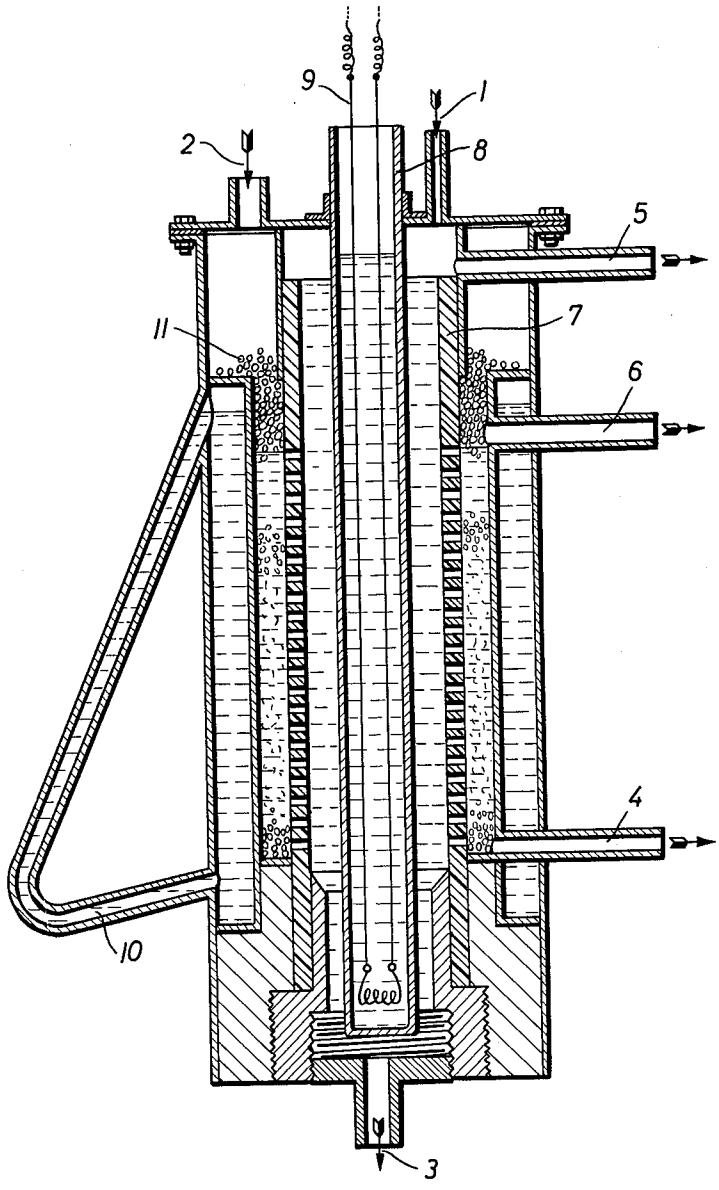
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PROCESS FOR THE ELECTROLYTIC PRECIPITATION OF SODIUM

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PROCESS FOR THE ELECTROLYTIC PRECIPITATION OF SODIUM

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This application is a continuation of application Serial No. 27,219, filed May 5, 1960, now abandoned.

This invention relates to a process for the electrolytic precipitation of sodium.

The production of metallic sodium by cathodic deposition of the metal in an electrolysis of sodium-containing compounds is known. A distinction must be made between two different types of sodium production. In one embodiment, fusion electrolyses are effected with sodium hydroxide or sodium chloride, the melting point of which is lowered by the addition of calcium chloride. Naturally, this mode of operation and especially the sodium chloride electrolysis required relatively high electrolysis temperatures.

In the second type of electrolytic sodium production, metallic sodium is first dissolved in a mercury cathode to form the amalgam by electrolysis of a warm sodium chloride solution. This amalgam must be freed from its sodium content in a secondary electrolysis in which it constitutes the anode and wherein the metallic sodium is deposited cathodically. This secondary electrolysis cannot be effected in the presence of water, the electrolyte being rather a molten bath of sodium hydroxide, sodium iodide and sodium bromide. The electrolysis temperature is about 250° C. It cannot be avoided at this high temperature that murcury enters the metallic sodium, the reason being probably the fact that the vapor pressure of mercury is very high at the high electrolysis temperature required. The molten electrolyte saturates with this mercury vapor and the sodium at the cathode will again absorb this mercury portions. The deposited sodium from the secondary electrolysis must be subsequently freed from mercury not only because of the usability of the sodium but also for economical reasons since otherwise the mercury losses would be prohibitive. This purification is accomplished by an additional treatment with some metallic calcium which combines with the mercury to form a solid calcium amalgam from which the molten mercury-free sodium can be decanted. The mercury may then be recovered from the calcium amalgam, e.g. by decomposition with an acid. In total, these operational measures are complicated and many process steps are necessary.

It is an object of this invention to provide a novel process for the electrolytic production of sodium, which process involves simplifications and facilitations in many respects over the prior art and which is particularly suited for the cathodic precipitation of pure sodium which contains only traces of foreign matter.

This object is accomplished in accordance with the invention by a process for the electrolytic precipitation of sodium which comprises subjecting to electrolysis molten baths of complex compounds of the general formula $MeAlR_3R'$ wherein Me is sodium or a mixture of sodium and potassium, R is an alkyl radical and R' is hydrogen, an alkyl, alkoxy, cycloalkoxy and/or an aroxy radical which, if desired, may be substituted, while preventing any free metal alkyls which may be formed anodically, especially aluminum trialkyls, from becoming commingled with the sodium deposited at the cathode. Suitable electrolytes for carrying out the process of the invention are especially those complex compounds of

the general formula given above, wherein R is a straight chain alkyl radical having preferably from 2 to 6 and especially 2 carbon atoms and R' is hydrogen, a straight chain alkyl radical having preferably 2 to 6 carbon atoms and especially 2 carbon atoms or an organic radical OR'' wherein R'' is an alkyl, cycloalkyl, phenyl or alkyl-substituted phenyl radical. Electrolytes wherein R' is hydrogen are preferably used only in specific embodiments of the invention which are dealt with hereinafter.

It has been found that it is one of the essential conditions for the deposition of pure sodium at the cathode that aluminum complex compounds are used as electrolytes, which are sufficiently stable in the molten bath at the temperature of the electrolysis, i.e. will not undergo decomposition into their individual components (free aluminum alkyl compound and complex-former) to an extent that the deposit of pure sodium is interfered with, and/or are not reactive with the sodium metal at the electrolysis temperatures used. This basic requirement of the process of the invention is met by the compounds of the general formula $MeAlR_3R'$ mentioned above.

In one of the most convenient embodiments of the process of the invention, the electrolysis is effected on electrodes which do not participate in the chemical reactions involved in the electrolysis, i.e. both the cathode and the anode consist of inert metals such as, for example, copper, silver, gold, platinum, palladium, iron, cobalt, nickel, manganese, osmium, iridium or other inert metals. Alloys such as brass may also be used. With these electrodes, sodium is deposited on the cathode while the gaseous decomposition products of the ethyl radical are evolved at the anode. When using the complex compound $MeAlR_4$, i.e. an aluminum tetraalkyl complex compound as the electrolyte, an aluminum trialkyl is simultaneously formed at the anode per metal equivalent deposited. If this evolved aluminum trialkyl would not be prevented from becoming commingled with the cathodically deposited sodium, the latter would diffuse through the electrolyte towards the cathode where it would disturb after a short period of time the deposit of sodium with simultaneous deposition of aluminum.

Accordingly, in accordance with the invention, the free metal alkyls formed at the anode are prevented from being mixed with the sodium deposited on the cathode. To this end, two different possibilities exist fundamentally, i.e. the use of mechanical or physical means which exclude such undesirable commingling and an intensional control of the chemical processes in the electrolyte which likewise prevent an undesirable back reaction involving the deposited sodium.

The mechanical or physical means include especially the following:

(a) Inserting a diaphraghm between the anode and cathode or

(b) Effecting the electrolysis in vacuo, the vacuum having to be such that the anodically formed metal alkyls distil out directly from the electrolyte liquid prior to being able of migrating through the electrolyte to the cathode. In this embodiment, it is not advantageous to use inert anodes since this would involve the necessity of constantly pumping off an excessively large amount of gas. This embodiment is suited for the use of anodes on which the alkyl radical is combined to form metal alkyl compounds rather than to be decomposed.

When operating with a diaphragm inserted between the cathode and the anode, it may be desirable to maintain a liquid flow from the cathode space into the anode space, which flow is preferably slow. This is, for example, accomplished in a convenient manner by maintaining the liquid level in the cathode space somewhat

higher than in the anode space so that this desirable continuous flow is maintained by the natural liquid equalization across the diaphragm. If necessary or desired, a plurality of diaphragms, e.g. two, may be used.

Examples of suitable materials for the diaphragm include compressed fibrous materials such as asbestos, glass wool, quartz wool or porous cellulose products such as, for example, filter paper which has been compressed or chemically impregnated to reduce the pore size and which may be fixed between fabrics of, for example, cotton.

If, however, the electrolysis is effected in a vacuum cell, very low pressures are generally required in the cell. For example, satisfactory operation can be achieved at pressures of below 1 mm. Hg. As has been found, the removal of the formed free metal alkyl compound by distillation must be effected so rapidly that specific maximum concentrations of these alkyl compounds in the electrolyte are not exceeded. In case of aluminum triethyl, this maximum concentration is about 3% and preferably about 1%. Apparatus suited for carrying out the process of the invention is disclosed in our U. S. Patent Nos. 2,985,568 and 3,069,334 which describe both the use of the diaphragms mentioned above and operation in vacuo.

The alternative of preventing the undesirable back reaction by controlling the chemical processes within the electrolyte is also realizable by different methods. If, for example, aluminum triethyl is evolved at the anode during the electrolysis, the same may in one embodiment of the process of the invention be prevented from reacting with the sodium by adding alkoxy or aroxy complex compounds of the general formula $MeAlR_3OR''$ wherein Me, R, and R'' have the meaning mentioned above. In doing so, the free aluminum trialkyl is converted into the alkali metal aluminum tetraalkyl compound, i.e. into an electrolyte which is among those electrolytes which are suitable for the process of the invention, while free aluminum compounds of the general formula AlR_2OR'' are simultaneously formed. It appeared surprisingly that an undesirable re-conversion does not occur in this embodiment of the process. While free aluminum trialkyl undergoes decomposition with sodium at temperatures of as low as about 100° C., such decomposition does not occur between an alkoxy or aroxy aluminum dialkyl and sodium metal in the temperature range which is suitable for carrying out the process of the invention, i.e. at temperature up to about 150°–160° C. An undesirable conversion will only occur if the temperature exceeds this limit. Addition of the complex compound $MeAlR_3OR''$ may be effected batchwise, i.e. in adequate amount at the beginning of the electrolysis, or preferably continuously during the electrolysis at the rate required.

Thus, when constantly converting any evolved portions of free aluminum trialkyl into the corresponding alkoxy or aroxy aluminum dialkyl compounds by the preferred continuous addition of the $MeAlR_3OR''$ compounds, pure sodium may be deposited cathodically up to about 150° C. even without the use of mechanical means. Besides the use of $MeAlR_4$ as the main electrolyte, it is also possible for carrying out this embodiment of the invention by adding at least the necessary amounts of $MeAlR_3OR''$ to use this seceond complex compound even as the sole electrolyte. However, due to the relatively poor electric conductivity of the alkoxy complex compounds, the use of the tetraalkyl complexes as the main electrolyte is preferred.

If anodic evolution of still other metal alkyl compounds occur which undergo no reaction with the aluminum alkoxy complex compound, the use of mechanical means for the separation of the anodic reaction product from the cathodically deposited metal is indispensable.

Of the compounds of the general formula $MeAlR_3R'$ to be used as the electrolyte in accordance with the invention those compounds wherein Me is potassium have a considerably better conductivity than the corresponding sodium compounds. It also appeared that if a mixture of potassium and sodium tetraalkyl complex compounds is subjected to electrolysis, pure sodium is deposited as long as the potassium portion does not exceed about 80% of the alkali metal. For this reason, it is preferred to use mixtures of sodium and potassium complex compounds of the general formula $MeAlR_3R'$ as the electrolytes. During the electrolysis, this electrolyte becomes poor in the sodium compound which must then be supplied batchwise or continuously at an appropriate rate such that the potassium content will not exceed about 80%.

For continuous operation, the amount of sodium aluminum complex compound decomposed during the electrolysis must be renewed batchwise or continuously even when working with no potassium compound. When operating with mechanical means for removing the anodically evolved free aluminum trialkyl, the same may advantageously be re-used for the production of the sodium-aluminum tetraalkyl compound. To this end, it is transferred together with fresh sodium into a pressure reactor and reconverted into the electrolyte compound by treatment with hydrogen and subsequently with the corresponding olefin. A suitable process for this conversion is, for example, that disclosed in German Patent No. 917,006. In this manner, cyclic processes may, for example, be carried out for the refining of sodium with the latter being introduced into the process cycle in the regeneration of the electrolyte, and the purified metal being cathodically withdrawn.

Cyclic processes of this type may also be carried out in cases where the formed free aluminum trialkyl compounds are converted within the electrolyte into the free alkoxy or aroxy aluminum dialkyl compounds by the addition of $MeAlR_3OR''$. For this purpose, the compounds of the formula AlR_2OR'' are then reconverted outside of the electrolytic cell into the compounds $MeAlR_3OR''$, and these are then again returned into the electrolyte as electrolyte or for reaction with the aluminum trialkyl compounds. The best possibility of regenerating the compounds of the general formula $MeAlR_3OR''$ is to react the compounds of the formula R_2AlOR'', together with alkali metal hydride, with the appropriate olefins, e.g. ethylene. The treatment with the olefins may be effected at temperatures between 130° and 220° C. and preferably between 150° and 200° C. and pressures up to 100 atmospheres and preferably between 1 and 20 atmospheres.

The deposition of sodium of highest purity for any period of electrolysis desired is also possible by a different and particularly preferred embodiment of the process. In this preferred embodiment of the process of the invention, the molten electrolyte body of compounds of the general formula $MeAlR_3R'$ is subjected to electrolysis at a cathode of an inert metal and a sodium-containing anode. It was found very surprisingly that this permits in most convenient manner to maintain the conditions for effecting the process of the invention for any period desired.

While the decomposition products of the remaining electrolyte residue in addition to the evolving aluminum trialkyl appear at an inert anode, this free residue dissolves under the same conditions, but with the use of a sodium-containing anode, sodium goes anodically into solution, and forms sodium alkyl. Since aluminum trialkyl in equivalent amount is simultaneously set free at the anode and immediately reacts with the sodium compound just formed anodically to form the sodium aluminum complex compound, constant electrolyte composition is always maintained in this manner. The need for the use of any mechanical means for preventing undesirable back decompositions is thus completely eliminated just as the batchwise or continuous renewal of consumed electrolyte.

Various sodium-containing materials may be used as the anode material. An example of a suitable material is

molten raw sodium. This involves the simplest form of electrolytic sodium refining in carrying out the process of the invention. Other anode materials are also usable.

Particularly preferred is the use of sodium amalgam as the anode material. This sodium amalgam is, for example obtained in large amounts in the electrolysis of aqueous sodium chloride solutions, which electrolysis is currently widely practised. As was already mentioned above, the recovery of pure sodium from these solutions has been relatively difficult and complicated up to the present. The process of the invention now provides a new route to the direct production of sodium of highest purity from this sodium amalgam, especially by the use of the novel electrolytes. Due to the possibility of effecting the electrolysis at considerably lower temperature than heretofore, but under at least equally favorable conditions with respect to current utilization, it is accomplished in accordance with the invention in a single operational step to obtain sodium of highest purity which needs not be subjected to further complicated purifying operations. The degree of purity of the sodium deposited at the cathode is further improved by the possibility of reducing the electrolysis temperature to a relatively low level. The sodium amalgam preferably used in this embodiment of the process of the invention is an amalgam which is obtained in the electrolytic production of alkyls of metals of group II and main groups III to V of the Periodic Table by electrolysis of aluminum-organic compounds. In such a process, electrolytes containing compounds of the general formula $Me[AlR_3R']$ are subjected to electrolysis on anodes of the metal the alkyls of which are to be produced and on a mercury cathode. In the general formula given above, R is an alkyl radical, R' is an alkyl, alkoxy or aroxy radical, which aroxy radical may be substituted, or fluorine and Me is sodium, potassium or a mixture of sodium and potassium. The electrolyte may in addition contain compounds of the general formula AlR_2R' wherein R is an alkyl radical and R' is an alkyl, alkoxy, or aroxy radical, it being possible in the case of R'=alkyl that the aluminum trialkyl compounds then present are added as etherates or trialkyl aminates. It may further be advantageous if all radicals R are identical and, in the case of R'=alkyl, the radicals R and R' likewise are the same alkyl radicals. The preferred starting electrolytes are compounds of the general formula $MeAlR_4$, $MeAlR_3OR'''$ (wherein R''' is an alkyl radical having preferably from 2 to about 20 carbon atoms and especially from 2 to 8 carbon atoms, a cycloalkyl radical or, if desired, a substituted phenyl radical), $NaF.AlR_3$, $NaF.2\ AlR_3$ and/or mixtures thereof. It is then possible, for example, to produce alkyls of the following metals: Beryllium, magnesium, mercury, aluminum, gallium, indium, lead, arsensic, antimony or bismuth.

Sodium amalgam is cathodically formed in an electrolysis of this type, it being preferred that the sodium content in the amalgam does not exceed about 1.5% by weight since this permits simple withdrawal of the sodium amalgam which is then still liquid. To permit the re-use of the mercury for the production of metal alkyls, it must be freed at least partially from its sodium content, which can be accomplished by the process of the invention.

It must be considered as extremely surprising that the performance of the process of the invention with formation of sodium ethyl from sodium amalgam is possible at all. As is known, mercury is among the metals which, when used as the anode metal in the electrolysis of aluminum-organic complex compounds, form volatile metal alkyls. Since the reactivity of sodium in the amalgam is considerably reduced as compared with that of pure sodium, it could not be predicted that it is actually possible to transfer the sodium out of the amalgam into sodium ethyl without the simultaneous formation of mercury alkyls. This is the more true when considering the fact that lithium amalgam and mercury alkyls can be produced by shaking lithium alkyls with mercury:

$$2\ LiR + Hg \rightleftarrows HgR_2 + 2Li$$

This is an equilibrium reaction and it is clear that, if such a conversion would play a part also in case of sodium, the smooth separation of sodium from the amalgam would not be possible.

The attack of the ethyl radical takes place at the surface of the amalgam layer, where the sodium is consumed so that the surface becomes more and more enriched with mercury.

When operating with electrolytes $MeAlR_3R'$ wherein R' is alkyl, alkoxy, or aroxy and using sufficiently high current densities that the formation of sodium alkyl proceeds at a rate higher than that of the diffusion of sodium metal from the interior to the amalgam surface, an undesirable formation of mercury alkyls may occur. It is preferred, therefore, to set an upper limit to the current densities used with the range up to about 80 a./dm.^{2} being particularly preferred. Particularly suitable is the range from about 10 to about 50 a./dm.^{2}. In addition, this deficiency may be remedied by agitation of the sodium amalgam.

If, furthermore, the amalgam becomes progressively poorer in sodium as the electrolysis proceeds, the risk of the undesirable formation of mercury alkyl becomes greater. This will with certainty occur after the last residue of sodium has been removed from the mercury.

It is, therefore, preferred in accordance with the invention to leave always a sufficient residual content of sodium in the amalgam rather than effecting the electrolysis until the sodium is completely removed. This residual sodium content may, however, range below 1% and is, for example about 0.2% to 0.5% of sodium. This does not restrict the applicability of the process of the invention since the mercury anyhow serves in a cyclic process as the receiving agent for the primarily precipitated sodium and any residual sodium content is, of course, unimportant in such a cyclic process.

When using sodium-containing anodes, the electrolysis is carried out particularly advantageously with the electrolytes of the general formula $MeAlR_3R'$ wherein R has the meaning referred to above and R' is hydrogen. In electrolyzing these compounds, the hydrogen radical rather than an ethyl radical is bonded to a sodium which goes into solution. However, as long as this reaction of hydrogen is preferred to the corresponding reaction of the ethyl radical, the risk of an undesirable formation of mercury compounds is excluded since sodium hydride and consequently the corresponding electrolyte complex compound (by reaction with the aluminum-containing compound simultaneously formed anodically from the decomposition of the electrolyte) but no mercury hydride can be formed. The hydride-containing electrolytes may also be electrolyzed advantageously on inert anodes. As long as the overvoltage of hydrogen on these anodes is not sufficient that the discharge of the ethyl radicals occurs easier, hydrogen is then anodically evolved in place of the gaseous decomposition products of the ethyl radical. This hydrogen may then be used in a simple manner to assist in the regeneration of the electrolyte. In the case of using anode metals of groups II to V of the Periodic Table which are converted into the corresponding alkyl compounds during the electrolysis, the use of the hydride-containing complexes is less suited since undesirable back reactions may occur within the electrolyte.

In a particularly simple and preferred embodiment of this modification of the process, the electrolysis is carried out as a "three layer processs" wherein the heavy amalgam layer is at the bottom followed by the molten electrolyte while any inert metal cathode, e.g. in the form of a net, is arranged at the surface of the electrolyte. The sodium is then precipitated round the cathode. It appeared, however, that the specific gravity of sodium is higher than that of the molten electrolyte so that if the electrolysis is effected at temperatures at which the sodium is present in molten state, this molten metal would drop downward through the electrolyte and onto the

amalgam anode thereby aggravating the process. According to a still further preferred embodiment of the process of the invention, this difficulty is overcome as follows:

The density differences between the molten electrolyte and the sodium are not very great. They are estimated to be 0.05 to 0.1, i.e. the sodium has only about 1/20 to 1/10 of its actual weight in the electrolyte. Furthermore, the surface tension of molten sodium in the molten electrolyte is very high. Thus, very important surface or capillary forces are existing at the interfaces between sodium and the electrolyte. The consequence hereof is that already a very wide-meshed net of a suitable insulating material which, for example, is arranged horizontally in the electroylte at a distance of a few millimeters above the mercury surface will suffice completely to keep a sodium layer having a thickness of even several centimeters floating and to prevent it from sinking down. The surface tension prevents the sodium from passing through the net. The net itself may consist of cellulose filaments or, still better, from a glass fiber fabric. In this case, the process may be operated with voltages of about 1 v.

The performance of the electrolysis is, however, not restricted to the mode of operation described above. Use may also be made of different electroytic cells. Thus, the electrolyses of truly inorganic electrolytes are effected with rotating vertical disc electrodes which are immersed with their lower parts in the amalgam, are wetted with the amalgam and which face metallic cathodes with their upper halves. If the cathodes are given a shape such that the deposited sodium glides along the cathode and sinks in downward direction, it can thereby be discharged laterally from the bottom of the electrolytic cell.

On principle, the process of the invention is operated at temperatures at which the sodium is deposited as a liquid on the cathode. Since the melting point of sodium is about 97° C., the preferred temperatures range about 100° C. and especially between about 100 and about 150° C. The lower temperatures are used for the production of particularly pure sodium so that, when working at a temperature slightly exceeding 100° C., a sodium product which contains only a few parts per mille of mercury can be obtained in a once-through electrolysis. However, included within the scope of the invention is also the use of temperatures below 100° C. at which, for example, the mercury content of the deposited sodium can be reduced still further. Since, however, temperatures in excess of 100° C. facilitate the performance of the process and favor the current yield, the use of the temperature range mentioned above is particularly advantageous.

Where a particularly high purity of the cathodically deposited sodium is desired, this can be achieved by repetition of the electrolysis described above. To this end, the sodium cathodically deposited in the first electrolysis is used as the anode in a second electrolysis and subjected to a still more extensive refining in the second electrolysis. Such a double electrolysis can be carried out in a particularly simple manner is a single cell by inserting between the cathode and anode of the three layer-electrolysis arrangement described above a second net which bears a sodium layer. The space below and above this central sodium layer is occupied by electrolyte so that, in current flow, the bottom face of this intermediate layer of sodium acts as the cathode and the top face as the anode. In this manner, the raw sodium derived from the sodium amalgam is first deposited in the intermediate layer and, finally, the pure sodium is deposited at the upper cathode in highest purity by repeated electrical refining of the middle layer of raw sodium. Since the distances between the cathode and anode need not be greater than a few millimeters, the current requirement of such a double cell is practically hardly increased as compared with a single cell. Relatively low voltages, e.g. of about 1.5 to about 5 v., may be used in the process.

When using inert electrodes in the process of the invention, i.e. if sodium ethyl or other metal alkyls are not formed at the anode, the process may be carried out in any electrolytic cell provided that care is taken that a connection with metallic conduction is not established between the cathode and the anode, e.g. by the depositing sodium metal. A device wherein the process of the invention can be carried out with the use of anodes of metal alkyl-forming metals of groups II to V of the Periodic Table is shown in the appended drawing. The electrolytic cell shown comprises an opening **1** through which the electrolyte may be introduced while being preferably in molten state. The metal whose metal alkyls are simultaneously formed my be charged through the opening **2** in the form of, for example, small spheres or as granules. During the electrolysis, sodium is deposited as a thin layer on the cylindrical cathode **8** (e.g. of copper) in the middle of the electrolytic cell. It flows downwardly and may be withdrawn from the electrolytic cell through the opening **3**. The cathode space is separated from the anode space by a perforated cylinder of insulating material **7** and a superimposed diaphragm. The latter 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 be constantly supplied with fresh metal at a rate corresponding to the quantity of metal dissolved in the electrolysis. This anode space is provided with two outlet openings **4**, **6** through which the metal alkyl formed may be withdrawn depending upon whether it sinks downward in the electrolyte or rises in upward direction. Contained 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 adjusted by the heating element **9**. It is possible thereby to control the temperature of the catholyte as desired while the temperature of the anolyte is adjustable by the heating element **10** which, in the present case, is operated with circulating liquid.

EXAMPLE 1

In an electrolytic cell having the shape of a closed kettle of glass-lined sheet steel is arranged in the center a cathode of sheet copper extended to the bottom of the kettle. Located on both sides thereof at a distance of about 1 to 2 cm. are anodes likewise made of sheet copper and being at least 10 to 20 cm. shorter than the cathode. A molten mixture of 80% potassium-aluminum tetraethyl and 20% sodium-aluminum tetraethyl is filled into the kettle under a nitrogen atmosphere. Moreover, a larger quantity of sodium butoxy aluminum triethyl is prepared by the process of our application Serial No. 792,614, filed February 11, 1959, now abandoned.

The electrolysis is effected at 140° C. and a current density of about 30 a./dm.^{2}. Prior to switching in the current, a small amount of the molten butoxy complex is allowed to flow into the eletcrolyte until its content in the mixture is about 5%. The current is now switched on and sodium butoxy aluminum triethyl is allowed to flow continuously into the electrolyte at a rate of 7.85 gms. per ampere-hours. The molten sodium deposits at the cathode at the correct rate, i.e. 0.86 gm. per ampere-hour. It flows down at the cathode and accumulates as a coherent layer at the bottom of the vessel from which it may be withdrawn. A 1:1 mixture of ethylene and ethane is evolved at the anode and a layer consisting of pure butoxy aluminum diethyl accumulates above the electrolyte. This layer is easily separated and reconverted into sodium butoxy aluminum triethyl by means of sodium hydride and ethylene by the process disclosed in our said application Serial No. 792,614 and continuously passed to the electrolyte. Care should be taken in the electrolysis that a certain quantity of the complex sodium butoxy aluminum triethyl is always maintained in the electrolyte. Normally, a very small stationary content will

be sufficient. However, since the proportioning is not always adjustable to be exactly equivalent to the passage of current due to occasional current fluctuation, it is preferable to operate with a content of a few percent of the alkoxy compound in the electrolyte.

EXAMPLE 2

3320 gms. (20 mols) of sodium aluminum tetraethyl are stirred for 5 hours at 150° C. with 740 gms. (10 mols) of potassium chloride. Upon settling of the sodium chloride formed, the formed equimolar mixture of sodium aluminum tetraethyl and potassium aluminum tetraethyl is subjected to electrolysis with a lead anode in the apparatus shown in the figure. The cathode is a copper cylinder. At a distance of 1 cm. therefrom is arranged a perforated cylinder of a material which is not electrically conducting and is not attacked by the electrolyte, such as porcelain or bakelite reinforced by a fabric. The cylinder is surrounded by a diaphragm of hardened filter paper or of a fine cloth or glas filter cloth. Behind the diaphragm is the anode space which is filled with lead spheres and may be supplied continuously with lead spheres at a rate corresponding to the lead dissolved in the electrolysis. Heating of the electrolyte or removal of the current heat evolved during the electrolysis is effected by recirculating a liquid of about 100° C. in the interior of the closed cathode cylinder. Heat supply or removal at the outer cylinder jacket is controlled such that the temperature in the anode space does not exceed 70° C. The temperature during the electrolysis is preferably about 100° C. in the cathode space and about 70° C. in the anode space. The conductivity of the mixture used is 4.5×10^{-2} (ohm-cm.)$^{-1}$ at 100° C. The current is adjusted to 20 a. corresponding to a cell voltage of 2 v.

The sodium deposited at the cathode flows down as a thin film at the surface of the cathode into the lower cathode space from where it may be withdrawn from time to time. The effluent from the anode space is adjusted such that a reaction mixture containing 10% lead tetraethyl flows off, which is the case when about 500 ml./hr. of liquid are withdrawn from the anode space. The supply of sodium aluminum tetraethyl to the cathode space should be controlled such that the liquid level in the cathode space is about 4 to 5 cm. higher than in the anode space. Yield of sodium: 23 gms. per 26.8 ampere-hours (100% of the theory).

EXAMPLE 3

Molten sodium aluminum tetrabutyl is subjected to electrolysis at 120° C. in the apparatus described in Example 2 using aluminum granules as the anode material. The sodium deposited at the cathode collects at the bottom of the cathode space and may be withdrawn therefrom from time to time. Moreover, the procedure is analogous to that described in Example 2 except that a reaction mixture containing 10% aluminum tributyl is withdrawn from the anode space, which reaction mixture is freed from aluminum tributyl at 100° C. and a vacuum of 0.1 mm. Hg. The yield of sodium is 23 grams per 26.8 amperes×hours, which corresponds to 100% of the theory.

EXAMPLE 4

Electrolysis is effected in the apparatus shown in the figure and described in Example 2, except that the anode space is not filled with metal granules, but a cylinder of metal wire, e.g. copper, is fastened in the anode space. The electrolysis temperature is 100° C. A melt of the complex compound sodium aluminum triethyl hydride is used as the electrolyte. A current of 15 a. is adjusted at a terminal voltage of 6 v. Under these conditions, 12.8 gms. of sodium (100% of the theory) are deposited per hour at the cathode while hydrogen gas at a rate of 6.3 liters/hr. is evolved at the anode. The supply of sodium aluminum triethyl hydride to the cathode space is adapted such to the effluent from the anode space that a difference of 4 to 5 cm. is maintained between the liquid level in the cathode space and that in the anode space.

The effluent from the anode space is collected and freed from aluminum triethyl at 100° C. under a vacuum of 1 mm. Hg. The distillation residue may be returned into the electrolytic cell. The hydrogen evolved at the anode may be used in the regeneration of aluminum triethyl to form complex $NaAl(C_2H_5)_3H$. The aluminum triethyl is reacted with NaH at 100° C. to form sodium aluminum triethyl hydride which may again be charged to the electrolysis.

EXAMPLE 5

The electrolytic cell consists of a cylindrical and internally enamelled steel kettle which contains at the bottom the raw sodium to be refined as a melt. Suspended in the kettle is a cylinder of enamelled sheet steel of somewhat smaller diameter, which is open at both ends and has horizontally tightened across the lower opening a wide-meshed glass fiber fabric having a mesh size of 1 to 3 mm. The net is arranged at a distance of 3 to 5 mm. above the surface of the liquid sodium. Arranged closely above the net is a net of copper or iron wire as the cathode. The electrolysis temperature is 150° C. Sodium aluminum tetraethyl is used as the electroyte. The level of the molten electrolyte must be above the upper edge of the suspended cylinder so that the sodium deposited at the cathode is surrounded by the electrolyte from above and below. An electrode current density of 20 a./dm.^{2} can be maintained at a terminal voltage of 2.0 v. The cathodically formed sodium collects above the glass fiber net and may be drained from this space from time to time. Care is taken by the addition of raw sodium during the electrolysis that the distance between the anode and cathode is kept constant. The yield of sodium is 23 grams per 26.8 amperes×hours, and 23 gms. of Na were dissolved anodically by the same amount of current. The yield is 100%.

EXAMPLE 6

The procedure is the same as that described in Example 5 except that a mixture of 20% sodium aluminum tetraethyl and 80% potassium aluminum tetraethyl is used as the electrolyte and the same volume of 1% sodium amalgam is substituted for the molten raw sodium. The electrolysis is effected at a temperature of 150° C., a current density of 30 a./dm.^{2} and a terminal voltage of 1.5 v. The cathodically deposited sodium collects as a coherent molten layer above the net of glass fiber fabric. To remove the joulean heat and for mixing the electrolyte, a greater electrolyte stock is recirculated through the electrolytic cell while maintaining the liquid in the electrolytic cell at a constant level. This is easily accomplished by allowing an equal volume of electrolyte per unit time to flow from a stock vessel into the space between the anode and cathode as that pumped back into the stock vessel from a point opposite of the inlet opening. The amount of sodium depoisted cathodically after 185 amperes× hours is 160 grams which are drained in molten state from the upper part of the electrolytic cell.

The sodium thus obtained still contains about 0.3% of Hg. The mercury content is further reduced when maintaining a temperature of 120° C. during the electrolysis. It is easy to achieve 0.01% of Hg and less in this case. This is that mercury content which, in the production of sodium from sodium amalgam with an electrolyte of molten sodium bromide, iodide and hydroxide, is only achieved after an additional treatment with metallic calcium. The primary mercury content in this prior art process is in the order of magnitude of 1%. Even the last traces of mercury can be removed when repeating the electrolysis in accordance with Example 5.

The Na content of the initial Na amalgam which was 1% has been reduced to about 0.2%. The amalgam is preferably removed from the cell and may be used for

another electrolysis after having been concentrated to 1% Na.

The yield of sodium is 23 gms. of Na per 26.8 amperes × hours (100% of the theory).

It is to be understood that due to the sensitivity of all electrolytes to air and water all operations must be carried out with exclusion of moisture and in an inert gas atmosphere such as, for example, nitrogen or argon.

What is claimed is:

1. Process for electrolytic production of sodium which comprises:

passing an electrolysis current between an anode and a cathode through an electrolyte comprising a complex compound of the general formula $MeAlR_3R'$ in which Me is alkali metal selected from the group consisting of sodium and a mixture of sodium and potassium, R is an alkyl radical and R' is selected from the group consisting of hydrogen, alkyl, alkoxy, cycloalkoxy and aroxy, said anode containing sodium, to electrolyze sodium from the anode and deposit sodium at the cathode, the sodium electrolyzed at the anode replacing in the electrolyte sodium deposited at the cathode.

2. Process according to claim 1, wherein the anode is a sodium amalgam, the sodium being electrolyzed from the amalgam without reaction of the mercury.

3. Process according to claim 2, wherein the electrolyte contains $MeAlR_3OR''$ wherein Me and R are as above and R'' is selected from the group consisting of alkyl and cycloalkyl.

4. Process according to claim 2, the sodium content of the amalgam being less than about 1.5% by weight.

5. Process according to claim 2, wherein the current density is less than about 80 a./dm.^{2}.

6. Process according to claim 2, wherein the current density is about 10–50 a./dm.^{2}.

7. Process according to claim 2, wherein the temperature of the electrolyte is about 100–150° C.

8. Improvement according to claim 2 in which R is a straight chain alkyl radical containing 2–6 carbon atoms.

9. Improvement according to claim 2 in which R is a straight chain alkyl radical containing 2 carbon atoms.

10. Improvement according to claim 2 in which Me is a mixture of sodium and potassium and containing up to about 80% potassium.

11. Improvement according to claim 2 in which said electrolysis is effected with the sodium amalgam as the lowermost layer, the electrolyte as the middle layer, and in which the cathodically deposited sodium is kept in suspension by a wide mesh net of insulating material as the uppermost layer.

12. Improvement according to claim 1 in which said anode consists of molten raw sodium.

13. Improvement according to claim 1 in which said anode is a sodium amalgam anode and in which the electrolysis current is only passed while there is sufficient sodium in the anode material to prevent the formation of mercury alkyls.

14. In the process for the electrolytic production of sodium in which an electrolysis current is passed between a cathode and an anode through a sodium electrolyte in the form of a complex compound of the general formula $MeAlR_3R'$ in which Me is a metal selected from the group consisting of sodium and mixtures of sodium and potassium, R is an alkyl radical, and R' is a member selected from the group consisting of hydrogen, alkyl, alkoxy, cycloalkoxy, and aroxy radicals, the improvement which comprises effecting the electrolysis with a sodium-containing anode as the lowermost layer, the electrolyte as the middle layer, and the cathodically deposited sodium kept in suspension by a wide meshed net of insulating material as the uppermost layer.

15. Improvement according to claim 14 in which said anode is a sodium amalgam anode.

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