May 23, 1961 K. ZIEGLER ET AL 2,985,568

ELECTROLYTIC PROCESS FOR THE PRODUCTION OF METAL ALKYLS

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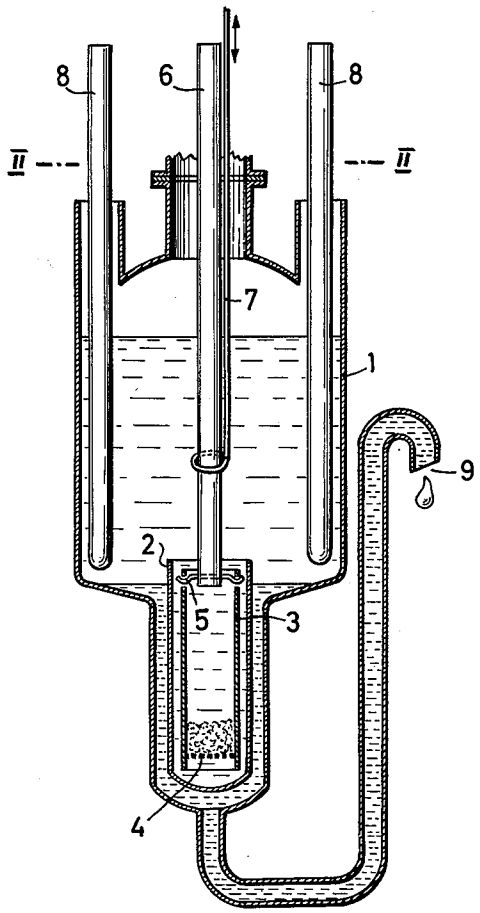

FIG.1

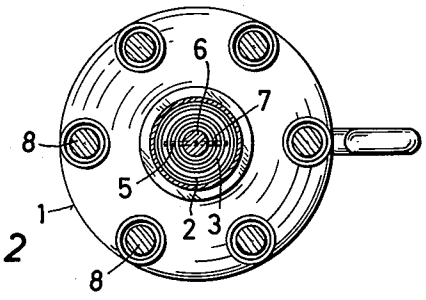

FIG.2

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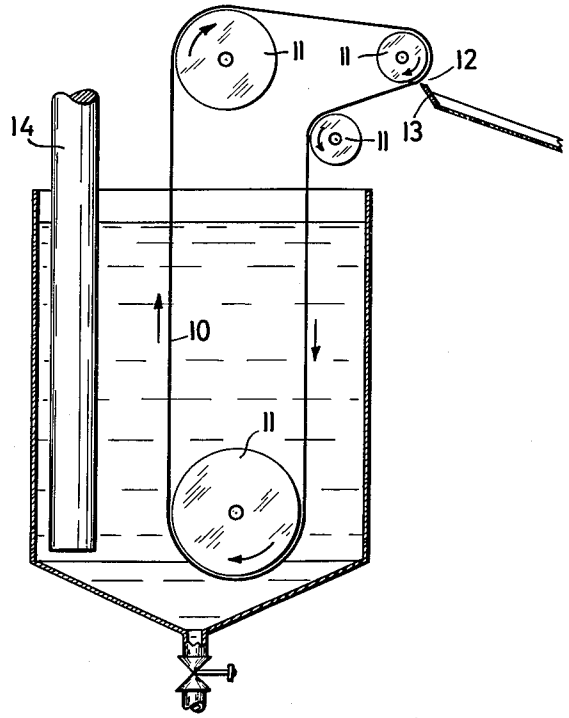
FIG.3



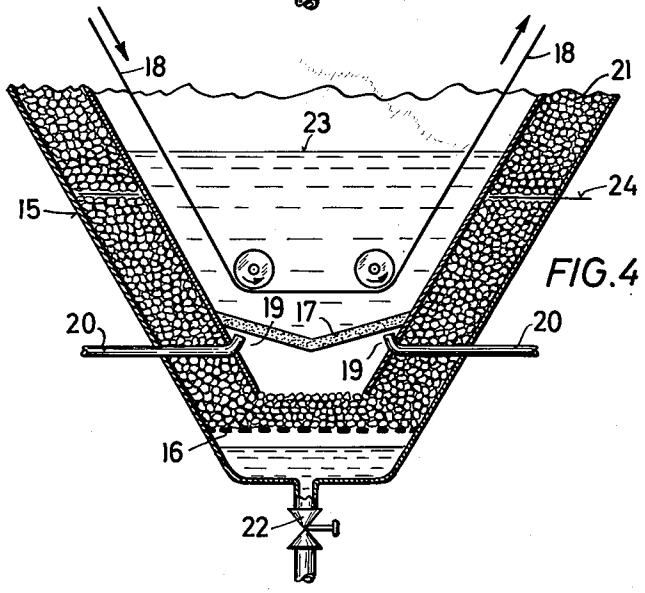


FIG.4

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ELECTROLYTIC PROCESS FOR THE PRODUCTION OF METAL ALKYLS

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Filed Nov. 25, 1955, Ser. No. 548,862

Claims priority, application Germany Nov. 26, 1954

34 Claims. (Cl. 204—59)

This invention relates to a process and apparatus for the production of metal alkyls. Lead tetraalkyls, especially lead tetraethyl, have hitherto been produced on a technical scale exclusively by reaction between a sodium-lead alloy and an alkyl chloride, especially ethyl chloride:

$$PbNa_4+4C_2H_5Cl=Pb(C_2H_5)_4+4NaCl$$

In this case, sodium and the alkly chloride are constantly used up, and these substances depreciate either completely, like the sodium, or partially, like the chlorine constituent in the alkyl chloride, with the formation of common salt.

The present invention provides a process in which such valueless waste products are not obtained or are obtained only in quite a subordinate amount. The object of the invention is to carry out the reaction represented by the empirical equation:

$$Pb+2H_2+4C_nH_{2n}=Pb(C_nH_{2n+1})_4$$

by combining lead, hydrogen and an olefine, in particular the production of the especially important lead tetraethyl by combining lead, hydrogen and ethylene, or, generally, the production of alkyl compounds of the metals Me of the 2nd to 5th groups of the periodic system as represented by the equation:

$$Me+mH+mC_nH_{2n}=Me(C_nH_{2n+1})_m$$

in which m represents the valency of the metal Me. However, it has not yet been possible to prove direct reaction between such metals, for example metallic lead, and the hydrogen and olefines. It is however possible by means of the present invention to effect this by a combination of two partial processes. In accordance with the invention, aluminium is first of all reacted with an olefine and hydrogen to form an aluminium trialkyl. In the second stage, the aluminium trialkyl is made electrically conducting by adding a suitable electrolyte, for example an alkali metal halide, and the resulting mixture is electrolysed using an anode of the metal of the 2nd to 5th groups of the periodic system of which it is desired to obtain the alkyl, and a cathode of any suitable metal. In this process, aluminium is deposited at the cathode, while the desired metal alkyl is formed at the anode; this alkyl can be separated from the electrolyte in a suitable manner. The aluminium deposited at the cathode is reacted afresh with an olefine and hydrogen to form an aluminium alkyl, which is returned to the process.

It is primarily lead tetraalkyls which can be produced by the process of the invention. However, the process is also suitable for the production of alkyl compounds of the other metals of the 4th group of the periodic system and for the production of alkyl compounds of the metals of the 2nd, 3rd and 5th groups of the periodic system. In particular, it is possible in a simple manner to produce the alkyl compounds of the metals of the main groups and sub-groups of the 2nd and 3rd groups of the periodic system, for example magnesium, calcium, zinc, mercury,

indium, the rare earths, for example in the form of the so-called "mixed metal" manufactured from lanthanum, cerium and other rare earth metals, thallium, and also the metals of the 4th and 5th main groups of the periodic system, for example germanium, tin and bismuth.

The reaction of the aluminium with the olefine and hydrogen in the first stage is preferably carried out in the presence of a dialkyl aluminium halide as catalyst or without a catalyst in accordance with the applicants' copending application Ser. No. 484,576 of January 27, 1955.

It can also be advantageous for the first stage to be split up into two partial reactions 1*a* and 1*b* in accordance with application Ser. No. 524,797, issued to Patent No. 2,835,689. In stage 1*a*, aluminium triisobutyl is prepared in accordance with copending application Ser. No. 484,576 of January 27, 1955, for example for aluminium, isobutylene and hydrogen, as set out in the following equation:

$$(1a)\qquad Al+1\tfrac{1}{2}H_2+3\ \text{iso}\ C_4H_8=Al(\text{iso}\ C_4H_9)_3$$

In stage 1*b*, the aluminum triisobutyl is then reacted with a second, preferably straight-chained, α-olefine in accordance with the following equation:

$$(1b)\qquad Al(\text{iso}\ C_4H_9)_3+3C_nH_{2n}=Al(C_nH_{2n+1})_3+3\ \text{iso}\ C_4H_8$$

The isobutylene is thereafter returned to the stage 1*a* again. It will be seen that by using a combination of the partial Reactions 1 and 2 or 1*a*, 1*b*, and 2 in accordance with the invention, metal alkyls, for example lead tetraalkyls, can be produced from constituents consisting of metal, for example lead, hydrogen and an olefine as set out in the equation already given. Secondary products of low value are formed only insofar as hydrogenation of the olefines into paraffins in secondary reactions occurs in stage 1 or 1*a*. By suitably carrying out the reaction, however, this hydrogenation can be restricted to affect only 5 to 15% of the total amount of olefine which is converted. Consequently, the consumption of material when using the process of the invention for manufacturing, for example, lead tetraalkyls is far lower than in the prior known processes, which operate with stoichiometric amounts of valuable auxiliary materials.

Nevertheless, the process of the invention necessitates the use of electrical energy in the second stage. However, the amount used can be kept exceptionally low, since it is possible by using suitable electrolytes to manage with very low voltages in the electrolysis cells, in the region of about 1 to 2 volts. The consumption of electrical energy per kilogramme of, for example, lead tetraethyl is then of the order of magnitude of 1 kw.h. The high molecular weight of the lead tetraalkyl, for example lead tetraethyl, formed is particularly favourable in such a case, since the weight of lead tetraethyl obtained is 9 times the weight of the aluminium recovered at the cathode.

Details of how stage 1 or stages 1*a* and 1*b* are to be carried out are given in the aforementioned copending application Ser. No. 484,576 of January 25, 1955, and application Ser. No. 524,797, issued to Patent No. 2,835,689 in the name of the applicants.

The electroylsis in the second stage of the process of the invention, using anodes of the metal of which it is desired to produce the alkyl, can advantageously be carried out in accordance with application Ser. No. 521,424, issued to Patent No. 2,849,349, by electrolysis of a homogeneous melt comprising a true organic aluminum compound of the general formula

$$AlR(R')_2$$

in which R represents an alkyl radical and R' an alkyl radical or a halogen atom, or a complex compound

thereof with an alkali metal compound of the general formula

$$MeR'$$

wherein Me represents an alkali metal.

A number of technological problems occur in the second stage and these are described in detail below.

The aluminum alkyls must be made electrically conducting. For this purpose, the aluminum trialkyls can be mixed with alkali metal halides, for example sodium fluoride. Instead of the latter, it is also possible to use quaternary ammonium salts, such as $(C_2H_5)_4NCl$. One particularly suitable electrolyte for the production of lead tetraethyl is the liquid complex compound having the composition $NaF.2Al(C_2H_5)_3$, which has been disclosed by the applicants in copending application Ser. No. 379,294 of September 9, 1953, issued to Patent No. 2,844,-615. However, it is also possible to use other electrolytes, for example either alkali metal-aluminum tetraalkyls or complex compounds of the true organic aluminum compounds of the general formula

$$AlR(R')_2$$

with alkali halides MeX, these complex compounds having the general formula

$$MeX.nAlR(R')_2$$

wherein Me represents an alkali metal, X a halogen atom, R an alkyl radical, R' an alkyl radical or a halogen atom and *n* either 1 or 2, for example the complex compound $KCl.Al(C_2H_5)_3$. Generally speaking, for the production of lead tetraethyl it is readily possible to use any electrolyte containing aluminum triethyl which evolves substantially equimolecular amounts of ethane and ethylene at a neutral metallic anode consisting for example of platinum, copper or iron, or generally for the production of metal alkyls, electrolytes can be used which evolve substantially equimolecular amounts of paraffin hydrocarbons and olefine hydrocarbons.

The electroylsis constantly uses up aluminum triethyl (or aluminum trialkyls). When $NaF.2Al(C_2H_5)_3$ is used as the electrolyte, the effect is that the electrolyte bath constantly becomes impoverished in aluminum and finally its composition approaches a ratio between NaF and $Al(C_2H_5)_3$ such as 1:1. The definite complex compound $Na(Al(C_2H_5)_3F)$ with a melting points of 74° C., corresponds to this ratio between NaF and $Al(C_2H_5)_3$, this compound having a substantially lower conductivity than the compound $NaF.2Al(C_2H_5)_3$. It is clear that constant proportions can be maintained in the electrolyte bath by constant addition of aluminum triethyl in the amount in which it is consumed by formation of the metal alkyl, for example lead tetraethyl, at the anode on the one hand, and by deposition of aluminum at the cathode on the other hand. The amount of electrolyte itself which is originally introduced remains unchanged in this case.

Aluminum trialkyls which have not been prepared with very great care almost always contain certain amounts of dialkyl aluminum hydrides, which can be formed very easily by partial decomposition of the aluminum trialkyls with splitting off of olefine. It has been found that such electrolyte baths containing hydride are not very suitable for use in the process of the invention. For example, during the electrolysis hydrogen is more readily liberated than the ethyl or other alkyl radical. Accordingly, with such hydride-containing baths, it is initially only hydrogen which is evolved at the anode and none, or only a very small amount, of the metal alkyl, for example lead tetraethyl, which is to be produced is formed. Moreover, electrolyte baths which contain hydride do not remain clear, but become dark in colour even when only a little lead tetraethyl has been formed, with precipitation of a lead sludge. Very considerably interference with the electrolysis can thereby result.

It is therefore necessary to take care that the aluminum

trialkyl used for the production of the electrolyte, and also the aluminum trialkyl which is constantly added, should be as far as possible free from hydride. This effect is obtained very easily by treating the aluminum trialkyl with an olefine at a temperature in the region of 60–70° C. prior to or during the use for electrolysis purposes, the treatment preferably being carried out with that olefine which had the same number of carbon atoms as the alkyl radical joined to the aluminum. The result of such a treatment is that the entire amount of dialkyl aluminum hydride which is present changes into aluminum trialkyl by addition of the olefine. Moreover, prepared electrolyte baths which are subsequently found to contain amounts of hydride can be made suitable for use in the second stage of the process of the invention by being heated with an olefine. However, it is not necessary to use an olefine having the same number of carbon atoms as the alkyl radical. For example, a hydride-containing sodium fluoride-aluminum triethyl electrolyte can be completely freed from the hydride components by being heated with α-octene at 120–130° C. Such an initial treatment with a "foreign olefine" is, however, only advantageous in the course of any desired improvement of an electrolyte. Such a procedure is not suitable for the initial treatment of the aluminum alkyl which is to be constantly supplied during the process, since it leads to non-uniform reaction products.

Depending on the nature of the electrolyte employed, the metal alkyl to be produced and the molecular weight thereof, various processes can be used for the deposition thereof. In the production of lead tetraethyl, for example, using $NaF.2Al(C_2H_5)_3$ as electrolyte, the lead tetraethyl is deposited at the anode directly in the form of heavy drops which are insolube in the electrolyte, sink in the liquid electrolyte and then unite at the bottom of the apparatus to form a coherent layer of lead tetraethyl, which can be withdrawn either intermittently or continuously. It is thus possible to operate in a particularly simple manner.

However, the lead tetraethyl constantly removes from the electrolyte bath a small amount of the electrolyte, which is to a certain degree soluble in the lead tetraethyl. This electrolyte can, however, easily be separated from the lead tetraethyl by simple vacuum distillaton. The electrolyte is in this case left behind and can also be returned to the electrolysis vessel. This also applies to other metal alkyls with a sufficiently low boiling point, such as antimony alkyls and mercury alkyls. Instead of using vacuum distillation, it is also possible to recover the lead tetraalkyls by extraction of the electrolyte. It is then preferable to make use of the fact that the complex organic aluminium compounds with an electrolyte character are sparingly soluble or insoluble in saturated aliphatic hydrocarbons, while the lead tetraalkyls generally have unlimited miscibility with such solvents.

In the production of zinc alkyls, the alkyls formed are advantageously separated by extraction of the electrolyte. Hydrocarbons, for example pentane or hexane, or propane or butane under pressure, are suitable as extraction media.

Magnesium alkyls can also be separated by extraction of the electrolyte, but for this purpose it is necessary to use a very specific extraction medium, namely an aluminium trialkyl, since the magnesium dialkyls are insoluble in other solvents which otherwise are suitable for such extraction processes. The magnesium alkyls dissolved in aluminium alkyls to form complex compounds of the formula $MgR_2.2AlR_3$, and these complex compounds can be readily split into magnesium alkyls and aluminium alkyls by heating in vacuo. The magnesium alkyls remain in the residue.

The extraction process can be carried out continuously by constantly withdrawing some of the electrolyte from the electrolysis vessel and subjecting it to vacuum distillation or an extraction treatment in a separate device and

recycling the electrolyte freed from the metal alkyl product to the cell. Such a procedure is particularly recommended when the metal alkyl is sufficiently soluble in the electrolyte.

However, the lead tetraalkyls can also be obtained by extraction in the electrolysis cell by passing the extraction medium upwardly through the cell to dissolve the lead tetraalkyl formed in the cell.

Metal alkyls which have a sufficiently low boiling point, such as mercury alkyls, antimony alkyls and lead tetraalkyls, can however, be separated in a simple manner by carrying out the electrolysis in vacuo at a temperature at which these metal alkyls distil off. This can be done by heating the entire electrolysis cell to a suitable temperature during the electrolysis in vacuo, it being in particular possible for the lower low-boiling lead tetraalykyl compounds to distil out of the electrolysis cell and to be obtained as liquid distillate after suitable cooling of the vapours. This separation by distillation can therefore be carried out several times, because those complex compounds of the aluminium triaalkyls used as electrolyte are not volatile or are only very sparingly volatile. Small amounts of aluminium trialkyls which may pass over with the electrolyte can be separated, for example, by stirring the lead tetraalkyls with a little sodium fluoride and distilling in vacuo. Those sodium fluoride complexes of the aluminium trialkyls which are left can be used to compensate for unavoidable losses of electrolyte. The lead tetraalkyls which are obtained can also be purified by simply treating them with water, any admixed aluminium trialkyls being completely decomposed.

It is readily apparent that, with the continuous introduction of aluminium trialkyls into the electrolysis apparatus and constant withdrawal of the lead tetraalkyls by one of the said processes, it is possible to develop semi-continuous procedures in which the replenishment of the dissolved lead anodes and also the extraction of the precipitated aluminium need only take place intermittently. A further development of the process of the invention in the direction of a fully continuous process is obtained if also the precipitated aluminium is continuously discharged from the electrolysis cell.

The electrolytic precipitation of aluminium from baths, as proposed in the process of the invention, is per se the subject of the separate patent application Ser. No. 521,424, issued to Patent No. 2,849,349. Where this precipitation is carried out with the intention of producing compact protective coatings of pure aluminium on foreign metals or of refining a crude aluminum, the aim will be to ensure that the aluminium is deposited in as coherent a layer as possible. This is possible if an current density of about 1 amp./dm.^{2} is not exceeded at the cathode. The process of the invention can be carried out under these conditions; in this case, the cathode is withdrawn from time to time from the electrolysis cell, but it is necessary first of all to ensure that the cathode is still in a protective gas atmosphere, for example nitrogen or argon, so that the cathode is freed from the adhering electrolyte by flushing with a suitable solvent before the cathode is placed in air.

In carrying-out the complete two-stage process of the invention, however, such a procedure is not very desirable, since in the first stage, comprising the redissolving of the aluminium with the aid of the olefine and hydrogen, it is necessary in every case for the aluminum metal to be in finely divided form. It would therefore be necessary for the aluminium deposited in compact form to be first of all further comminuted. It is therefore preferred to arrange that the aluminium is deposited on the cathode in a loose finely divided form during the electrolysis by choosing a suitable higher current density; this is possible, for example, by using current densities higher than 1 amp./dm.^{2}, preferably higher than 2 amp./dm^2. Such a finely divided aluminium can be stripped from the cathode without it being necessary to interrupt the electrolysis, and can then be discharged by suitable devices from the electrolysis cell, either at intervals or continuously.

The electrolysis is carried out above the melting point of the electrolyte at a temperature between room temperature and 200° C., preferably between 60 and 120° C., depending on the electrolyte used.

The lead anodes dissolve in the course of the electrolysis, and are replaced from time to time. It is also readily possible to provide a continuous advance of relatively long lead rods, which are lengthened from time to time in a continuous process by casting liquid lead on to the upper end, which actually projects from the apparatus.

As the anode, it is also possible to use lead in lump form, for example granulated lead, in perforated vessels, for example baskets, consisting of insulating material, which are suspended in the electrolyte bath and which are replenishd from time to time with lead granules by suitable charging devices in an inert gas atmosphere.

The following examples further illustrate the invention.

Example 1

An electrolysis cell which permits a substantially continuous process for the production of lead tetraalkyl with only brief interruptions is shown in Figure 1 of the accompanying drawings. A cylinder **2** which is closed at the bottom end and is made of glass is positioned at the bottom end of a cylindrical electrolysis vessel **1**, and a second cylinder **3** also made of glass and open at the bottom end is located inside the cylinder **2**, the bottom end of the cylinder **3** being closed by a screen **4**. The inner cylinder is suspended by means of hooks **5** from a cylindrical cathode **6**, made of iron, copper or aluminium. The cathode is surrounded by a scraper **7** which can be operated from above. Arranged in a circle around the cathode **6** are six anodes **8**. During operation, the aluminium deposited on the cathode is scraped downwardly from time to time, this aluminium collecting in the cylinder **3**. When the cylinder **3** is full of aluminium, the cathode and also the cylinder **3** are withdrawn in an upward direction and removed under a nitrogen atmosphere by means of a discharge device which is not shown, and are then replaced by a second similar cathode **6** and a second cylinder **3** in a protective gas atmosphere. The method of supplying aluminium triethyl is not shown. The lead tetraethyl discharges at **9**. The arrangement of the anodes **8** around the cathode **6** is shown as a section A—B in Figure 2.

Example 2

Another embodiment of the electrolysis cell, in which the aluminium also is continuously extracted, is shown in Figure 3. In this embodiment, a travelling endless thin metal belt **10** serves as the cathode, this belt running over rollers **11** and the aluminium deposited thereon being scraped off at **12** by means of a knife **13**. In this case also, the anode consists of a lead rod **14**.

As has already been stated, copending application Ser. No. 521,424, issued to Patent No. 2,849,349, describes a process for the electrolytic deposition of aluminium by means of which aluminium can be refined very effectively and with a low current consumption, using specified electrolytes. The electrolytes used in such a case are homogeneous melts of true organic aluminium compounds of the general formula $AlR(R')_2$, in which R represents an alkyl radical and R' represents an alkyl radical or a halogen atom, and the complex compounds of which are used with alkali compounds of the general formula MeR', in which Me represents an alkali metal, or with quaternary ammonium compounds. Such electrolytes are also suitable for the process of the present invention.

For the production of aluminium trialkyls, especially aluminium triethyl, in accordance with the second stage of the process of the invention, it is possible without disadvantages to use ordinary foundry aluminium with

an aluminium content of for example 99.7%. The usual impurities of this ordinary foundry aluminium are left behind in the formation of the aluminium trialkyl in the second stage. The metal present in an aluminium trialkyl is consequently extraordinarily pure. Hence on electrolysis of an electrolyte containing this aluminium trialkyl, the aluminium deposited at the cathode should be of a higher degree of purity than the foundry aluminium.

It has in fact been found that the previously described process for the production of metal alkyls, such as lead tetraalkyls, can be modified so that it is possible to deposite cathodically pure aluminium as well as to produce metal alkyls, such as otherwise obtained by the process according to copending application Ser. No. 521,424, issued to Patent No. 2,849,349. For this purpose ordinary foundry aluminium is supplied to the process instead of the same aluminium being constantly re-used. However, in order to be able constantly to extract refined aluminium from the process, it is necessary to overcome the following difficulty.

If for example the electrolyte $NaF.2Al(C_2H_5)_3$, which is particularly satisfactory for the production of lead tetraethyl, is electrolytically treated, without special precautionary measures, with a lead anode and a cathode of any other desired metallic material, the cathodically deposited aluminium does not have the same degree of purity as is usually found for aluminium which is obtained with otherwise the same arrangement but using an aluminium anode. In fact, if lead tetraethyl is also produced in the electrolyte, the cathodically deposited aluminium contains lead. The reason for this is no doubt that lead tetraethyl is in fact practically insoluble in the said electrolyte and is deposited as a sparingly soluble layer at the base of the apparatus serving for the electrolysis, but small amounts apparently pass in dissolved form into the electrolyte and react with the cathodically deposited aluminum to form lead and aluminium triethyl. Due to this secondary reaction, only a very small part of the lead tetraethyl produced is lost. The lowering of the yield is so small that in practice it is of no importance for the lead tetraethyl, but the very small traces of lead deposited together with the aluminium lower the quality of the latter and do not permit the manufacture of lead tetraethyl to be combined with the refining of the aluminium.

According to one form of the invention for the purpose of depositing pure aluminium at the cathode, the electrolysis cell used has a cethode space which is separated by a diaphragm from the anode space, and the electrolyte is continuously withdrawn from the anode space above the liquid lead tetraethyl layer and is extracted with a solvent and recycled to the cathode space again in such a manner that the electrolyte flows through the diaphragm from the cathode space into the anode space throughout the entire electrolysis period.

As regards the electrolysis cell used for carrying out the process of the invention, the cathode space is preferably arranged above the anode space as well as being separated from the latter by a diaphragm. The diaphragm can consist of a wide variety of materials. Pressed fibrous materials, such as asbestos, glass wool or quartz wool, between perforated plates of insulating material, are particularly suitable, or also porous polyethylene of high molecular weight and with a high melting point, such as obtained by the low pressure polymerisation of ethylene. When solid lead anodes are used, these must be perforated or arranged substantially in the form of a horizontally disposed grid, so that the lead tetraethyl can flow downwardly into the space beneath the anode. The arrangement preferably has a construction such as that shown in Figure 4, if the process is to be carried out continuously.

Example 3

The electrolysis is carried out in an electrolytic cell in the form of a double-walled trough **15** of V-shaped cross-section, as shown in Figure 4. The inner wall is provided with openings at the bottom. The apex of the V is bridged by a screen **16** which is a non-conductor of electricity. Lead granules **21** are disposed between the walls of the trough. A diaphragm **17** is formed as a shallow V. Located in the cathode space above the diaphragm **17** is a device **18** for continuously removing aluminum by means of a travelling metal web or belt as described in Example 2. Small amounts of gas are formed at the anode: these can be discharged at **19** by means of the pipes **20**. The same pipes can also serve for discharging electrolyte from the anode space. Both walls of the V-shaped trough **15** consist of steel and are covered with an electrically insulating enamel layer over the area which is immersed in the electrolyte. The lead is introduced in the form of granules **21** between the walls of the trough **15**, and these granules are replenished at the top at the rate at which they are dissolved at the bottom. The lead alkyl formed is discharged at **22**. (Unessential parts such as the covering and discharge means for the aluminium are omitted.)

The levels of the electrolyte in the cathode space and of the electrolyte in the anode space are indicated by the reference numerals **23** and **24** respectively.

The diaphragm **17** can alternatively be rounded as a section of a cylinder.

The necessary or preferred speed of circulation of the electrolyte depends on various factors. If a specific difference in the electrolyte level is maintained between the cathode space and the anode space, the circulation speed is automatically produced by the permeability of the diaphragm. If the diaphragm has very fine pores, it is possible to use a low circulation speed. However, if the pores are large, it will be necessary to choose a higher circulation speed or the operation will in this case be carried out with a smaller difference in level. In each case, the flow conditions in the diaphragm must be such that rediffusion from the lead-containing anode space into the cathode space is reliably avoided. Diaphragms with fine pores are more reliable in this respect than those with large pores. On the other hand, the total electrical resistance of the cell is also very dependent on the size of the pores in the diaphragm. The best technical effect is thus a compromise in each case between different influences which oppose one another, and it is very easy for the pore sizes, level differences and flow velocities which are preferred in each case to be found by a number of experiments. The energy needed for circulation which is saved by using a diaphragm with very fine pores must however be used by increasing the cell voltage, that is to say, increasing the electrical energy. Generally speaking, the energy consumed by repeated circulation is smaller than that required for an increase in the cell voltage. However since energy is required not only for the circulation but also for the larger amounts of liquid which must be constantly extracted with an increased speed of circulation, the comparison is not as simple as it seems at first sight, and the conditions chosen are entirely dependent on the energy costs in each individual case.

Hydrocarbons are particularly suitable for treatment of the electrolyte in order to extract the traces of lead tetraethyl contained therein.

In the production of lead tetraethyl, the amount of refined 99.99% aluminium which is obtained in this way is about ⅛ of the weight of the amount of lead tetraethyl which is produced. The aluminium deposited has the same quality as the refined aluminium obtained by the process of copending application Ser. No. 521,424, issued to Patent No. 2,849,349.

With various metal alkyls, for example antimony alkyls, it is possible to proceed as described in Examples 1 and 2, as well as by the method described in Example 3, since, with a certain content of electrolyte based on the metal alkyl compound, the metal which entered the

solution at the anode is not deposited at the cathode. However, it is recommended for the anode space to be separated from the cathode space by a diaphragm if it is desired to obtain an aluminium with a high degree of purity as secondary product.

On the other hand, with other metals, for example zinc and magnesium, it is always preferred for a diaphragm to be used for producing good results. In the electrolysis, zinc and magnesium dissolve in exactly the correct amount at the anode. Magnesium alkyls and zinc alkyls, however, have a comparatively high degree of solubility in the electrolyte, so that in the production of these compounds the complication arises that it is not aluminium, but magnesium or zinc, which is deposited at the cathode. In this and similar cases, therefore, the electrolysis will be most effective if the anode space and cathode space are separated by a diaphragm and provision is made for a constant flow of electrolyte from the cathode space into the anode space. The metal alkyls formed are in this case separated from the circulated electrolyte in a separate step of the process.

Example 4

The electrolyte $NaF.2Al(C_2H_5)_3$ is electrolysed at a temperature of 70–100° C. in an electrolytic cell without a diaphragm as described in Example 1 or 2, using an antimony anode and a cathode consisting of aluminium or iron. The correct amount of antimony dissolves, and aluminum is deposited at the cathode. At first, no other alterations are observed, and in particular the antimony triethyl formed is not deposited as an insoluble layer in this case. If such an amount of current is passed through that the ratio between aluminium triethyl and sodium fluoride drops from 2 to about 1.7, the electrolysis is interrupted and the liquid electrolyte is treated with hexane for extraction of antimony triethyl. After the hexane has been distilled off, a residue is left which, upon being distilled in vacuo (20 mm.) at a temperature between 60 and 100° C., yields a colourless distillate of antimony triethyl in an amount which corresponds to about 80 to 90% of the amount to be obtained from the number of coulombs passed through. This distillate scarcely rises in temperature on being mixed with water and therefore contains practically no aluminium triethyl. The distillate is distilled again with steam, and pure antimony triethyl with a boiling point of 158° C. at normal pressure is obtained by absorption in pentane after the usual working up process. In this first distillation of the antimony triethyl in vacuo, (prior to the steam distillation), a sparingly volatile residue is left which consists substantially of the aluminium triethyl-sodium fluoride compound $NaF.Al(C_2H_5)_3$.

This residue is returned to the main quantity of the original electrolyte and then such an amount of aluminium triethyl is added that a liquid layer of aluminium triethyl remains above the electrolyte even after stirring for a relatively long time. This liquid layer is withdrawn and then the electrolyte is again ready for a fresh experiment. The cathodically deposited aluminium is used again in the usual way for the production of the aluminium triethyl. Even during the electrolysis the electrolyte can be covered with aluminium triethyl and provision may be made by gentle stirring for the electrolyte to remain always saturated with aluminium triethyl. The electrolysis is then carried out until the layer of aluminium triethyl has disappeared. The operation is carried out in a protective gas atmosphere, since all the substances used or formed within the scope of the example, especially the antimony compounds, are sensitive to air.

Example 5

The procedure is as described in Example 4, but a tin anode is used. The tin tetraethyl formed is deposited below the electrolyte as an insoluble layer and can be extracted. The electrolyte is constantly replenished by aluminium triethyl in an amount corresponding to the rate of removal of the tin tetraethyl.

Example 6

In an apparatus such as that described in Example 3, the electrolysis is carried out with an electrolyte consisting of aluminium triethyl and sodium fluoride and having the composition $NaF.2Al(C_2H_5)_3$, but using a magnesium anode. The electrolyte constantly withdrawn from the anode space is supplied to an extraction device, in which the product is extracted from the electrolyte with liquid aluminium triethyl. The electrolyte in this case is simultaneously saturated again with aluminium triethyl, that is to say, the loss resulting from the electrolysis is again made up. The electrolyte having the aforementioned composition is practically insoluble in aluminium triethyl, so that the extraction can be carried out without any difficulty. By evaporating the aluminium triethyl used for the extraction, the complex compound

$$Mg(C_2H_5)_2.2Al(C_2H_5)_3$$

is left as a thick oil. By heating in vacuo at about 120° C., this complex compound can be split into solid magnesium diethyl, which remains in the residue, and aluminium triethyl, which distils over. The electrolyte from which the product has been extracted is made up again by saturating it with aluminium triethyl and is returned to the anode space. The cathodically deposited aluminium is converted into aluminium triethyl, or a relatively impure crude aluminium is used for the production of the aluminium triethyl which is constantly required and a high-grade refined aluminium is then constantly recovered from the electrolysis. All operations are carried out in a protective gas atmosphere, for example nitrogen.

Example 7

The procedure of Example 6 is followed, using a zinc anode and an electrolyte consisting of $NaF.2Al(C_2H_5)_3$. Hexane is used for extraction purposes. The zinc tripropyl can be readily distilled from the extract in vacuo. There is a certain residue of electrolyte which has also been extracted, and this residue is returned to the process. The losses in electrolyte caused by the cathodic deposition of aluminium and the anodic formation of zinc propyl are constantly made up by adding aluminium tripropyl.

Example 8

The procedure of Example 6 is followed, using an indium anode. Pentane is used for the extraction of the electrolyte containing indium triethyl. After evaporation of the pentane, the indium triethyl can easily be obtained in a pure form from the extract by vacuum distillation. The losses in electrolyte caused by the cathodic deposition of aluminium and the anodic formation of indium triethyl are constantly made up by adding aluminium triethyl.

What we claim is:

1. Process for the production of metal alkyl compounds which comprises passing an electrolysis current between a cathode and an anode through an electrolyte containing an aluminium trialkyl, said anode being a member selected from the group consisting of a metal of the second to fifth groups of the periodic system, to thereby dissolve the anode metal with the formation of the alkyl compound thereof having alkyl radicals corresponding to the alkyl radicals of said aluminium trialkyl, and recovering the metal alkyl compound so formed.

2. Process according to claim 1 in which said anode is a lead anode.

3. Process according to claim 2 in which said aluminium trialkyl is aluminium triethyl and in which the metal alkyl compound formed is tetraethyl lead.

4. Process according to claim 1 in which said electrolyte comprises a mixture of aluminium trialkyl and an alkali metal halide.

5. Process according to claim 1 in which said electrolyte comprises a complex compound of an aluminium compound and an alkali halide having the general formula

$$MeX.nAlR(R')_2$$

in which Me represents an alkali metal, X a halogen atom, R an alkyl radical, R' a member selected from the group consisting of alkyl radicals and halogen atoms and n is a whole number between 1 and 2.

6. Process according to claim 5 in which said electrolyte is

$$NaF.2Al(C_2H_5)_3$$

7. Process according to claim 1 in which said metal alkyl compound is recovered by extraction.

8. Process according to claim 7 in which said extraction is effected with a hydrocarbon extracting agent.

9. Process according to claim 1 in which said group member is magnesium and in which said metal alkyl compound is recovered by extraction with an aluminum trialkyl.

10. Process according to claim 1 in which said metal alkyl is recovered by layer separation and vacuum distillation.

11. Process according to claim 1 in which said metal alkyl compound is recovered by layer separation and extraction.

12. Process according to claim 1 in which said metal alkyl compound is recovered by withdrawing electrolyte from the electrolysis, separating the formed metal alkyl compound by vacuum distillation and recycling electrolyte to the electrolysis after said separation.

13. Process according to claim 1 in which said metal alkyl compound is recovered by withdrawing a portion of the electrolyte from the electrolysis, extracting the formed metal alkyl therefrom and recycling the residual electrolyte to the electrolysis.

14. Process according to claim 1 in which said metal alkyl compound is recovered by effecting said electrolysis under vacuum and substantially continuously distilling off the metal alkyl compound formed.

15. Process according to claim 1 in which said electrolysis is effected at a temperature between about room temperature and 200° C.

16. Process according to claim 1 which includes effecting said electrolysis with said cathode in a cathode space and said anode in an anode space while maintaining said cathode space and said anode space separated by a diaphragm.

17. Process according to claim 16 which includes maintaining a constant flow of said electrolyte from said cathode space to said anode space.

18. Process according to claim 1 which includes maintaining said cathode in a cathode space and said anode in an anode space while maintaining said cathode space separated from said anode space by a diaphragm, substantially continuously withdrawing electrolyte from said anode space, extracting the metal alkyl compound formed therefrom and substantially continuously recycling the electrolyte after said extraction to said cathode space.

19. Process according to claim 1 which includes maintaining said cathode in a cathode space and said anode in an anode space while maintaining a diaphragm separating said cathode and said anode spaces and which includes substantially continuously passing electrolyte from the cathode space into the anode space at a flow rate sufficient to prevent diffusion of electrolyte from the anode space into the cathode space.

20. Process according to claim 1 which includes maintaining said cathode in a cathode space and said anode in an anode space while maintaining a diaphragm separating said cathode and said anode spaces and which include substantially continuously passing electrolyte from the cathode space into the anode space while maintaining a higher pressure on the cathode space side of the diaphragm than on the anode space side of said diaphragm to prevent diffusion of electrolyte back from said anode space to said cathode space.

21. Process for the production of metal alkyl compounds which comprises passing an electrolysis current between a cathode and anode through a homogeneous electrolyte melt comprising an organic aluminum compound of the general formula $AlR(R')_2$ in which R represents an alkyl radical and R' represents a member selected from the group consisting of alkyl radicals and halogen atoms and complex compounds thereof with an alkali compound having the general formula MeR' in which Me represents an alkali metal, said anode being a member selected from the group consisting of metals of the second to fifth groups of the periodic system, to thereby dissolve the anode metal with the formation of an alkyl compound thereof and recovering the metal alkyl compound so formed.

22. Process for the production of metal alkyl compounds which comprises reacting aluminum with an olefin and hydrogen to thereby form an aluminum trialkyl, passing an electrolysis current between a cathode and an anode through an electrolyte containing said aluminum trialkyl, said anode being a member selected from the group consisting of metals of the second to fifth groups of the periodic system, to thereby dissolve the anode metal with the formation of the alkyl compound thereof having alkyl radicals corresponding to the alkyl radicals of said aluminum trialkyl and recovering the metal alkyl so formed.

23. Process according to claim 22 in which said anode is a lead anode.

24. Process according to claim 23 in which said olefin is ethylene, said aluminum trialkyl aluminum triethyl and in which the metal alkyl compound formed is tetraethyl lead.

25. Process according to claim 22 in which said electrolyte comprises a complex compound of an aluminum compound and an alkali halide having the general formula

$$MeX.nAlR(R')_2$$

in which Me represents an alkali metal, X a halogen atom, R an alkyl radical, R' a member selected from the group consisting of alkyl radicals and halogen atoms and n is a number between 1 and 2.

26. Process according to claim 25 in which said electrolyte is

$$NaF.2Al(C_2H_5)_3$$

27. Process according to claim 25 which includes replacing consumed aluminum trialkyl by adding fresh aluminum trialkyl to said electrolyte.

28. Process according to claim 22 in which said electrolyte is substantially free from alkyl aluminum hydrides.

29. Process according to claim 22 which comprises contacting the aluminium trialkyl present in the electrolyte with an olefin at a temperature between about 60° and 70° C. prior to said electrolysis, to thereby free the same of any alkyl aluminium hydrides present.

30. Process according to claim 22 which includes contacting said aluminium alkyl present in the electrolyte with an olefin at a temperature of about 60 to 70° C. during said electrolysis to free the same of any alkyl aluminium hydrides present.

31. Process according to claim 22 in which said cathode is an iron cathode.

32. Process according to claim 22 which includes recovering aluminium from the cathode and reacting the recovered aluminium with an olefin and hydrogen for the formation of further aluminium trialkyl for use in the process.

33. Process according to claim 22 in which said electrolysis is effected with a current density in excess of 1 amp./dm.^{2} and which includes recovering the aluminium formed at the cathode in loose finely divided form.

34. The process for producing tetra alkyl lead compounds which comprises passing a direct electric current

between a cathode and a lead anode through an electrolyte consisting essentially of a composition prepared by admixing a trialkyl aluminum compound with an alkali metal halide, the alkali metal halide being added in a sufficient quantity to render the composition conductive, to thereby dissolve the anode metal with the formation of a tetra alkyl lead compound having alkyl radicals corresponding to the alkyl radicals of said aluminum compound.

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