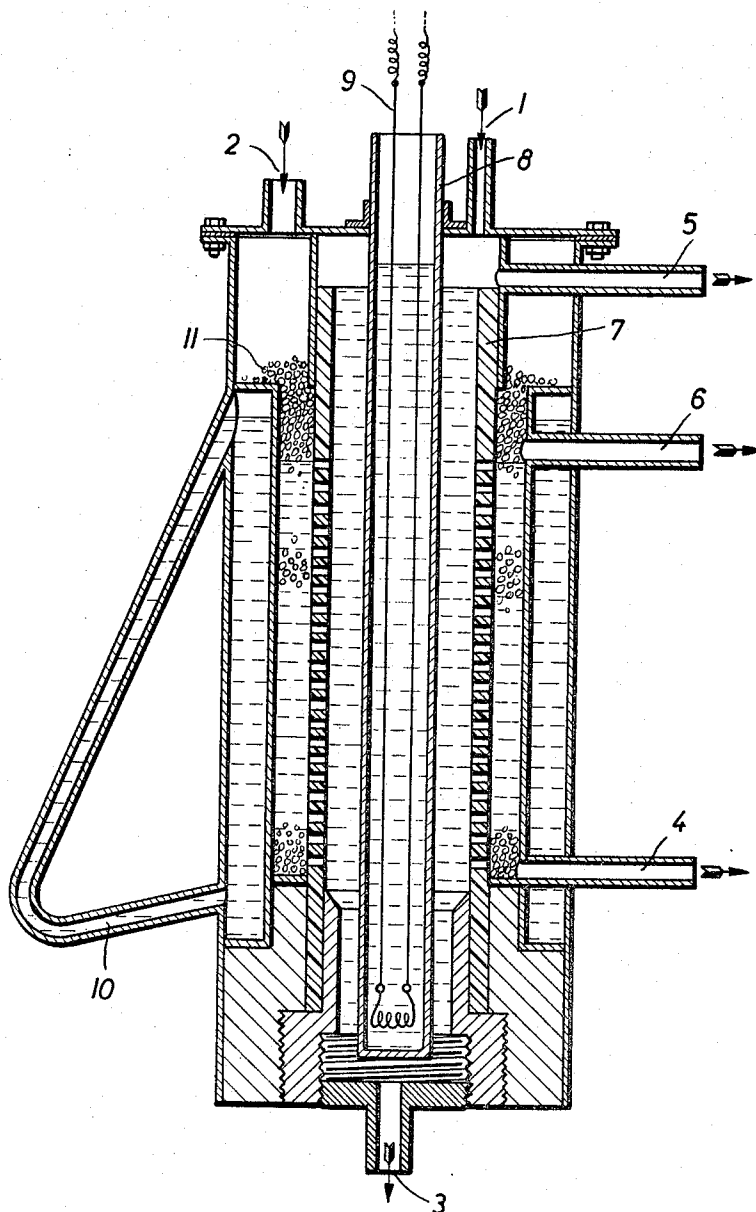


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PROCESS FOR THE ELECTROLYTIC PRODUCTION OF  
MAGNESIUM DIALKYL AND  
ALUMINIUM TRIALKYL  
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3,306,836

## PROCESS FOR THE ELECTROLYTIC PRODUCTION OF MAGNESIUM DIALKYLS AND ALUMINIUM TRIALKYLS

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Claims priority, application Germany, May 6, 1959,

Z 7,316

15 Claims. (Cl. 204-62)

Processes for the electrolytic production of metal alkyls are described in co-pending applications Nos. 792,614 filed February 11, 1959, 792,467, filed February 11, 1959, which applications by mesne applications matured into U.S. Patent No. 3,254,009; and U.S. Patents Nos. 2,985,568 and 3,069,334 of which this application is a continuation-in-part. This application is a continuation of application Serial No. 27,218, filed May 5, 1960.

This invention relates to a process for the electrolytic production of magnesium dialkyls and aluminium trialkyls.

While aluminium is generally deposited at the cathode in the processes described in the specifications referred to above, the two last-mentioned specifications describe processes wherein sodium is deposited at the cathode while the metal alkyls desired are formed at the anode and may be separated from the electrolyte.

In our co-pending patent application 792,614 the electrolyte used is an aluminium alkoxy or alkoxy complex compound or a mixture of these complex compounds with compounds of the general formula  $\text{MeAlR}_4$ . In the process of our co-pending patent application 792,467 the electrolysis is first carried out with a compound of the general formula  $\text{MeAlR}_4$ . The resultant reaction product is reacted with an aluminium alkoxy or alkoxy complex compound.

Both of the processes exhibit certain disadvantages for the production of aluminium trialkyl while the production of magnesium dialkyl is not possible by the processes described therein.

This invention relates to a new process for the production of these two metal alkyls, which process offers considerable simplifications and improved economy over the prior art processes.

It is an object of the present invention to provide a process for the electrolytic production of magnesium dialkyl and aluminium trialkyl, which process comprises electrolyzing a compound of the general formula  $\text{MeAlR}_4$  wherein Me is sodium or a mixture of sodium and potassium and R is an alkyl radical containing especially from 2 to 6 carbon atoms, with the use of anodes of magnesium or aluminium while maintaining the content of free aluminium trialkyl in the electrolyte at the cathode below 3%. At the same time, sodium is deposited at the cathode in accordance with the invention. It is particularly preferred to maintain the content of free aluminium trialkyl in the electrolyte in the neighborhood of the cathode below 1%.

Suitable cathode materials are all good conductors of electric current, which do not form alloys with the sodium deposited at the cathode under the reaction conditions.

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The metal alkyl forming from the anode metal and free aluminium trialkyl as a decomposition product of the electrolyte are formed at the anode during the electrolysis.

It may be desirable for carrying out the process of the invention to separate the anode space from the cathode space by a diaphragm which may be made of, for example, asbestos, glass wool, quartz wool and preferably of porous cellulose products, e.g., filter paper. Suitable diaphragm materials and electrolytic cells equipped with such diaphragms are described in the earlier filed patent specifications mentioned above.

The diaphragm prevents the anodically formed and uncomplexed aluminium trialkyl or the resulting magnesium dialkyl from mixing with the electrolyte liquid in the neighborhood of the cathode, which mixing would interfere in an undesirable manner with the deposition of sodium and the anodic formation of metal alkyl.

It may be preferable when using aluminium anodes to effect the electrolysis in vacuo. In this case, the anodically formed aluminium trialkyl is distilled out of the electrolyte immediately after its formation. It is advantageous, however, to use as high a vacuum as is possible. Thus, for example, final pressures of below 1 mm. Hg may be used. The free aluminium trialkyl will then have no opportunity of proceeding into the neighborhood of the cathode but will leave the electrolyte prior to proceeding close to the cathode. Another possibility is the use of liquid extracting agents which do not mix with the electrolyte. In this embodiment of the process of the invention, the electrolyte is constantly flushed with the extracting agent during the electrolysis. The extracting agent absorbs the organometallic compounds anodically formed and thereby excludes them from the undesirable reaction with the sodium deposited at the cathode. The extraction liquid which, for example, collects on top of the electrolyte may be withdrawn from the electrolytic cell intermittently or continuously and then separated into extracting agent and organometallic compound. As extracting agents, there may be used saturated hydrocarbons and preferably aliphatic and hydroaromatic hydrocarbons which are immiscible with the electrolyte.

The operation of the process of the invention is extremely simple. The uncomplexed metal alkyl compounds formed during the electrolysis do not commingle with the complex electrolyte. Instead, they separate as the lighter liquid phase on the electrolyte and may thence be withdrawn intermittently or continuously from the electrolyzer. When operating with magnesium anodes, the resultant mixture of magnesium dialkyl and aluminium trialkyl which is present in the form of a loose complex compound is easily separated, e.g., by distillation. In doing so, the volatile aluminium trialkyl distills while the magnesium dialkyl is left as the residue. The distillation is preferably effected under a slight vacuum. When using aluminium anodes, only aluminium trialkyl is formed. Three equivalents of aluminium trialkyl are simultaneously formed from the decomposition of the electrolyte per equivalent of the aluminium trialkyl formed from the anode metal. Thus, a total of four equivalents of aluminium trialkyl is obtained.

It is preferred for the economic execution of the process of the invention to reconvert into the complex aluminium tetra-alkyl compound these portions of aluminium trialkyl formed by the decomposition of the complex elec-

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trolyte. This may be accomplished advantageously by treating the compound together with sodium with hydrogen and olefins by the process described in our Patent 2,826,598.

For this purpose, the sodium deposited cathodically in the electrolysis may be used to advantage.

It is possible in this manner to carry out cyclic processes for the production of aluminium trialkyl and magnesium dialkyl. In accordance with the invention, a complex compound of the general formula  $\text{MeAlR}_4$  mentioned above is electrolyzed while maintaining the content of uncomplexed aluminium trialkyl in the electrolyte low in the neighborhood of the cathode by the method described above. The organometallic compounds formed at the anode and comprising a mixture of magnesium dialkyl and aluminium trialkyl or only aluminium trialkyl are separated from the electrolyte and separated into aluminium trialkyl derived from the decomposition of the electrolyte and metal alkyl formed from the anode metal. The aluminium trialkyl formed by decomposition of the electrolyte, together with the sodium deposited at the cathode, is then treated with hydrogen and the appropriate olefin outside of the electrolytic cell to be reconverted into the complex compound of the general formula  $\text{MeAlR}_4$ . The latter is subsequently introduced intermittently or preferably continuously into the electrolytic cell. The only starting materials constantly used in this embodiment of the process are the anode metal, hydrogen and olefin. The adjuvants further used in the electrolysis are recycled. Except for unavoidable losses, they are not introduced continuously but only once, i.e., at the beginning of the process.

Since sodium melts at about  $97^\circ$  and the deposition of molten sodium is desirable, temperatures in excess of about  $100^\circ \text{C}$ . are preferred in accordance with the invention. Particularly preferred is the temperature range from about  $100^\circ$  to about  $140^\circ \text{C}$ .

The process may be operated at relatively low voltages. Suitable voltages are, for example, in the range from about 0.5 to about 5 volts and preferably from 1.5 to 3 volts. It is preferred for economic utilization of the process to operate at higher current densities, particularly preferred being current densities up to about 80 a./dm.<sup>2</sup>. However, higher current densities may be used. Furthermore, it is preferred to operate with current densities of at least about 2 to about 5 a./dm.<sup>2</sup>. Particularly suited is a range from about 30 to about 50 a./dm.<sup>2</sup>. Of the complex compounds of the general formula  $\text{MeAlR}_4$ , the potassium compounds are better conductors of current than the sodium compounds. It is particularly preferred, therefore, to use mixtures of sodium and potassium complex compounds as the electrolytes. From these, sodium is always deposited at the cathode with potassium contents up to about 80% so that it is furthermore preferred to use not more than about 80% by weight of potassium in these mixtures. An apparatus in which the process of the invention is operable is shown in the appended drawing. The electrolytic cell shown comprises an opening 1 through which the electrolyte which is preferably in molten state may be introduced. The metal whose metal alkyls are to be produced may be introduced through the opening 2 in the form of, for example, small spheres or granules. During the electrolysis, the sodium is deposited at the cylindrical cathode 3 of, for example, copper in the center of the electrolysis vessel. It flows to the bottom and may thence be withdrawn from the electrolyte cell through the opening 3. The cathode space is separated from the anode space by a perforated cylinder of insulating material 7 with a superimposed diaphragm. This may, for example, consist of hardened filter paper or a fine cloth or glass filter cloth. At the outside is the anode space which is filled with the small metal spheres 11 and may continuously be supplied with fresh metal at the rate at which the metal dissolved in the electro-

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lysis. The anode space is provided with two outlet openings (4 and 6). The metal alkyl (aluminium trialkyl or a mixture of aluminium trialkyl and magnesium dialkyl) formed during the electrolysis rises in upward direction in the anode space and may be withdrawn through the opening 6. Disposed in the inner space of the perforated cylinder 7 is the catholyte which, for example, may be withdrawn from the apparatus through the overflow 5. The cathode cylinder 8 may be filled in its interior with a heating or cooling liquid the temperature of which is controlled by the heating element 9. It is possible in this manner to adjust the temperature of the catholyte as desired while the temperature of the anolyte is adjustable by the heating element 10 which, in this case, is operated by recirculating liquid.

#### Example 1

Sodium-aluminium tetraethyl which is preferably in molten state is introduced into an electrolyzer as shown in the appended drawing. The cathode is constituted by a copper cylinder. Arranged at a distance of 1 cm. from this cylinder is a perforated cylinder of porcelain or a plastic composition, e.g., Bakelite reinforced by a fabric. Tightened round the cylinder is a diaphragm of hardened filter paper or a fine cloth or glass filter fabric. Behind the diaphragm is the anode space which is filled with aluminium granules and may be supplied continuously with aluminium granules at the rate at which aluminium is dissolved in the electrolysis. Heating of the electrolyte or removal of the Joulean heat formed during the electrolysis is effected by recirculating a liquid of  $140^\circ \text{C}$ . in the interior of the closed cathode cylinder. The current is adjusted to 15 amperes with a terminal voltage of 3 volts. With the present dimensioning of the apparatus, this corresponds to an anodic current density of 14 a./dm.<sup>2</sup> and a cathodic current density of 10 a./dm.<sup>2</sup>. The cathodically formed sodium flows as a thin film down at the surface of the cathode into the lower cathode space where it is intermittently withdrawn in molten state. The anodically formed aluminium triethyl is sparingly soluble in the electrolyte and rises as droplets to the electrolyte surface where it forms a second liquid phase in the anode space, which is intermittently withdrawn. The influx of  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  into the cathode space should be adjusted such that the liquid level in the cathode space is by 4 to 5 cm. higher than in the anode space.

The yields of newly formed aluminium triethyl is 1.4 gms. per ampere hour (corresponding to 99% of the theoretical yield). A total of 5.7 gms. of  $\text{Al}(\text{C}_2\text{H}_5)_3$  is separated in the anode space per ampere hour. Three-quarters of this amount are derived from the electrolyte and are reacted with NaH and ethylene at  $180^\circ \text{C}$ . and an ethylene pressure of 10 atmospheres to be reconverted into sodium-aluminium tetraethyl.

#### Example 2

The sodium-aluminium tetrapropyl obtained in accordance with Example 4 of our Patent 2,826,598 is introduced into the electrolyzer as shown in the appended drawing while being preferably in molten state. The temperature during the electrolysis is maintained at the preferred level of about  $100^\circ \text{C}$ . The current is adjusted to 15 amperes at a terminal voltage of 8 volts, which corresponds to an anodic current density of 4 a./dm.<sup>2</sup> and a cathodic current density of 10 a./dm.<sup>2</sup>. The sodium deposited at the cathode flows downwardly as a thin film on the surface of the cathode and into the lower cathode space from where it is intermittently withdrawn in molten state. The effluent from the anode space is adjusted such that a reaction mixture containing about 20% of aluminium tripropyl flows off, which will be the case if a total of about 550 ml. of liquid per hour is withdrawn from the anode space. The influx of molten sodium-aluminium

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tetrapropyl into the cathode space should be adjusted such that the liquid level in the cathode space is by 4 to 5 centimeters higher than that in the anode space.

Aluminium tripropyl is separated from sodium-aluminium tetrapropyl in a film evaporator (at 100° C. and 1 mm. Hg). One-fourth of the distillate obtained is newly formed aluminium tripropyl and is removed from the cycle. The remaining ¾ of the quantity obtained are reacted with sodium hydride and propylene according to the process of our Patent 2,826,598 to form sodium-aluminium tetrapropyl which is returned into the cycle. Aluminium tripropyl in amount of 1.8 gms. per ampere hour (corresponding to 94% of the theoretical yield) is newly formed.

#### Example 3

The procedure is the same as in Example 2 except that sodium-aluminium tetrabutyl is used as the electrolyte and a mixture of 30% of aluminium tributyl and sodium-aluminium tetrabutyl is withdrawn from the anode space. Pure aluminium tributyl (B.P., 100° C./0.5 mm. Hg) is obtained after appropriate processing.

#### Example 4

The procedure and the apparatus are the same as in Example 1, except that  $\text{NaAl}(\text{C}_2\text{H}_5)_4$  is electrolyzed with the use of magnesium granules as the anode material. The electrolysis temperature is 120° C. The current intensity is adjusted to 15 amperes with a terminal voltage of 4 volts. The anodically formed compound of the composition  $\text{Mg}(\text{C}_2\text{H}_5)_2 \cdot 2\text{Al}(\text{C}_2\text{H}_5)_3$  dissolves only sparingly in the sodium aluminium tetraalkyl (about 10%), rises in droplets to the surface where it forms a second liquid phase which may be withdrawn from time to time. The obtained compound  $\text{Mg}(\text{C}_2\text{H}_5)_2 \cdot 2\text{Al}(\text{C}_2\text{H}_5)_3$  is heated at 100° C. under high vacuum. In doing so, the aluminium trialkyl distills off completely. The residue is pure magnesium diethyl.

The yield of  $\text{Mg}(\text{C}_2\text{H}_5)_2$  is 39 gms. per 26.8 amps. hrs. corresponding to 95% of the theoretical yield.

#### Example 5

Use is made of an electrolytic cell which simply consists of a vacuum-resistant steel kettle which has arranged in the center a cathode of sheet copper and, on both sides at a distance of about 1 to 2 cm. therefrom, anodes of thick aluminium plates. The anodes are led in with insulation. The cathode is connected with the steel shell of the kettle with metallic conduction.

The cathode is sufficiently long to touch with its lower end the bottom of the kettle while a free space of about 20 cm. is left between the kettle and the lower end of the anode. An electrolyte comprising 80% of potassium-aluminium tetraethyl and 20% of sodium-aluminium tetraethyl is introduced into the kettle under a nitrogen atmosphere. The kettle is connected with a cooled receiver and a vacuum pump via a descending condenser. The kettle is heated to 130–140° C. and evacuated 0.1 mm. Hg and preferably less. The current is then switched on and molten sodium-aluminium tetraethyl at a rate equivalent to the amount of current passed through is allowed to flow in through a separate line arranged at the kettle. The current is adjusted to a current density of 10 to 30 a./dm.<sup>2</sup> and 166 gms. of sodium-aluminium tetraethyl are allowed to flow in per 26.8 amps. hrs.

The anodically formed aluminium triethyl continuously distills off at a rate of 150 gms. per 26.8 amps. hrs. of which 38 gms. are newly formed (corresponding to 100% of the theoretical yield). In this setup, the electrolyte containing complex potassium and sodium remains practically unchanged in the kettle and only the inflowing sodium-aluminium tetraethyl is decomposed. The molten sodium collects at the correct rate, i.e., 23 grams per 26.8 amps. hrs., at the bottom of the kettle. The electrolysis may be run until the sodium level in the kettle is high enough that short-circuit with the aluminium anodes would occur. The sodium may, of course, be withdrawn in

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molten form from the apparatus, perhaps after having temporarily interrupted the vacuum and switched off the current. One-fourth of the amount of distillate is put aside as newly recovered aluminium triethyl. The balance is reacted with NaH and ethylene as described in Example 1 to form sodium-aluminium tetraethyl which may be returned into the electrolysis.

It should still be noted that due to the sensitivity of the electrolytes and the reaction products to air and moisture all of the operations must be carried out with exclusion of moisture and under an inert atmosphere of, for example, nitrogen or argon.

What we claim is:

1. In the process for the electrolytic production of a compound selected from the group consisting of magnesium dialkyls and aluminium trialkyls in which an electrolysis current is passed between a cathode and an anode selected from the group consisting of magnesium and aluminium anodes through an electrolyte in the form of a complex compound of the general formula  $\text{MeAlR}_4$  in which Me is a metal selected from the group consisting of sodium and mixtures of sodium and potassium and R is an alkyl radical to thereby form an alkyl compound of the anode metal and deposit sodium at the cathode, the improvement for depositing sodium uncontaminated with aluminium at the cathode which comprises maintaining the content of free aluminium trialkyl in the electrolyte at the cathode below 3%.

2. Process according to claim 1 in which R in said general formula represents an alkyl radical containing from 2 to 6 carbon atoms.

3. Improvement according to claim 1 in which the content of free aluminium trialkyl in the electrolyte in the neighborhood of the cathode is maintained below 1%.

4. Improvement according to claim 1 which includes separating the anode space from the cathode space by a diaphragm.

5. Improvement according to claim 1 in which said electrolysis is effected to produce aluminium alkyls and is carried out in vacuo.

6. Improvement according to claim 5 in which said electrolysis is effected at a pressure below about 1 mm. Hg.

7. Process according to claim 1 which includes continuously extracting the alkyl compound formed from the electrolyte with a saturated hydrocarbon immiscible therewith.

8. Improvement according to claim 1 which includes continuously extracting the alkyl compound formed from the electrolyte with a hydrocarbon immiscible therewith and selected from the group consisting of aliphatic and hydroaromatic hydrocarbons.

9. Improvement according to claim 1 in which the electrolysis is effected for the production of a magnesium alkyl and in which the anodically formed mixture of magnesium dialkyl and aluminium trialkyl is separated from the electrolyte liquid and separated into its components.

10. Improvement according to claim 9 in which said separation into components is effected by distilling off of the volatile aluminium trialkyl in vacuo.

11. Improvement according to claim 1 in which those portions of aluminium trialkyl which are anodically formed during the electrolysis as aluminium-containing decomposition products of the electrolyte are treated together with sodium outside of the electrolytic cell with hydrogen and an olefin to be converted into compounds of the general formula  $\text{MeAlR}_4$ .

12. Improvement according to claim 1 in which the electrolysis is effected at a temperature between about 100–140° C., at a voltage between about 0.5 to 5 volts using current densities of up to about 80 a./dm.<sup>2</sup>.

13. Improvement according to claim 1 in which Me in said general formula is a mixture of sodium and potassium having a potassium content of up to 80%.

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14. Improvement according to claim 1 in which said cathode is of a metal which will not alloy with the deposited sodium.

15. Improvement according to claim 1 which includes separating the anodically formed organometal compounds from the electrolyte, separating from the latter the aluminium alkyls formed by decomposition of the electrolyte, recovering the sodium deposited at the cathode, reacting a portion of the separated aluminium alkyls with the sodium, hydrogen, and an olefin to form the compound of the general formula  $\text{MeAlR}_4$  and recycling said compound to the electrolysis.

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