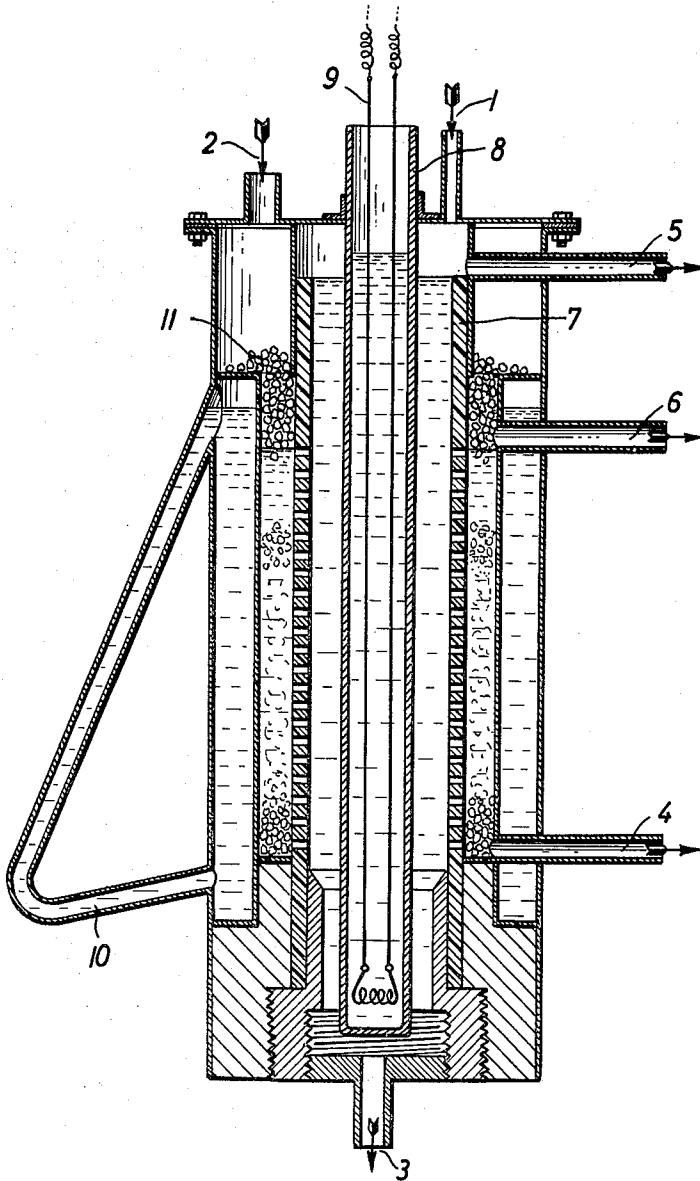May 31, 1966   K. ZIEGLER ET AL   3,254,009

PRODUCTION OF METAL ALKYLS

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3,254,009
PRODUCTION OF METAL ALKYLS
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6,509; Feb. 14, 1958, 6,510
52 Claims. (Cl. 204—59)

This application is a continuation of application Serial
No. 129,195, filed July 25, 1961, now abandoned, and
which was a continuation-in-part of applications Serial
No. 792,467, filed February 11, 1959, and 792,614, filed
February 11, 1959, both now abandoned.

This invention relates to new and useful improvements
in the production of metal alkyls and particularly of
alkyls of the metals lead, tin, antimony, bismuth, zinc,
cadmium, mercury. One preferred embodiment of the
invention concerns the production of lead tetraalkyls.

In the production of metal alkyls use is frequently
made, as alkylating agent, of complex aluminum com-
pounds having the grouping Me[Al(R')₃—] in which
Me is an alkali metal and R' is alkyl. Thus mixtures of
the desired metal alkyl with aluminum trialkyl are often
obtained. The separation of the desired alkyl metal com-
pounds is often connected with difficulties because of the
relative closeness of boiling points of the components
and/or the formation of hydrides and their deteriorat-
ing influence upon the alkyl compounds.

Such mixtures are for instance typically formed in the
electrolytic production of metal alkyls and especially
alkyls of the metals lead, tin, antimony, bismuth, zinc,
cadmium, mercury.

Thus, when subjecting an alkali metal aluminum alkyl
complex, as for instance sodium or potassium aluminum
tetraethyl to electrolysis using one of these metals, such
as, for instance lead, as the anode, the corresponding
metal alkyl compounds, such as tetraalkyl lead are
formed. Trialkyl aluminum is formed or liberated at the
same time. If the alkali metal aluminum tetraalkyl com-
pound was a tetraethyl compound, triethyl aluminum is
liberated which establishes its own independent liquid
layer and does not intermix with the sodium aluminum
tetraethyl complex which under the conditions of re-
action is normally present in molten condition. The
aluminum trialkyl, and particularly aluminum triethyl,
may thus be readily separated from the metal aluminum
tetraalkyl complex. On the other hand, the separation
of the aluminum trialkyl and particularly of the alumi-
num triethyl from the other metal alkyl compounds,
and particularly the metal ethyl compounds, which are
formed during electrolysis, offers in most cases consid-
erable difficulties. This is particularly true for the mix-
ture of lead tetraalkyl and aluminum trialkyl and most
specifically for lead tetraethyl and aluminum triethyl be-
cause the boiling points of these products are normally
so relatively closely adjacent that separation by distilla-
tion of mixtures of these materials is difficult if not im-
possible. Furthermore, mixtures of tetraalkyl lead and
aluminum trialkyl and particularly mixtures of tetraethyl
lead and aluminum triethyl will decompose relatively
readily because the lower aluminum trialkyls and par-
ticularly aluminum triethyl will slowly degenerate with
heat, being dissociated into dialkyl aluminum hydride
and the corresponding hydrocarbon. Thus, a mixture of
tetraethyl lead and triethyl aluminum will, with heat,
form diethylaluminum hydride and ethylene. Further-
more, such diethylaluminum hydride has a reducing effect
upon the tetraethyl lead converting the same to metallic
lead with the formation of ethane.

One object of the invention comprises an improvement

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in the production of metal alkyls with an alkylating agent
having the general grouping Me[Al(R')₃—], such that
there is substantial freedom from trialkyl aluminum in
the product containing the formed metal alkyl.

Other objects of the invention comprise processes sub-
stantially assuring such freedom from trialkyl aluminum
respectively in avoidance of its formation, by conversion
as it is formed and by conversion after its formation.

A further object of the invention comprises a novel
process for the separation of metal alkyls from alumi-
num-trialkyls in mixtures containing the same.

Still further objects of the invention comprises novel
electrolytic processes for the production of metal alkyls.

The foregoing and still further objects of the inven-
tion will be apparent from the following description:

In accordance with the broadest aspect of the inven-
tion, a metal alkyl production with the use of an alkyl
radical supplying agent having the general grouping
Me[Al(R')₃—] is effected, at a point between the metal
alkyl formation and the separation of formed metal alkyl,
in the presence of a complex compound of the general
formula: Me[Al(R')₃OR] in which Me is an alkali metal
of the group consisting of sodium and potassium, R' is
an alkyl radical with up to 6 carbon atoms and R is an
organic radical selected from the group consisting of
alkyl and cycloalkyl radicals to thereby substantially
assure freedom from AlR'₃ and to react said complex
compound to form AlR'₂OR.

As shown below in greater detail, one limiting case
of the metal alkyl production in accordance with the in-
vention is that in which the alkylating agent itself is said
alkali metal alkyl aluminum alkoxy complex compound.
In that case the formation of trialkyl aluminum is avoided
ab initio as for instance in an electrolytic alkylation in
which the metal of the desired metal alkyl is used as
anode and the said complex compound constitutes the
electrolyte. The other limiting case is that in which a
mixture of the desired metal alkyl and aluminum tri-
alkyl (regardless of its derivation) is present and is to
be used for the metal alkyl production. In that case
the trialkyl aluminum is eliminated by reaction with said
alkoxy complex compound i.e. it is converted to an alkali
metal tetraalkyl aluminum complex compound. This is
accomplished in an electrolytic alkylation in which the
metal of the desired metal alkyl is used as anode and
an alkali metal aluminum tetraalkyl is employed as al-
kylating electrolyte. The trialkyl aluminum containing
electrolysis product being acted with said alkoxy complex
compound for the elimination of the aluminum trialkyl.
A further case of metal alkyl production in accordance
with the invention is presented by conducting the alkyla-
tion, as for example electrolytic alkylation, with the use
of alkali metal tetraalkyl aluminum and said alkali metal
trialkyl aluminum alkoxy complex compound. In that
case the products resulting from the alkylation are sub-
stantially free from trialkyl aluminum.

In accordance with an embodiment of the invention a
mixture containing aluminum trialkyl and an alkyl of a
metal other than aluminum is reacted with a complex
compound of the general formula Me[Al(R')₃OR], in
which Me is an alkali metal preferably sodium or potas-
sium, R' is an alkyl radical up to 6 carbon atoms and
advantageously a straight chain alkyl radical with up to
4 and preferably 2–4 carbon atoms and in which R is
a member of the group consisting of alkyl and cyclo-
alkyl radicals, the alkyl radicals having advantageously
2 to 12 preferably 2 to 8 and especially 4 carbon atoms.
This reaction results in the substantial conversion of the
trialkyl aluminum as for instance illustrated in accord-
ance with the following general equation:

$$AlR'_3 + Me[Al(OR)R'_3] \rightarrow Me[AlR'_4] + Al(OR)R'_2$$
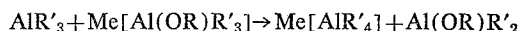
The reaction thus results in the elimination of the tri-alkyl aluminum compound and the formation of an alkali metal tetraalkyl aluminum compound and an alkoxy aluminum dialkyl compound in admixture with the desired metal alkyl compound. This mixture may now be further treated for the separation, such as by distillation of the desired alkali metal compound. The invention in its application readily lends itself to the separation of the alkyls and particularly lower alkyls of the metals lead, zinc, mercury, cadmium, antimony, bismuth and tin. Specific examples are, for instance, lead tetraethyl, zinc diethyl, mercury diethyl, cadmium diethyl, antimony triethyl, bismuth triethyl, tin tetraethyl, lead tetramethyl, and the corresponding propyl and higher and lower alkyl derivatives of these metals. By a suitable selection of the residue OR the boiling points of the components of the mixture containing the desired metal alkyl may be fixed at any desired, suitable differential so that separation by distillation may be readily accomplished.

One electrolytic embodiment of the invention concerns the electrolytic production of alkyls of metals other than aluminum and particularly of the metals lead, tin, antimony, bismuth, zinc, cadmium, mercury and especially of lead tetraalkyls from complex compounds of the general formula $Me[Al(R')_4]$ in which Me and R' have the above given connotation. When proceeding in this manner, the metal, as for instance, lead, of which the alkyl compound is to be produced is used as the anode together with the alkali metal aluminum tetraalkyl compounds preferably present in substantially molten condition as the electrolyte. The preferred electrolyte is a mixture of potassium and sodium aluminum tetraalkyl compounds with the potassium component predominating. This increases the electric conductivity of the electrolyte. There is anodically produced a mixture of n mol aluminum trialkyl, where n is the valence of the metal the alkyl compound of which is produced, and lead tetraalkyl, such as, for instance 4 mol aluminum triethyl and lead tetraethyl which is practically insoluble in the electrolyte mixture of, for instance, potassium and sodium aluminum tetraethyl with the potassium component predominating. Such a mixture is, therefore, readily separable from the electrolyte. The resulting mixture is, on the other hand, not readily separable by distillation into its components for the recovery of the desired metal alkyls because, for instance, aluminum triethyl and tetraethyl lead have boiling points that are closely adjacent. If, however, in accordance with the invention, there is added to this mixture 4 molecules of alkali metal alkoxy-aluminum-triethyl, immediately the following double reaction takes place:

$$Al(C_2H_5)_3 + Me[Al(OR)(C_2H_5)_3]$$
$$\rightarrow Me[Al(C_2H_5)_4] + Al(OR)(C_2H_5)_2$$
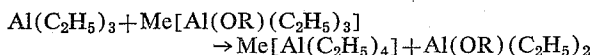
In accordance with this reaction the tetraethyl lead is mixed with the alkoxy-aluminum-diethyl while the alkali metal aluminum tetraethyl, in case the same is sodium, for instance, will separate at temperatures above 110° C. as a liquid layer while the same will be separated in substantially solid form when operating at temperatures below 110° C. A separation of the mixture of tetraethyl lead and the diethyl-alkoxy-aluminum is then readily possible. Tetraethyl lead may be removed by distillation, particularly with the suitable selection of the OR to assure an advantageous boiling point differential. Good results are thus obtained when there is selected for R a butyl radical. Instead of first separating the alkali metal tetraalkyl aluminum electrolyte, as for instance, aluminum tetraethyl sodium, the mixture containing the three components may be subjected to distillation for the removal of the tetraethyl lead whereupon the alkoxy aluminum dialkyl, such as the alkoxy-aluminum-diethyl, is distilled off or separated out by mechanical separation of nonmiscible phases. The sodium aluminum tetraethyl is returned to the electrolyte and balances the amount

of this material used up in the electrolysis. The compound of the general formula $ROAl(C_2H_5)_2$ may then be worked up and reconverted into the compound

$$Na[Al(OR)(C_2H_5)_3]$$

as below set forth in detail in connection with an alternative embodiment of the invention.

An alternative electrolytic embodiment of the invention concerning the electrolytic production of alkyls of metals other than aluminum and particularly of lead, tin, antimony, bismuth, zinc, cadmium, mercury and especially of lead tetraalkyls resides in the use as electrolyte of the said complex compound of the general formula $Me[Al(R')_3OR]$, using as anode, the metal of which the desired alkyl is to be formed. When proceeding in this manner, metallic potassium or preferably sodium are deposited at the cathode, either as such or in the form of their alloys, while there is deposited at the anode a mixture of the alkyl compound of the metal of the anode together with n molecules of the compound of the formula $Al(R')_2OR$, n being the valence of the metal in the formed metal alkyl. In the case of, for instance, a lead anode and an alkali metal alkoxy aluminum triethyl, as the material in the electrolysis, there results at the anode a mixture composed of tetraethyl lead and four molecules of the compound $Al(C_2H_5)_2OR$. The equation of the complete chemical reaction involved in the electrolysis is in this case as follows:

$$4Me[Al(C_2H_5)_3OR] + Pb + \text{Electric Energy}$$
$$= 4Me + 4Al(C_2H_5)_2OR + Pb(C_2H_5)_4$$
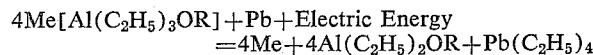
Besides the alkali metal there is obtained as reaction product a mixture of alkoxy aluminum dialkyl compounds and the desired metal alkyl. This mixture, however, can easily be separated by distillation because of the higher boiling point of the aluminum alkoxy compound compared with aluminum trialkyl compound.

In this manner the alkyl of other metals, such as zinc, mercury, cadmium, antimony, bismuth, and tin, may be conveniently obtained. Specific examples are thus, for instance, lead tetraethyl, zinc diethyl, mercury diethyl, cadmium diethyl, antimony triethyl, bismuth triethyl, tin tetraethyl, and the corresponding propyl and lower and higher alkyl derivatives of these metals.

The compounds of the formula $ROAl(R')_2$ do normally not possess the reactivity of aluminum trialkyls. Especially, they will not give the characteristic sodium fluoride compounds of the aluminum trialkyls which possess an excellent conductivity. Accordingly the electrolytic conductivity of the complex compounds of the formula $Me[Al(R')_3OR]$ is relatively bad so that when electrolyzing these compounds alone a relatively high current consumption will have to be taken into account. In spite of the higher current consumption, the advantages of the process according to the invention are so considerable because of the facilitated separability of the reaction products, that in comparison thereto the disadvantages are unimportant.

The current consumption may be appreciably lowered when using as the electrolyte a mixture of the complex compounds $Me[Al(R')_3OR]$ with complex compounds of the general formula $Me[Al(R')_4]$ of which the latter possess a much better conductivity. For this reason there is to be used as the principal electrolyte a compound of the formula $Me[Al(R')_4]$ to which the compound of the formula $Me[Al(R')_3OR]$ has been given as an addition.

When using a compound of the formula $Me[Al(R')_4]$ in which Me is sodium, it presents the considerable advantage that the electrolysis may be so regulated that metallic sodium can be obtained at the cathode in a continuous liquid phase. The corresponding potassium compounds do present somewhat more difficulty in this respect in their cathodic separation but do have a considerably higher current conductivity than the sodium com-

pounds. For this reason best electrolytes are composed of the potassium aluminum tetraalkyls and sodium alkoxy aluminumtrialkyls. If the electrolyte contains more sodium than corresponds to the last named compound, the same consists of the following three components:

$$K[Al(R')_4], Na[Al(R')_4]$$

and

$$Me[Al(R')_3OR]$$
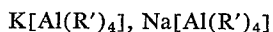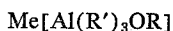
For the practical operation of the electrolysis, it is important that the alkyl metal, such as the tetraalkyl lead, and in a specific case, the tetraethyl lead is readily separable from the alkoxy-aluminumdiethyl or other dialkyl compound. By a suitable selection of the residue OR the boiling points of both components may be fixed at any desired, suitable differential. In selecting OR, however, it may be necessary to obtain an optimum compromise. OR should not be too small because otherwise the boiling point will be too low. OR, on the other hand, shall not be too large because otherwise the "ballast" of the OR which is otherwise immaterial for the process becomes too large and the conductivity of the complex electrolyte will be reduced. As compound for the production of, for instance, tetraethyl lead, the butoxy-diethylaluminum may be used successfully. The 1:4 mixture $Pb(C_2H_5)_4$-$(C_2H_5)_2AlOC_4H_9$ has the weight proportionate composition ratio of 323:632, that is, the same consists of approximately ⅓ of tetraethyl lead and ⅔ of the butoxydiethyl-aluminum. A simple single and very easily entirely continuously conductible distillation will yield the lead compound as the distillate and the lead free aluminum compound as the residue. In this manner, the problem of the separation of the tetraethyl lead is solved in the most simple manner. Appropriately, there should be used in this case as an essential component of the electrolyte preferably a compound

$$Me[Al(C_2H_5)_3OC_4H_9]$$

It is, of course, understood that depending upon the reaction conditions other corresponding compounds may be used in accordance with the invention.

An important advantage of the use of the compounds of the general formula $Me[Al(R')_3OR]$ is that their mixtures with, for instance tetraalkyl lead, and especially tetraethyl lead and corresponding metal alkyls do not tend towards decomposition with heat.

The compounds of the general formula
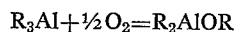
$$Me[Al(R')_3OR]$$

may be produced in various ways. One mode of production comprises the reaction of complex compounds of the formula $Me[Al(R')_4]$ with alcohols in accordance with the following equation:

$$Me[Al(R')_4]+HOR=Me[Al(R')_3OR]+HR'$$
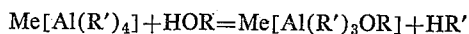
A further possibility is the reaction of aluminum trialkyl with sodium or potassium alcoholates in accordance with the following equation:

$$Al(R')_3+MeOR=Me[Al(R')_3OR]$$
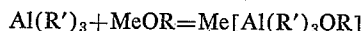
A still further possibility is the careful oxidation of aluminumtrialkyls with exactly ½ mol of oxygen whereby, however, only compounds are obtained in which R=R'. In accordance with an appropriate equation the reaction may be expressed as follows:

$$R_3Al+\tfrac{1}{2}O_2=R_2AlOR$$

A suitable method for the production of compounds of the general formula $Me[Al(R')_3OR]$ proceeds from the compound $(R')_2AlOR$ obtained at the anode during the electrolysis and the reaction of this compound with aluminumtrialkyl and sodium or potassium in accordance with the following equation:

$$3(R')_2AlOR+Al(R')_3+3Me=3Me[Al(R')_3OR]+Al$$
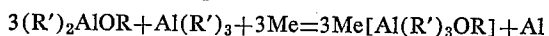
The aluminum obtained when proceeding in this manner may then be converted in known procedure into aluminum trialkyl.

The best possibility for the purpose of producing or regenerating compounds of the general formula
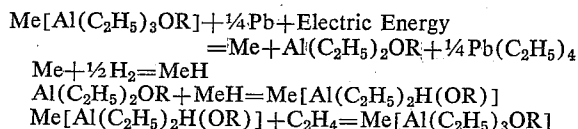
$$Me[Al(R')_3OR]$$
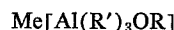
is the addition of alkali metal hydrides to the compounds of the general formula $(R')_2AlOR$ which are produced at the anode and to react the addition products with ethylene or olefins of the type $C_nH_{2n+1}-CH=CH_2$ whereby in the case of ethylene compounds, for instance, the following reaction takes place:

$$MeH+(C_2H_5)_2AlOR=Me[(C_2H_5)_2AlHOR]$$
$$Me[(C_2H_5)_2AlHOR]+C_2H_4=Me[(C_2H_5)_3AlOR]$$
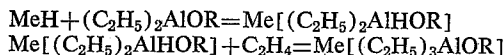
The practical execution of this embodiment may be effected by transferring the spent electrolyte, or, when operating with a diaphragm separating the cathode and anode spaces, the catholyte, together with the sodium or potassium into a pressure reactor and, after the addition of the compound $(C_2H_5)_2AlOR$ obtained in the anode space, convert by treatment with hydrogen into the compound $Me[(C_2H_5)_2AlH(OR)]$ and to treat the same with ethylene. The amount of alkali metal separated at the cathode during the electrolysis is just sufficient for this regeneration.

The treatment with ethylene is preferably carried out at 130 to 220° C., particularly 150 to 200° C. with a pressure of up to 100 atmospheres, particularly 1 to 20 atmospheres.

In accordance with the above-described manner, a substantially closed cycle process may be carried out in accordance with the illustrated cycle for, for instance, tetraethyl lead:

$$Me[Al(C_2H_5)_3OR]+\tfrac{1}{4}Pb+Electric\ Energy$$
$$=Me+Al(C_2H_5)_2OR+\tfrac{1}{4}Pb(C_2H_5)_4$$
$$Me+\tfrac{1}{2}H_2=MeH$$
$$Al(C_2H_5)_2OR+MeH=Me[Al(C_2H_5)_2H(OR)]$$
$$Me[Al(C_2H_5)_2H(OR)]+C_2H_4=Me[Al(C_2H_5)_3OR]$$

This cycle may be considered as an electrolysis of alkaliethyl in the compound $Al(C_2H_5)_2OR$ as solvent with a lead anode.

The potassium aluminumtetraalkyl useable in accordance with the invention may be obtained in a relatively simple manner by reaction of sodium aluminumtetraalkyl with potassium chloride in accordance with the following equation:

$$Na[Al(R')_4]+KCl=NaCl+K[Al(R')_4]$$
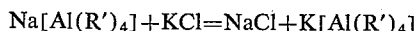
For this purpose the molten sodium complex compound is stirred with powdered potassium chloride at about 120° C. whereupon the same is decanted from undissolved sodium chloride. By use of less than one mol of potassium chloride, in accordance with the above equation, any desired ratio of sodium to potassium complex may be obtained.

Even with a relatively high potassium content, up to about 80% potassium calculated on the whole alkali metal content, there will first appear at the cathode only molten sodium. Nevertheless, the conductivity can be increased by the use of the potassium compound by about 100%.
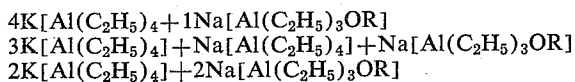
It is of advantage to so regulate the electrolysis conditions that liquid alkali metal is separated at the cathode. This may be achieved by operating the cathode cell at at least 100° C. since sodium will melt at 96° C. Procedural conditions at which substantially pure or almost pure potassium would be separated at the cathode are not always as desirable.

The cathodically deposited sodium runs downwardly on the cathode as a liquid film and can there easily be removed from the electrolytic device.

In a particularly advantageous and simple form of electrolysis arrangement, the anode and cathode are

vertically concentrically arranged tubes, the anode portion being composed of perforated electrically insulated material behind which the metal to be dissolved is arranged in the form of granules. The diaphragm is equally present in tubular form and is inserted between anode and cathode. For purposes of the invention, the electrolysis itself may be thus constituted relatively simply. The anode space may be appropriately separated from the cathode space by a diaphragm. There is then preferably used an anolyte and catholyte of substantially the same composition. The anolyte is advantageously saturated with $(R')_2AlOR$ so that upon electrolysis, already the first small amount of the metal alkyls and of the compounds of the formula $(R')_2AlOR$ which are formed will separate in substantially liquid form.

A valuable composition of the electrolyte for the production of the ethyl compounds of different metals, best expressed in mol percent by way of the ions in question, may be the following: Sodium 100 to 20%, potassium 0 to 80%, $[(C_2H_5)_4Al]^-$ 95 to 50%, $[(C_2H_5)_3AlOR]^-$ 5 to 50%. Suitable electrolytes are, for instance, the following mixtures, indicated in mols:

$$4K[Al(C_2H_5)_4]+1Na[Al(C_2H_5)_3OR]$$
$$3K[Al(C_2H_5)_4]+Na[Al(C_2H_5)_4]+Na[Al(C_2H_5)_3OR]$$
$$2K[Al(C_2H_5)_4]+2Na[Al(C_2H_5)_3OR]$$

Particular advantages are obtained in accordance with the invention by not adding the alkali metal alkoxy aluminum compound to the electrolyte before the beginning of the electrolysis. Said alkali metal alkoxy aluminium compound is rather added preferably continuously to the electrolyte during the electrolysis in such amounts sufficient for the desired reaction, i.e. in such amounts as used up by the electrolytic reaction. In this manner it is possible to work constantly with maximum conductivity. It is furthermore of advantage to maintain a relatively small distance from the cathode or anode and to select the same, for instance, from 1 to 5 centimeters. Still further it is of advantage to use a current flow of electrolyte such that a relatively weak current of flow passes from the cathode to the anode space which may be, for instance, accomplished by arranging the electrolyte level in the cathode space higher than that in the anode space. It is finally possible to operate with electrolytic cells similar to those described in U.S. applications Serial Nos. 548,862 filed November 25, 1955, now Patent No. 2,985,568, and 740,623 filed June 9, 1958, now Patent No. 3,069,334.

The separation of the metal alkyls produced in accordance with the invention from the aluminum organic materials of the type AlR'_2OR and from the electrolyte has been described here in its modus of operation as it is used in accordance with the lower alkyl compounds and especially for tetraethyl lead and in which advantage is taken of the two layer separation of the anolyte in the course of the electrolysis, one of which layers then contains the principal portion of the metal alkyl produced in accordance with the invention. This two layer procedure is not an absolute necessity, however. It is also possible to obtain by vacuum distillation of the total anolytes the desired metal alkyl from both the compound AlR'_2OR and the metal alkyl. This is indicated particularly for those cases where layer separation does not occur which is especially true in the case, when the electrolyte contains compounds of the general formula $Me[Al(R')_3OR]$ in high concentrations.

A particularly preferred method according to the invention is carried out by electrolyzing the mixture of the electrolyte compounds in a cell under vacuo, whereby the metal alkyl formed or the metal alkyl together with the alkoxy aluminum dialkyls is continuously distilled off. Under these circumstances it is not necessary to employ a diaphragm in the electrolytic device.

The practical operability of the method is for an alkyl radical corresponding to about hexyl. Electrolytes with

higher alkyl possess such a relatively low conductivity that current consumption is much too high.

The second described electrolytic embodiment of the invention possesses a number of considerable advantages. One of the principal benefits is the relatively simple, readily immediate separability of the desired metal alkyls from the electrolysis by-products, which are formed in accordance with the invention, which advantage is particularly true and of great value for the production of tetraalkyl lead such as tetraethyl lead. A further advantage resides in the preferred embodiment involving the regeneration of compounds of the general formula $Me[Al(R')_3OR]$ however avoiding the necessity of making aluminum trialkyl from aluminum hydrogen and olefins. This is especially important in the production of ethyl compounds which might otherwise lead to difficulties because in the second stage of this method in accordance with the equation

$$(C_2H_5)_2AlH+C_2H_4=(C_2H_5)_3Al$$
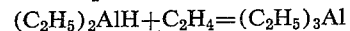
there is usually formed by the addition of a second ethylene some aluminum butyl compounds which may then be contained as impurity in the ethyl compound produced in accordance with the invention. On the other hand, the complex $Me[Al(C_2H_5)_3OR]$ will not further add any ethylene even in the presence of an excess of ethylene and even at higher temperatures.

Furthermore, the method in accordance with the invention is characterized by a better space time yield in the hydrogenation phase of the cyclic process. The sodium hydride formation under pressure proceeds more rapidly than the synthesis of the diethylaluminum hydride in accordance with the equation

$$2Al(C_2H_5)_3+Al+1\tfrac{1}{2}H_2=3HAl(C_2H_5)_3$$
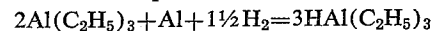
A still further advantage resides in the relatively small current requirement of the electrolysis in view of the relatively high conductivity of the electrolyte. A most important advance, however, when proceeding in accordance with the method of the invention, is the fact that by depositing an alkali metal preferably sodium at the cathode there a liquid metal is obtained, the separation and removal of which liquid metal can be effected without any difficulties and does not involve any more any danger or problem of short circuiting within the cell.

On the other hand though the aggregate of the results obtained when proceeding in the electrolytic preparation of the desired metal alkyls in accordance with said second described electrolytic embodiment are the same as compared with that in accordance with said first described electrolytic embodiment, the latter nevertheless also affords a number of decided advantages. The electrolyte, in accordance with said second described embodiment, has a decidedly lower electric conductivity than the substantially pure alkali aluminum tetraalkyl complex electrolyte in accordance with the first described embodiment. It is thus possible when proceeding, in accordance with the latter, to electrolytically produce the desired metal alkyl compounds with materially lowered energy requirements of the electrolysis cell for the same yields or, alternatively, to obtain yields of about 50% higher with the same energy.

Furthermore, in the case of certain alkyl compounds of some of the metals, and particularly the ethyl compounds of zinc and lead, the mutual miscibility of the phase aluminum triethyl and methal ethyl, on the one hand, molten alkali aluminum tetraethyl, on the other, is less than is normally the case for the miscibility of the phases $Al(OR)(C_2H_5)_2$, metal ethyl, on the one hand, and the molten mixed electrolyte, in accordance with the method of said second described electrolytic embodiment, on the other. It is possible in this manner to reduce the residual content of the electrolyte of lead or zinc in comparison to the method of said latter embodiment which will have an advantageous effect upon the course of the total process.

Example 1

3320 g. (=20 mol) of sodium aluminum tetraethyl are stirred with 740 g. (10 mol) of potassium chloride for five hours at 150° C. After settling of the sodium chloride which forms, the resultant equimolar mixture of sodium aluminum tetraethyl and potassium aluminum tetraethyl is subjected to electrolysis while in molten condition. The cathode is a copper cylinder and at a distance of about 1 centimeter a perforated synthetic resin cylinder of teflon, polypropylene or high molecular weight low pressure polyethylene is positioned. A diaphragm consisting of hardened filter paper or of a fine textile or glass filter fabric is stretched over the synthetic resin cylinder. The anode space is situated behind the diaphragm and is filled with lead spheres and any lead dissolved during electrolysis can be continuously replenished with additional lead spheres in the anode space. The heating of the electrolyte or removal of any current produced heat during the electrolysis is effected by circulating a liquid having a temperature of about 100° C. through the interior of the closed cathode cylinder. Heat input or heat removal at the outer cylinder is so regulated that the temperature within the anode space does not exceed about 70° C. During electrolysis the temperature within the anode space is preferably maintained at about 100° C. while that within the anode space is maintained at about 70° C.

The conductivity of the electrolyte mixture used is 4.5×10^{-2} (Ω cm.)$^{-1}$ at 100° C. Current intensity is adjusted to about 20 A. corresponding to a cell voltage of 2 volts.

The flow-off from the anode space is adjusted to 15 cc. per ampere hour so that a reaction mixture with about 20% lead tetraethyl runs off. During the course of 12 hours, about 3,600 g. electrolyte are flown through the electrolytic cell at 20 A. The electrolyte drained from the anode space consists of two layers. The upper layer which mainly consists of sodium aluminum tetraethyl is freed from small amounts of dissolved lead tetraethyl and aluminum triethyl under a vacuum of 0.5 mm. Hg and 120° C. and may subsequently be again used as electrolyte for a new electrolysis. The distillate is combined with the lower layer which now consists of 700 g. lead tetraethyl and 1,020 g. aluminum triethyl. The separation of the mixture of lead tetraethyl and aluminum triethyl may be effected in accordance with the process described in the following examples.
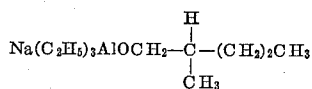
Example 2

A mixture of 700 g. lead tetraethyl and 1,020 g. aluminum triethyl is stirred for 1 hour at 100° C. with 1,880 g. of sodium butoxy aluminum triethyl. Upon termination of the agitation, the reaction mixture separates into 2 liquid layers. The upper layer is freed from small amounts of dissolved lead tetraethyl under a vacuum of 0.5 mm. Hg and at 100° C. The distillation residue is sodium aluminum tetraethyl and may be again used for the electrolysis. The lower layer consisting of a mixture of lead tetraethyl and butoxy diethyl aluminum with about 30% by weight of lead tetraethyl is distilled under vacum of 0.5 mm. Hg and at 70–80° C. (measured in the liquid). Pure lead tetraethyl distills under these conditions. The total yield of lead tetraethyl is 695 g. (99% of theory).
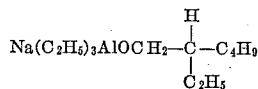
Example 3

Instead of the 1880 g. sodium butoxy aluminum triethyl used in Example 2, the mixture of 700 g. lead tetraethyl and 1020 g. aluminum triethyl formed according to Example 1 may, for example, also be reacted with 2130 g. of sodium-hexyl-oxy-aluminum triethyl
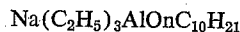
$$Na(C_2H_5)_3AlOnC_6H_{13}$$
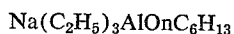
or 2130 g. sodium isohexyl-oxy-aluminum triethyl

$$Na(C_2H_5)_3AlOCH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-(CH_2)_2CH_3$$

or 2370 g. of sodium, isooctyl oxy aluminum triethyl

$$Na(C_2H_5)_3AlOCH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle C_2H_5}{|}}{C}}-C_4H_9$$

or 2620 g. of sodium decyl oxy aluminum triethyl

$$Na(C_2H_5)_3AlOnC_{10}H_{21}$$

Working-up of the resulting reaction mixture is effected in a manner analogously to that of Example 2.

Example 4

3320 g. of sodium aluminum tetraethyl and 740 g. of potassium chloride are stirred for 5 hours at 140° C. After settling of the sodium chloride which forms the mixture comprising equivalent amounts of sodium aluminum tetraethyl and potassium aluminum tetraethyl is subjected to electrolysis in the apparatus described in Example 1 using an anode of lead. The procedure is the same as in Example 1 except that the flow-off from the anode space is so adjusted that a reaction mixture with 10% lead tetraethyl is obtained, i.e. 30 cc. per ampere hour are withdrawn. After 6 hours, the total electrolyte stock has passed through the apparatus. The reaction mixture withdrawn consists of two phases. The upper layer consisting preponderantly of potassium aluminum tetraethyl is freed from lead tetraethyl and aluminum triethyl by distillation at a mercury pressure of 0.5 mm. and 100° C. The distillate is combined with the lower layer.

The separation of the lower layer consisting of 350 g. of lead tetraethyl and 510 g. of aluminum triethyl may be effected by the procedures set forth in Examples 2 and 3.

The regeneration of the complex sodium alkoxy aluminum trialkyl compounds obtained in accordance with the preceding examples may be effected by the following procedure described with reference to the butoxy compound.

742 g. (4.7 mols) Al(C$_2$H$_5$)$_2$(OC$_4$H$_9$) are heated with 4.7 mols sodium hydride under stirring in a nitrogen or argon atmosphere at 120 to 140° C. for ½ hour. After this time the reaction mix is transferred into a two liter autoclave filled with nitrogen and 50 to 60 atmospheres of ethylene are pressed on to the autoclave. The autoclave is then heated with rolling and shaking at 140 to 150° C. until no pressure change is further observable. This is usually the case after about 4 to 5 hours. The autoclave content is pure Na[Al(C$_2$H$_5$)$_3$(OC$_4$H$_9$)]. The yield is 990 g. (=100% of theory). This compound may again be used for separating lead tetraethyl from the electrolyte consisting of sodium aluminum tetraethyl and potassium aluminum tetraethyl.

Example 5

The procedure is the same as in Example 1 except that instead of sodium aluminum tetraethyl the equivalent amount of sodium aluminum tetrapropyl is charged to the electrolysis. The electrolyte withdrawn from the cell and containing the organometallic compounds formed is mixed with 2750 g. of the compound

$$Na[Al(C_3H_7)_3OCH_2CH(C_2H_5)C_4H_9]$$

and then distilled, preferably in a continuous film evaporator in as high as possible a vacuum (0.1 mm. mercury) at 100° C. There are obtained 800 g. of lead tetrapropyl (=95% of theory).

Lead tetra-n-butyl can be obtained in an analogous manner, it being only necessary to start with the butyl compounds corresponding to the propyl compounds mentioned above.

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The auxiliary materials needed for the process of the invention can be prepared as follows:

(1) Monoalkoxy aluminum dialkyls, are prepared by allowing 1 mol of the alcohol to react with 1 mol of the corresponding aluminum trialkyl.

(2) The complex compounds are prepared in a similar manner by adding dropwise 1 mol of the alcohol into the corresponding sodium aluminum tetraalkyls or by the procedure described in Example 4 with respect to the regeneration.

Example 6

The procedure is the same as in Example 1 except that zinc, cadmium, tin, antimony and bismuth, preferably in granular form, are used as the anode metal instead of lead. When using mercury as the anode metal, the anode space of the apparatus described in Example 1 is provided with superposed channels of an insulating material such as porcelain or polypropylene for receiving the liquid mercury. With a flow-off of about 15 cc. per ampere hour from the anode space, a reaction mixture with 15% zinc diethyl, 20% cadmium diethyl, 14% tin tetraethyl, 17% antimony triethyl, 24% bismuth triethyl and 32% mercury diethyl, respectively, is obtained depending upon the anode metal used. The particular reaction mixture is heated to 120° C. under a vacuum of 0.5 mm. mercury. There distills a mixture of the particular metal ethyl formed and aluminum triethyl. The separation may be effected by the procedures described in the following examples.

Example 7

A mixture of 123 g. of zinc diethyl and 228 g. of aluminum triethyl is stirred at 100% C. together with 364 g. of sodium ethoxy aluminum triethyl for 30 minutes. Then the zinc diethyl is distilled off from the mixture at a mercury pressure of 100 mm. and 80° C. The distillation residue consists of 2 phases. The upper layer is ethoxy aluminum diethyl and the lower layer consists of sodium aluminum tetraethyl with a small amount of dissolved ethoxy aluminum diethyl.

Example 8

A mixture of 235 g. of tin tetraethyl and 456 g. of aluminum triethyl is stirred at 100° C. for ½ hour together with 840 g. of sodium butoxy aluminum triethyl. The reaction mixture which forms is freed from the tin tetraethyl at a mercury pressure of 10 mm. and 90° C. (measured in the liquid). The distillate is pure tin tetraethyl and the yield is 230 g. (=98% of theory).

Example 9

With the same procedure set forth in Example 8, mixture of 170 g. of cadmium diethyl (boiling point, 54° C. at 11 mm. mercury) and 228 g. of aluminum triethyl; 258 g. of mercury diethyl (boiling point, 60° C. at 10 mm. mercury) and 228 g. of aluminum triethyl; and 209 g. of antimony triethyl (boiling point, 60° C. at 10 mm. mercury) and 342 g. of aluminum triethyl are separated.

Example 10

The procedure is the same as in Example 5 except that anodes of zinc instead of lead are used. The mixture of 330 g. of zinc dipropyl and 1370 g. of aluminum tripropyl separated by distillation from the residual electrolyte is stirred by distillation from the residual electrolyte is stirred at 100° C. for ½ hour together with 2710 g. of Na[(C₃H₇)₃AlOCH₂CH(C₂H₅)C₄H₉] and then distilled at a mercury pressure of 0.1 mm. and 100° C., the distillation being most preferably carried out in a continuously operating film evaporator. The yield is 320 g. (=97% of theory) of zinc dipropyl.

Example 11

By a procedure analogous to that of Example 10, a mixture consisting of 314 g. of mercury dibutyl, 396 g. of

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aluminum tributyl and 1000 g. of unchanged sodium aluminum tetrabutyl obtained by electrolysis in accordance with Examples 1 and 6, respectively, can be separated. 700 g. of sodium octyl oxy aluminum tributyl is added to the mixture which is then distilled under as high as possible a vacuum of 10⁻² mm mercury and at 100° C. to separate pure mercury dibutyl. The yield is 290 g. (94% of theory).
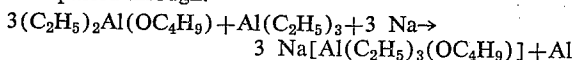
Example 12
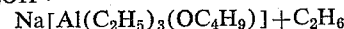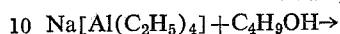
$$Na[Al(C_2H_5)_4]+C_4H_9OH \rightarrow Na[Al(C_2H_5)_3(OC_4H_9)]+C_2H_6$$

10 mol (=1660 g.) NaAl(C₂H₅)₄ are dissolved in three liters of dry and air-free benzene and are then admixed drop-wise in an inert atmosphere in a six liter three-neck flask under vigorous stirring with 10 mol (=740 g.) n-butanol. The solution of the complex salt heats up until the benzene comes to a obil. The addition of the butanol is so adjusted that the reaction mixture will boil under slight reflux. The solvent is removed by vacuum vaporization after the completion of the reaction. The resulting complex compound Na[Al(C₂H₅)₃(CO₄H₉)] will solidify upon cooling The yield is 2100 g. (=100% of theory). The electric conductivity is 2.2×10⁻³Ω⁻¹cm.⁻¹ at 100° C.

The complex compound is filled, preferably in molten condition into an electrolysis arrangement as shown on the appended drawing. This arrangement is provided with an opening 1 for introducing the electrolyte, a further opening 2 for adding the metal the alkyl compound of which is intended to be produced, means 3 for withdrawing the separated alkali metal and an outlet 4 for the reaction mixture from the anode space. 5 is the overflow for the cathode liquid and 6 that for the anode liquid. Between the cathode 8 and the anode metal 11 is arranged a perforated cylinder of an insulating material 7 and a diaphragm. Heating and cooling means 9 are provided within the cathode space to heat the cathode liquid to the appropriate temperature while the anode liquid is maintained at the temperature desired by means of the heating device 10 using a recirculated medium. The cathode is a copper cylinder 8 and at a distance of about 1 centimeter a perforated synthetic resin cylinder 7 of polypropylene or high molecular weight low pressure polyethylene is positioned. A diaphragm consisting of hardened filter paper or of a fine textile or glass filter fabric is stretched over the synthetic resin cylinder The anode space is situated behind the diaphragm and is filled with lead spheres 11 and any lead dissolved during electrolysis can be continuously replenished through opening 2 with additional lead spheres in the anode space The heating of the electrolyte or removal of any current produced heat during the electrolysis is effected by a liquid 9 having a temperature of about 100° C. in the interior of the closed cathode cylinder. Heat input or heat removal at the outer cylinder is so regulated that the temperature within the anode space does not exceed about 70° C. During electrolysis the temperature within the cathode space is preferably maintained at about 100° C. while that within the anode space is maintained at about 70° C. Current intensity is adjusted to about 15 A. at 30 volts between electrodes which corresponds to an anodic current intensity of 4 A./dm.² and a cathodic current intensity of 10 A./dm.². The cathodically formed sodium will flow away from the cathode into the lower cathode space from which it may be removed in molten condition from time to time. The flow away from the anode space is so adjusted that a reaction mixture with about 10% lead tetraethyl runs off whereby the inflow into the cathode space is so adjusted that the liquid level within the cathode space is by about 4–5 centimeters higher than that within the anode space. In the course of about 5 hours, the entire electrolyte has flown through the electrolysis cell. By distillation in vacuo at 0.5 to 0.3 mm. mercury and 40 to 42° C., at first the tetraethyl lead can be separated from the Al(C₂H₅)₂(CO₄H₉) and the remaining complex compound. The aluminum diethylbutoxy is separated by distillation at 120° in vacuo at 0.5 mm. mer-

cury. The yield of tetraethyl lead is 210 g. (=93% of theory), and $Al(C_2H_5)_2(OC_4H_9)$ is 400 g. (=2.5 mol).

These yields are relative to the amounts of current that have passed through.

$$3(C_2H_5)_2Al(OC_4H_9)+Al(C_2H_5)_3+3\ Na\rightarrow$$
$$3\ Na[Al(C_2H_5)_3(OC_4H_9)]+Al$$

400 g. (=2.5 mol) $Al(C_2H_5)_2(OC_4H_9)$ are heated with 58.2 g. (=2.5 gram atom) sodium and 96.2 g. (=0.84 mol) $Al(C_2H_5)_3$ with stirring in an inert atmosphere, while at a temperature of about 180° C. The aluminum is permitted to deposit from the hot melt and the supernatant liquid is separated.

The newly formed, as well as the complex salt which has remained unchanged during the electrolysis may now be again used for further electrolysis.

Example 13

10 mol (=1660 g.) $Na[Al(C_2H_5)_4]$ are dissolved in three liters of dry and air free benzene and are then admixed in an inert atmosphere in a six liter flask as described in Example 12 with 5 mol (=370 g.) n-butanol. After completion of the reaction the benzene is removed by vaporization and there is obtained a mixture of 5 mol (=830 g.) $Na[Al(C_2H_5)_4]$ and 5 mol (=1050 g.) $Na[Al(C_2H_5)_3(OC_4H_9)]$. The conductivity of this mixed electrolyte is $10^{-2}\Omega^{-1}cm.^{-1}$ at 100° C.
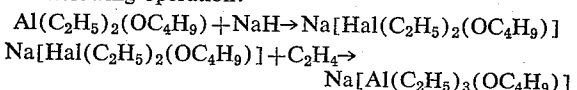
This electrolyte is subjected to electrolysis in the arrangement described in accordance with Example 12 between a copper cathode and a lead anode at the conditions of temperature there set forth. At a voltage of 9 volts between electrodes a current passage of 20 A. is obtained which corresponds to an anodic current intensity of 5.3 A./dm.² and a cathodic current intensity of 13 A./cm.². The cathodically formed sodium is removed in liquid condition from time to time and the efflux from the anode space is so adjusted that a reaction mixture with 20% tetraethyl lead flows off. By adjusting appropriately the inflow into the cathode space a liquid level differential between cathode and anode liquid of about 4 centimeters is maintained. During the course of about 6.3 hours, the entire electrolyte has passed through the electrolysis cell.

The tetraethyl lead is removed from the reaction mix by distillation at 40° C. and 0.5 to 0.3 mm. mercury. The yield of tetraethyl lead is 360 g. (=95% of theory). The lead free distillation residue separates into two phases. The upper is practically pure
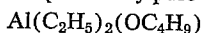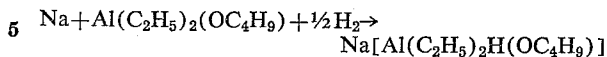
$$Al(C_2H_5)_2(OC_4H_9)$$

which may be converted into $Na[Al(C_2H_5)_3(OC_4H_9)]$ by the following operation:

$$Al(C_2H_5)_2(OC_4H_9)+NaH\rightarrow Na[Al(Hal(C_2H_5)_2(OC_4H_9)]$$
$$Na[Hal(C_2H_5)_2(OC_4H_9)]+C_2H_4\rightarrow$$
$$Na[Al(C_2H_5)_3(OC_4H_9)]$$

742 g. (=4.7 mol) $Al(C_2H_5)_2(OC_4H_9)$ are heated with 4.7 mol sodium hydride under stirring in a nitrogen or argon atmosphere at 120 to 140° C. for ½ hour. After this time the reaction mix is transferred into a two liter autoclave filled with nitrogen and 10 atmospheres of ethylene are pressed on to the autoclave. The autoclave is then heated with rolling and shaking at 170° C. until no pressure change is further observable. This is usually the case after about 4 to 5 hours. The autoclave con-

tent is pure $Na[Al(C_2H_5)_3(OC_4H_9)]$. The yield is 990 g. (=100% of theory).

Example 14

$$Na+Al(C_2H_5)_2(OC_4H_9)+\tfrac{1}{2}H_2\rightarrow$$
$$Na[Al(C_2H_5)_2H(OC_4H_9)]$$

Electrolysis is carried out as described in Example 13 using the same mixed electrolyte. After separation of the tetraethyl lead by vacuum distillation and preparation of the upper layer of $Al(C_2H_5)_2(OC_4H_9)$ from the complex salt, the 742 g. (=4.7 mol) butoxy aluminum diethyl are placed into a nitrogen filled 2 liter autoclave together with 4.7 gram atoms (=108 g.) sodium, which has formed cathodically. Thereupon 250 atmospheres of electrolyte hydrogen are pressed on and the autoclave is heated under rolling to 130 to 140° C. After about 7 to 8 hours, there is usually no further pressure reduction observable. Excess hydrogen is then blown off and about 5 atmospheres of ethylene are pressed on. The reaction proceeds quantitatively at 200° C. and is completed after about 4 to 5 hours in accordance with the following equation:

$$Na[Al(C_2H_5)_2H(OC_4H_9)]+C_2H_4\rightarrow$$
$$Na[Al(C_2H_5)_3(OC_4H_9)]$$
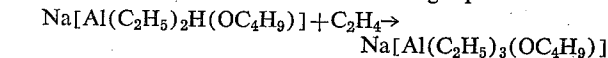
The newly formed electrolyte is then admixed with residual electrolyte and the cycle can begin anew.

Example 15

(a) 5 mol (=830 g.) sodium aluminum tetraethyl are heated under stirring to 140 to 150° C. in an inert atmosphere together with 6 mol (=447 g.) of dry potassium chloride. The reaction

$$Na[Al(C_2H_5)_4]+KCl\rightarrow K[Al(C_2H_5)_4]+NaCl$$
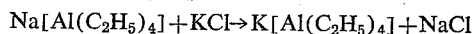
is completed in about three to four hours. After settling of the sodium chloride, the melt of potassium aluminum tetraethyl is decanted from the sodium chloride. The yield of $K[Al(C_2H_5)_4]$ is 820 g. (=90% of theory).

(b) 5 mol (830 g.) sodium aluminum tetraethyl are admixed with 5 mol n-butanol as described in Example 12. The resulting sodium butoxy aluminum triethyl is then mixed with the potassium aluminum tetraethyl obtained in accordance with the reaction (a) and there is thereby obtained a mixed electrolyte, the electrolytic conductivity of which at 100° C. is $4.5\times10^{-2}\Omega^{-1}cm.^{-1}$. In the electrolyses of this electrolyte the procedure set out in Example 12 is followed. The electrolysis was effected for 5 hours at 15 A. The mixed electrolyte of potassium and sodium compound will cathodically separate under these conditions a substantially pure sodium. The yield of sodium is quantitative. The separation of tetraethyl lead is effected by distillation in high vacuum as described in Example 13. The conversion of the butoxy aluminum diethyl into sodium butoxy aluminum triethyl may be effected in accordance with the procedure set out in Example 12 to 14. The yield is 210 g. of lead tetraethyl (=93% of theory).

Example 16

When proceeding in the same manner, set forth in Example 13, except that instead of lead there are used as anodic materials the metals: zinc, tin, antimony, bismuth, cadmium, and mercury respectively, the ethyl compounds of these metals were obtained as set forth in the following table:

| Anode	Current Intensity	Anode, A./dm.²	Met. Alkyl	Dist. Temp.	Yield	Remarks
Zn	15	4	$Zn(C_2H_5)_2$	24–26°/10 mm	91	
Sn	15	4	$Sn(C_2H_5)_4$	64°/10 mm	85	Diaphragm not necessary.
Sb	15	4	$Sb(C_2H_5)_3$	60–65°/20 mm	96	
Bi	15	4	$Bi(C_2H_5)_3$	60°/10 mm	95	
Cd	15	4	$Cd(C_2H_5)_2$	64°/19 mm	81	
Hg	5	4	$Hg(C_2H_5)_2$	60°/10 mm	82	(¹).

[1] For the production of the mercury diethyl there were used in the anode space of the electrolysis arrangement troughs of insulating material (porcelain, polyethylene) to hold the liquid mercury.

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Example 17

1140 g. of aluminum triethyl are diluted with 1 liter of dry and air-free hexane. Then 1580 g. of n-decyl alcohol are added dropwise with stirring. The heat of the reaction causes the hexane to boil vigorously. Therefore, a reflux condenser is used. The hexane is subsequently withdrawn under a moderate vacuum. There is left the decyl oxy aluminum diethyl as rather fluid oil.

This is the most simple process to produce a compound of this type if an electrolysis has not yet been carried out. The following prescription is then equally applicable to a produce freshly prepared in this manner as well as to a product recovered from the electrolysis.

The 2420 g. of the decyl oxy aluminum diethyl obtained are mixed with 1 liter of a 24 wt. percent sodium hydride suspension in decaline or with a corresponding amount of a similar suspension of different sodium hydride content and the entire mixture is filled into a pressure vessel. Ethylene of 20 to 50 atmospheres is pressed on with stirring and the mixture is heated to 170° C. The ethylene is absorbed and the pressure is maintained at a constant level by pressing on additional ethylene until an ethylene absorption does no longer occur. This is the case after about 6 hours. A sample drawn of the reaction mixture, when carefully hydrolized, should now furnish only ethane but no hydrogen. In most cases, however, a small residual content of hydrogen of about 0.5% will be observed in the gas obtained in the hydrolysis. This is, however, not disturbing. The pressure is released, the temperature is allowed to drop somewhat to about 130° C., the pressure vessel is provided with a descending condenser, and a vacuum is applied. Now the decaline introduced by the sodium hydride suspension distills. Finally, the temperature is increased again to 150 to 170° C. and the pressure is reduced to a few mm. mercury. There are left in the pressure vessel about 2900 g. which may be removed under nitrogen. The complex compound

$$Na[(C_2H_5)_3AlOC_{10}H_{21}]$$
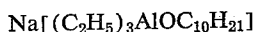
is a very viscous oil which does not show a tendency to crystallize.

The cathode and anode spaces of the electrolysis cell described in Example 12 first contain sodium aluminum tetraethyl in molten state. Sodium decyl oxy aluminum triethyl or, optionally, sodium isohexyl oxy aluminum triethyl is allowed to flow continuously into the anode space from above at a rate which is to be adapted to the current flowing through. The current circuit is closed as this addition starts. An amount of 11 g./hr. of sodium decyl oxy aluminum triethyl (or 8.9 g. of sodium isohexyl oxy aluminum triethyl) is allowed to flow in per ampere of current flowing through. At the bottom of the anode space, there separates a liquid layer consisting of a mixture of decyl oxy aluminum diethyl (or isohexyl oxy aluminum diethyl) and lead tetraethyl, which contains rather exactly 25% (30%) by weight of lead tetraethyl. This layer is continuously withdrawn at a rate that the main electrolyte, the molten alkali aluminum tetraethyl, remains unchanged in the anode space. The electrolyte level in the cathode space should be higher by about 4 centimeters than that in the anode space. Both of the spaces are preferably provided with overflows and sodium aluminum tetraethyl, preferably in molten state, is continuously introduced into the cathode space at a rate that only a small amount flows over. The amount flowing over from the cathode space is returned into the stock of the sodium aluminum tetraethyl.

Some sodium aluminum tetraethyl will also flow over in the anode space, this amount being the higher the more permeable the diaphragm is. This portion of the sodium aluminum tetraethyl is not capable of being directly returned into the stock since it contains lead. It must first be freed from lead tetraethyl by heating to about 100° C. under vacuum. For an electrolysis cell

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of the size set forth in Example 12, about 10 to 30 A. are allowable, i.e., on an hourly base, 110 to 330 g. of sodium decyl oxy aluminum triethyl (or 89 to 267 g. of sodium isohexyl oxy aluminum triethyl) can be converted and 120 to 360 g. of the mixture of lead tetraethyl and decyl oxy aluminum diethyl (or 100 to 300 g. of the mixture of lead tetraethyl and iso-hexyl oxy aluminum diethyl) can be recovered, from which the lead tetraethyl is distilled off at a mercury pressure of about 1 mm. and a bath temperature up to 100° C.

The regeneration of the decyl oxy aluminum diethyl compound into the complex sodium decyl oxy aluminum triethyl is effected by the procedure set forth in the first paragraph of this example.

Example 18

In this example, the electrolysis cell used simply consists of a vacuum-resistant steel container, in the center of which a cathode of a copper plate and on both sides of the cathode at a distance of about 1 to 2 centimeters therefrom anodes consisting of thick lead plates are arranged. The cathode is connected with the steel shell of the container to provide metallic conduction. Moreover, the cathode is of sufficient length as to contact the bottom of the container while between the container and the lower end of the anode a free space of about 20 centimeters is left. The container is filled under nitrogen with an electrolyte consisting of 80% of potassium aluminum tetraethyl and 20% of sodium aluminum tetraethyl. Moreover, a larger quantity of sodium aluminum ethoxy is prepared as follows: 1140 g. of aluminum triethyl are mixed under nitrogen with 680 g. of completely dry and alcohol free sodium ethylate and the mixture is heated to about 100° C. until a clear melt has formed. Upon cooling, the melt solidifies at 80° C.

By means of a descending cooler, the container is connected with a cooled receiver tank and a vacuum pump. The container is heated to 130 to 140° C. and evacuated to less than 0.1 mm. mercury if possible. Now, through a special line mounted at the container and provided with a valve, the molten sodium aluminum ethoxy triethyl is allowed to flow in slowly and the current is applied in that moment where the content of this compound added at least has reached 5% in the contents of the container. The current is now adjusted to a current density of 10 to 30 A./dm.^{2} and now the second electrolyte is allowed to flow in continuously at a rate corresponding to the current density, i.e. 6.78 grams per ampere hour. There distills continuously a mixture of lead tetraethyl and diethyl ethoxy aluminum, i.e. 3 g. of lead tetraethyl in mixture with 4.85 g. of ethoxy diethyl aluminum per ampere hour. In this arrangement, the complex electrolyte containing potassium and sodium remains practically unchanged in the container, and only the inflowing sodium ethoxy aluminum triethyl is decomposed. The molten sodium accumulates in correct amount, i.e. 0.86 grams per ampere hour. The electrolysis may be operated until the sodium level in the container is sufficiently high as to cause a short circuit with the lead anode. Of course, the sodium may also be dissolved out of the container in liquid state after temporary interruption of the vacuum and the current supply. The distillate is separated into lead tetraethyl (boiling point, 38° C./1 mm.,) and ethoxy aluminum diethyl (boiling point, 72° C./1 mm.) using a column which needs not be very efficient. The sodium formed in the electrolysis is further processed in conventional manner to form sodium hydride which is added to the electrolyte for regeneration as described above (Examples 12–14).

Example 19

1560 g. of aluminum tripropyl are mixed under nitrogen with 1240 g. of alcohol-free sodium hexylate

$$NaO(CH_2)_5—CH_3$$
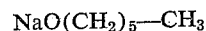
and the mixture is heated to about 100° C. until a clear

melt has formed. The resultant complex compound which is sodium hexoxy aluminum tripropyl is mixed with an equimolar amount of sodium aluminum tetrapropyl and the electrolyte mixture obtained is subjected to electrolysis in accordance with the procedure set forth in Example 12.

With a current of 10 amperes passing through, the flow-off from the anode space is so adjusted that a reaction mixture with 10% of lead tetrapropyl runs off. After 5 hours, about 1500 g. of electrolyte has flown through the electrolysis cell. The reaction mixture is freed from lead tetrapropyl at a mercury pressure of 0.1 mm. and 100° (measured in the liquid). The yield of lead tetrapropyl is 160 g. (=90% of theory).

Example 20

2780 g. of sodium aluminum tetrabutyl are dissolved in 3 liters of dry benzene. To the solution, 790 g. of n-decanol-1 are slowly added dropwise with vigorous stirring. After the total amount is added, the benzene solvent is distilled off at 120° C. (measured in the liquid). There is obtained a mixture of equimolar amounts of the complex compounds sodium aluminum tetrabutyl and sodium decyloxy aluminum tributyl.

This mixed electrolyte is subjected to electrolysis between a copper cathode and a lead anode using the apparatus described in Example 12. The procedure is otherwise the same as set out in Example 12. The resulting reaction mixture with 10% of lead tetrabutyl is freed from lead tetrabutyl at a mercury pressure of 10^{-3} mm. and 120° C. (measured in the liquid). The yield of lead tetrabutyl is 80% of theory.

Example 21

The procedure of Example 18 is followed except that zinc plates are used as anodes instead of thick lead plates. When proceeding as described in Example 18, a mixture of zinc diethyl and ethoxy aluminum diethyl distills off, i.e., 2.3 g. of zinc diethyl and 4.85 g. of ethoxy aluminum diethyl per ampere hour. The distillate is separated by distillation at 10 mm. mercury. The distillate boiling at 26–28° C. is pure zinc diethyl while the distillation residue is ethoxy aluminum diethyl. The yield of zinc diethyl is 100%.

Example 22

The equimolar mixture of sodium aluminum tetrapropyl and sodium hexyl oxy aluminum tripropyl obtained in accordance with Example 19 is subjected to electrolysis by the procedure set forth in Example 12 using an anode of antimony.

With a current of 10 A. flowing through, 310 g./hr. of the reaction mixture containing about 10% of antimony tripropyl are withdrawn. After 5 hours, about 1.7 liters of electrolyte have flown through the cell. The reaction mixture is freed from antimony tripropyl at a pressure of 10^{-3} mm. mercury and 90° C. (measured in the liquid). The yield of antimony tripropyl is 135 g. (=89% of theory).

Example 23

The mixed electrolyte produced in accordance with Example 20 is subjected to electrolysis by the procedure set forth in Example 20 using zinc granules as the anode material. With a current intensity of 10 A., 33 g. of reaction mixture are withdrawn from the anode space per ampere hour. This corresponds to a content of zinc dibutyl of about 10%.

The reaction mixture obtained is freed from zinc dibutyl at a vacuum of 0.1 mm. mercury and 90° C. (measured in the liquid). The yield of zinc dibutyl is 3.0 g. per ampere hour (=82% of theory).

Example 24

A mixture of 267 g. (=1 mole) Pb(CH₃)₄ and 288 g. (=4 moles) Al(CH₃)₃ obtained by electrolysis of
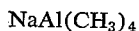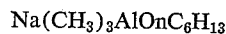
$$NaAl(CH_3)_4$$

with the use of a lead anode is stirred for 1 hour at 80° C. with 672 g. (=4 moles) of Na(CH₃)₃AlOC₄H₉. The reaction mixture consists of a liquid phase in which the insoluble NaAl(CH₃)₄ formed is suspended. The solids are separated by filtration in an inert gas atmosphere. The solids are identified by analysis as pure NaAl(CH₃)₄ and may thus be used as electrolyte in another electrolysis operation. The filtrate which consists of a mixture of Pb(CH₃)₄ and (CH₃)₂AlOC₄H₉ is separated by fractional distillation in a 50 cm. Vigreux column at about 100 mm. Hg. The first fraction obtained comprises 250 gms. Pb(CH₃)₄ corresponding to 93.5% of the theory. After withdrawal of a small intermediate fraction of about 20 to 30 ml. which contains both lead alkyl and aluminum alkyl, the residue from distillation is substantially free from lead alkyl and may be reconverted into the complex compound Na(CH₃)₃AlOC₄H₉ by processes known per se. The intermediate fraction is preferably combined with the next batch to be separated.
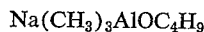
Example 25

If the separation of the mixture of 267 gms. of Pb(CH₃)₄ and 288 gms. of Al(CH₃)₃ obtained by electrolysis is effected by reaction with 784 gms. of

$$Na(CH_3)_3AlOnC_6H_{13}$$

with 896 gms. of

$$Na(CH_3)_3AlOCH_2-CH-C_4H_9$$
$$\qquad\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad C_2H_5$$
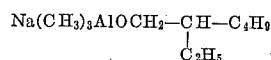
or with 1008 gms. of Na(CH₃)₃AlOnC₁₀H₂₁ likewise effected at 80° C. in place of the reaction with

$$Na(CH_3)_3AlOC_4H_9$$

the lead tetramethyl can be easily, i.e., without a column, distilled from the filtrate at about 100 mm. Hg and a bath temperature of 70 to 80° C. after filtration and recovery of the NaAl(CH₃)₄. The yields of lead tetramethyl are equally good as those mentioned in the preceding example.

We claim:

1. In the production of metal alkyls of metals other than aluminum by the use, as an alkyl radical supplying agent, of a complex compound having the general grouping Me[Al(R′)₃—] in which Me is an alkali metal and R′ an alkyl radical, said complex compound being other than an alkoxy derivative, the improvement which comprises effecting such production, at a point between the metal alkyl formation and the separation of formed metal alkyl, in the presence of a complex compound of the general formula: Me[Al(R′)₃OR] in which Me is an alkali metal of the group consisting of sodium and potassium, R′ is an alkyl radical with up to 6 carbon atoms and R is an organic radical selected from the group consisting of alkyl and cycloalkyl radicals to thereby substantially assure freedom from AlR′₃ and to react said complex compound to form AlR′₂OR.

2. Improvement in accordance with claim 1 in which R represents an alkyl radical with four carbon atoms.

3. In the production of metal alkyls, the improvement according to claim 1 in which said trialkyl aluminum is substantially continuously produced in said material and is reacted with said compound substantially as it is produced.

4. In the production of alkyls of metals selected from the group consisting of lead, tin, antimony, bismuth, zinc, cadmium and mercury from a material containing such metal alkyl and aluminum trialkyl, the improvement comprising reacting said material with a compound of the general formula: Me[Al(R′)₃OR] in which Me is an alkali metal of the group consisting of sodium and potassium, R′ is a straight chain alkyl with up to 6 carbon atoms and R is an organic radical selected from the group consisting of alkyl and cycloalkyl radicals and separating said metal alkyl compound from the reaction product formed.

5. In the production of metal alkyls the improvement according to claim 4, in which said material is substantially continuously supplied from the electrolysis, with one of said metals as anode, of alkali metal tetraalkyl aluminum, in which said metal alkyl separating is substantially continuously effected by distillation, and in which said alkali metal tetraalkyl aluminum is recycled to said electrolysis.

6. In the production of metal alkyls the improvement according to claim 5, in which the alkyl radical of said trialkyl aluminum is the same as is defined by R', and in which said anode metal is lead.

7. Improvement according to claim 4, in which R is an alkyl with from 2 to 12 carbon atoms.

8. Improvement according to claim 4, in which R is an alkyl with from 2 to 8 carbon atoms.

9. Improvement in accordance with claim 4, in which R represents an alkyl radical with four carbon atoms.

10. Improvement according to claim 4, in which R' represents a straight chain alkyl with up to 4 carbon atoms.

11. Improvement in accordance with claim 4, in which R' represents the ethyl radical.

12. Improvement according to claim 4, in which said metal of the metal alkyl compound is lead, in which R' represents the ethyl radical, and in which R represents an alkyl radical.

13. In the production of metal alkyls the improvement according to claim 4 in which said separating is effected by distillation.

14. In the process for the production of metal alkyls, the improvement which comprises subjecting to electrolysis, while using as an anode a metal selected from the group consisting of lead, tin, antimony, bismuth, zinc, cadmium, and mercury, an electrolyte comprising a complex compound of the general formula $Me[Al(R')_3OR]$ containing admixed therewith an amount of a compound having the general formula $Me[Al(R')_4]$ sufficient to increase its electric conductivity, in said general formulas R representing a member selected from the group consisting of alkyl and cycloalkyl, Me representing a member selected from the group consisting of potassium and sodium, and each R' representing a straight chain alkyl radical containing from 2–6 carbon atoms, to thereby form at the anode an alkyl compound of said anode metal together with an alkoxy aluminum dialkyl compound of the general formula $Al(R')_2OR$, while depositing substantially metallic alkali metal at the cathode, and separating said alkyl compound from said alkoxy aluminum dialkyl compound.

15. Improvement according to claim 14 in which said alkoxy aluminum dialkyl compound is regenerated to said complex compound by reacting said alkoxy aluminum dialkyl compound with hydrogen and olefin and a member selected from the group consisting of sodium and potassium and in which the regenerated compound is returned to said electrolysis.

16. Improvement according to claim 15 in which said cathodically deposited alkali metal is used for said regeneration with aluminum trialkyl.

17. Improvement in accordance with claim 14 in which said alkoxy aluminum dialkyl compound is regenerated to said complex compound by reacting said alkoxy aluminum dialkyl compound with alkali metal hydride, and treating the product, formed in said reaction, with olefin and in which the regenerated compound is returned to said electrolysis.

18. Improvement according to claim 17 in which said olefin is ethylene, in which said anode metal is lead, in which R' is an ethyl radical, in which said alkali metal hydride is sodium hydride and in which said sodium hydride is obtained by hydrogenation of the cathodically produced sodium.

19. Improvement according to claim 14, in which R is an alkyl with from 2 to 8 carbon atoms.

20. Improvement in accordance with claim 14, in which R represents an alkyl radical with four carbon atoms.

21. Improvement according to claim 14, in which R' represents a straight chain alkyl with up to 4 carbon atoms.

22. Improvement in accordance with claim 14, in which R' represents the ethyl radical.

23. Improvement in accordance with claim 14 in which said anode metal is lead, and in which R' is the ethyl radical.

24. Improvement according to claim 14 in which R is an alkyl radical with from 2 to 12 carbon atoms.

25. Improvement according to claim 14 in which said anode metal is lead, in which R' is the ethyl radical and in which R is an alkyl radical.

26. Improvement according to claim 14 in which said compound of the formula $Me[Al(R')_4]$ is in the form of a mixture of the potassium and sodium compound.

27. Improvement according to claim 14, in which said alkoxy aluminum dialkyl compound is regenerated to said complex compound by reacting said alkoxy aluminum dialkyl compound with sodium and hydrogen under pressure and treating the product formed in said reaction with olefins and in which the regenerated compound is returned to said electrolysis.

28. Improvement according to claim 14, in which for 100 to 20 mol percent sodium and 0 to 80 mol percent potassium, each calculated to the whole alkali metal content, there is used 95 to 50 mol percent of the ion of the formula $[(C_2H_5)_4Al]^-$ and 5 to 50 mol percent of the ion of the general formula $[(C_2H_5)_3AlOR]^-$.

29. Improvement according to claim 14, in which said complex compound is added continuously to said electrolyte during the electrolysis in such an amount as it is used up in the electrolysis.

30. Improvement according to claim 14, in which as said $Me[Al(R')_4]$ is used a mixture of potassium aluminum tetraalkyl and sodium aluminum tetraalkyl, which mixture has been produced by reacting 1 mol sodium aluminum tetraalkyl with less than 1 mol potassium chloride.

31. Improvement according to claim 14 in which R' is the ethyl radical, in which R is an alkyl radical, in which anodically produced liquid is permitted to separate into layers one of which contains said metal alkyl compound and said alkoxy aluminum diethyl compound, and in which said metal alkyl compound is recovered from said last-mentioned layer.

32. Improvement in accordance with claim 14, in which the electrolysis is carried out at a temperature sufficiently high to assure the cathodic separation of alkali metal in substantially liquid form.

33. In the process in the production of metal alkyls, the improvement which comprises subjecting the electrolysis, while using as an anode a metal selected from the group consisting of lead, tin, antimony, bismuth, zinc, cadium and mercury, an electrolyte comprising a complex compound of the general formula

$$Me[Al(R')_3OR]$$
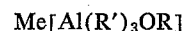
containing admixed therewith an amount of a compound of the general formula $Me[Al(R')_4]$ sufficient to increase its electric conductivity, in said general formulas R representing a member selected from the group consisting of alkyl and cycloalkyl radicals, Me representing an alkali metal selected from the group consisting of potassium and sodium, and R' representing a straight chain alkyl radical with from 2 to 6 carbon atoms to thereby form at the anode an alkyl compound of said anode metal, together with an alkoxy aluminum dialkyl compound of the general formula $Al(R')_2OR$, and separating the mixture of said alkyl compound, said alkoxy aluminum dialkyl compound and the remaining electroylte by distillation.

34. Improvement according to claim 33, in which a phase containing substantially a mixture of said metal alkyl compound and said alkoxy aluminum dialkyl compound is mechanically separated from the remaining electrolyte and said metal alkyl compound is separated from said alkoxy aluminum dialkyl compound by distillation in vacuo.

35. Improvement according to claim 34, in which the remaining electrolyte is purified from traces of said metal alkyl compound by distillation in vacuo and at elevated temperature.

36. Improvement according to claim 33, in which the separation of said mixture is effected by distillation in vacuo.

37. Improvement according to claim 33, in which a mixture of said metal alkyl compound and said alkoxy aluminum dialkyl compound is separated from the remaining electrolyte by distillation in vacuo.

38. Improvement according to claim 33, in which said alkoxy aluminum dialkyl compound is separated from the remaining electrolyte by distillation in vacuo.

39. Improvement according to claim 33, in which said metal alkyl compound is separated from said alkoxy aluminum dialkyl compound and the remaining electrolyte by distillation in vacuo during the electrolysis of the mixture of said first and said second electrolyte compound.

40. Improvement according to claim 33, in which said metal alkyl compound and the alkoxy aluminum dialkyl compound is separated from the remaining electrolyte by distillation in vacuo during the electrolysis of the mixture of said first and said second electrolyte compound.

41. Improvement according to claim 33, in which R′ is the ethyl radical and the electrolyte during the electrolysis saturated with the alkoxy aluminum diethyl compound.

42. In the process for the production of metal alkyls, the improvement which comprises subjecting the electrolysis, while using as an anode a metal selected from the group consisting of lead, tin, antimony, bismuth, zinc, cadmium and mercury, an electrolyte comprising a complex compound having the general formula Me[Al(R′)$_3$OR] containing admixed therewith a sufficient amount of a compound having the general formula Me[Al(R′)$_4$] to increase its electrical conductivity, in said general formulas, R representing a member selected from the group consisting of alkyls and cycloalkyl radicals, Me representing an alkali metal selected from the group consisting of potassium and sodium, and R′ representing a straight chain alkyl radical containing from 2 to 6 carbon atoms, to thereby form at the anode an alkyl compound of said anode metal, together with an alkoxy aluminum dialkyl compound of the general formula Al(R′)$_2$OR, separating said metal alkyl compound and said alkoxy aluminum dialkyl compound from the remaining elec-

trolyte by distillation, adding to said alkoxy aluminum dialkyl compound sodium hydride, treating the resulting product formed with an olefin to thereby produce said complex compound and adding the complex compound formed to the electrolyte.

43. Improvement according to claim 42 in which R is an alkyl with from 2 to 12 carbon atoms.

44. Improvement according to claim 42 in which R is an alkyl with from 2 to 8 carbon atoms.

45. Improvement according to claim 42 in which R′ represents the ethyl radical.

46. Improvement according to claim 42 in which said anode metal is lead, in which R′ represents an ethyl radical, and in which R represents an alkyl radical.

47. Improvement according to claim 42 in which the electrolysis is carried out at a temperature sufficiently high to assure the cathodic separation of alkali metal in substantially liquid form.

48. Improvement according to claim 42 in which for 100 to 20 mol percent sodium and 0 to 80 mol percent potassium, each calculated to the whole alkali metal content, there is used 95 to 50 mol percent of the ion of the formula [(C$_2$H$_5$)$_4$Al] and 5 to 50 mol percent of the ion of the general formula [C$_2$H$_5$)$_3$AlOR].

49. Improvement according to claim 42 in which the intermingling of the cathode liquid with the anode liquid is inhibited without impeding the current transfer in the electrolyte.

50. Improvement according to claim 42 in which the electrolysis is carried out under vacuo without any separation of the cathode liquid from the anode liquid.

51. In the production of metal alkyls of metals other than aluminum from a material containing such metal alkyl and trialkyl aluminum, the improvement which comprises reacting said trialkyl aluminum with a compound of the general formula: Me[Al(R′)$_3$OR] in which Me is an alkali metal of the group consisting of sodium and potassium, R′ is an alkyl radical with up to 6 carbon atoms and R is an organic radical selected from the group consisting of alkyl and cycloalkyl radicals to thereby convert said trialkyl aluminum to an alkali metal tetraalkyl aluminum and separating metal alkyl from the reaction product formed.

52. Improvement according to claim 4, wherein said reaction is carried out in an electrolysis cell wherein said metal alkyl and said aluminum trialkyl are produced by electrolysis.

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