene and forming sodium boron tetraethyl and returning the sodium boron tetraethyl to the electrolyte.

References Cited in the file of this patent

UNITED STATES PATENTS

2,849,349 Ziegler et al. ---------- Aug. 26, 1958

FOREIGN PATENTS

214,834 Australia ---------- Apr. 24, 1958