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INORGANIC MOLTEN ELECTROLYTE FOR THE ELECTROLYSIS OF TITANIUM

Filed Sept. 18, 1952

2 Sheets-Sheet 1

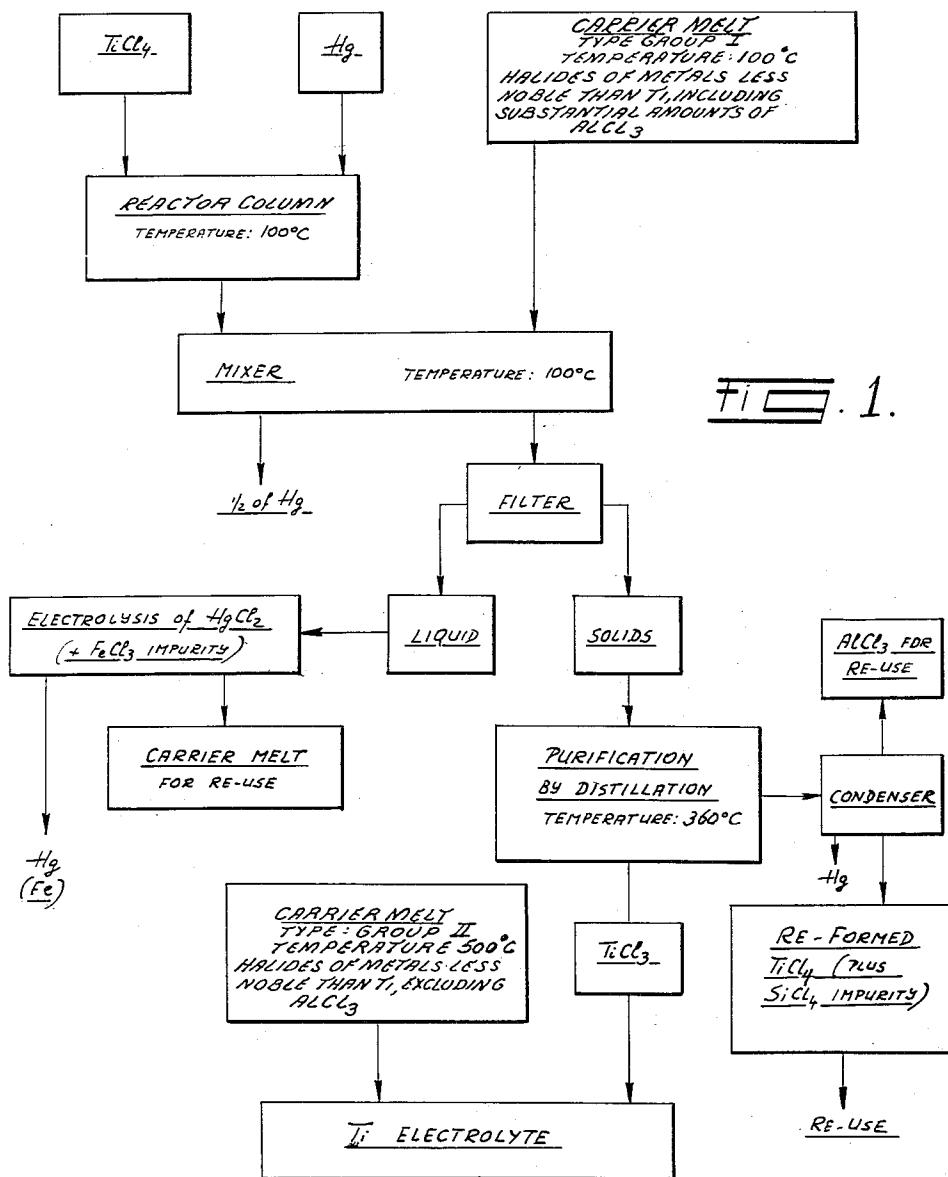


FIG. 1.

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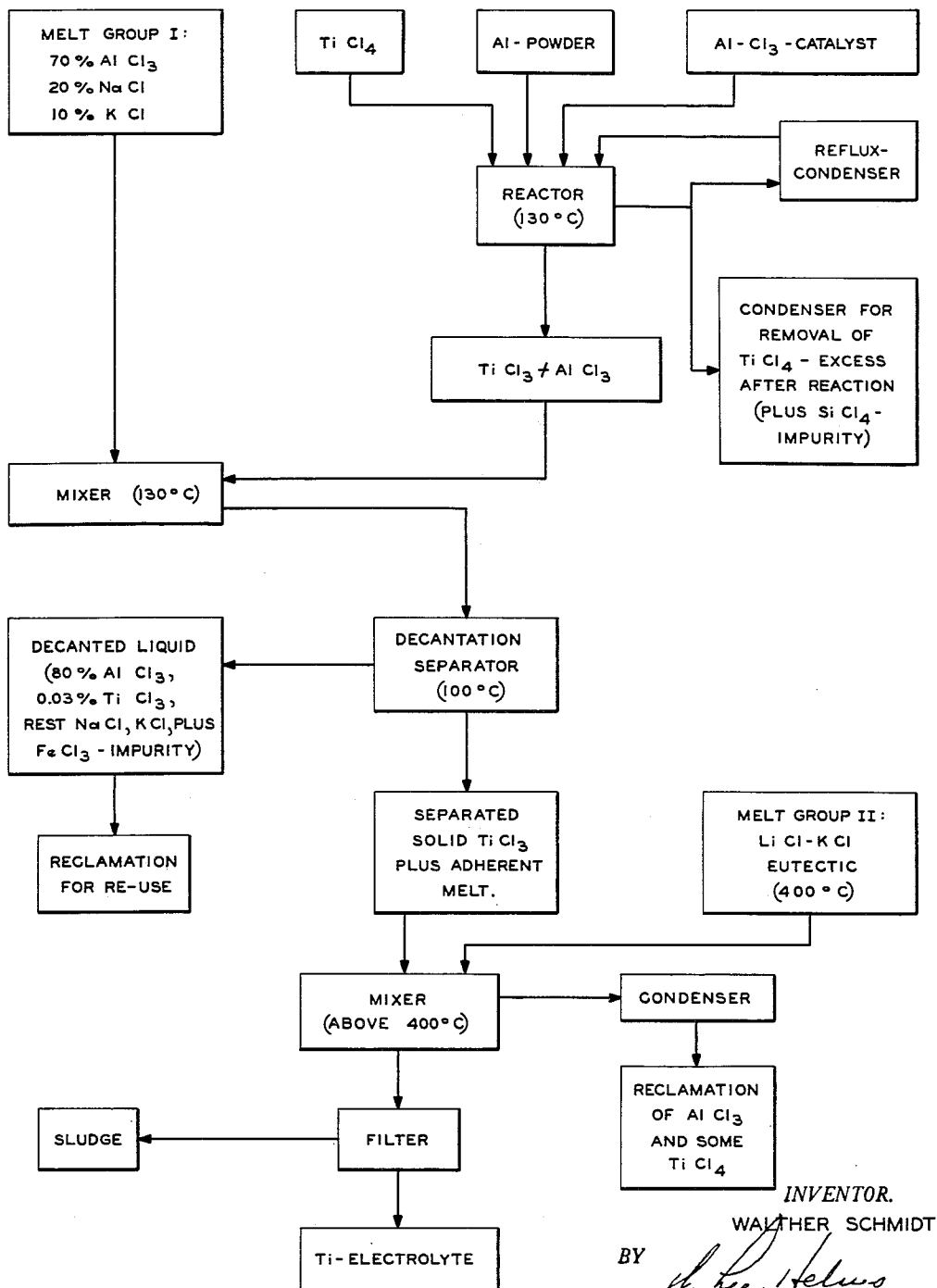
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2 Sheets-Sheet 2

FIG 2



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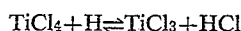
INORGANIC MOLTEN ELECTROLYTE FOR THE ELECTROLYSIS OF TITANIUM

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Application September 18, 1952, Serial No. 310,365

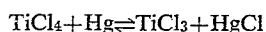
7 Claims. (Cl. 204—64)

This invention relates to preparing an inorganic molten electrolyte for the electrolysis of titanium. Previous attempts have been made to electrolyze Ti from inorganic salt melts containing TiCl_3 . The eutectic of KCl and LiCl has been used for dissolving TiCl_3 followed by electrolysis of the melt, using electrodes of tungsten and a temperature range of $500^\circ\text{--}550^\circ\text{C}$. Pure anhydrous TiCl_3 is needed for such operations. This was prepared by reacting purified TiCl_4 with hydrogen according to the reversible reaction:



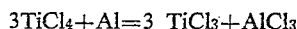
This reaction proceeds in the desired direction, forming TiCl_3 , at a temperature above 500°C . The products to the left side of the equation are reformed upon cooling. It is, therefore, necessary to counteract this reformation by quenching, but the yield is never complete, and the process yields substantial amounts of all four substances in the final product. In addition, TiCl_2 is also formed, and its formation can be suppressed only with the use of still higher temperatures, e.g. 800°C . It is, however, difficult to work with the corrosive HCl and explosive H_2 at high temperatures. This process of forming TiCl_3 is, clearly, costly with respect to energy consumption, yield, and maintenance of equipment.

It is also known that anhydrous TiCl_3 can be formed at much lower temperatures from TiCl_4 by the reducing action of many metals. On example is:



This reaction proceeds in the desired direction, rather slowly at normal temperature, and quite speedily at about 100°C ., the speed depending mostly on distribution, e.g. by stirring. The reaction reverses at high temperatures, e.g. above 180°C .

Another example is the reaction:



This reaction proceeds with Al-powder slowly at a temperature of about 130°C . The speed of the reaction is considerably increased at 180°C – 200°C . The conditions for reversing this reaction are not well established as to temperature and speed, but indications are that it reverses slowly at higher temperatures, probably above $220^\circ\text{--}250^\circ\text{C}$., especially if AlCl_3 and TiCl_3 are in contact within a salt melt.

A combination of these metals may be used for breaking down TiCl_4 , e.g. Al-amalgam.

All of these reducing reactions proceed at low temperatures. They do not require much energy, are easily controlled as to reversibility and speed, and can be accomplished with low-cost equipment, as compared with the use of hydrogen as the reducing agent.

These reactions, however, do not produce pure TiCl_3 , but a mixture of TiCl_3 and the equivalent amount of chloride of the reducing metal. The literature also reports efforts to separate these chlorides, e.g. the attempt to use Al for the reduction and to remove AlCl_3 by dis-

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tillation. The aim was, however, always directed to the goal of recovering TiCl_3 as a pure chemical.

This invention is described with reference to the accompanying drawings, in which,

Fig. 1 is a flow sheet using Hg as a reducing metal;

Fig. 2 is a flow sheet using Al as a reducing metal.

In both Figs. 1 and 2 a carrier melt of the type of group I, consisting of AlCl_3 plus a minor quantity of halides of alkali metals is employed for removing a major part of the HgCl_2 (in Fig. 1) or AlCl_3 (in Fig. 2) originating from the reaction of TiCl_4 with Hg or Al. Further purification in both cases is accomplished by distillation after the major part of HgCl_2 or AlCl_3 has been selectively dissolved in that carrier, and undissolved TiCl_3 has been separated.

Fig. 1 shows the reversal of the reaction, given on page 2, for purification during a separate distillation step.

Fig. 2 shows the purification by distilling off vapors of AlCl_3 and some TiCl_4 , the latter being formed by reversed reaction at the higher temperature at which the TiCl_3 is mixed to the final carrier-electrolyte.

In both cases the final electrolyte is one of group II, comprising an anhydrous inorganic melt of halides less noble than Ti, excluding AlCl_3 , however, in amounts larger than a minor contamination.

This invention makes use of the known reactions with the purpose of developing a suitable electrolyte. It was found that in many cases it would not be necessary to separate TiCl_3 from the chloride of the reducing metal, but an electrolyte could be prepared by adding with mixing both the TiCl_3 and the chloride of the reducing metal to a carrier electrolyte, the latter consisting of halides of metals less noble than Ti.

As indicated above, two groups of carriers are used in the process, the first one serving as an intermediate melt for the purpose of selective dissolution and separation, the second one being the final electrolyte. The first group contains a substantial, preferably a predominant amount of AlCl_3 , e.g. the binary or ternary eutectics of AlCl_3 with NaCl, KCl, and LiCl. Carriers of this group can be made to have a melting point as low as 70°C ., e.g. the ternary eutectic of AlCl_3 , NaCl, KCl containing approximately 80% AlCl_3 , 10% KCl, 10% NaCl. AlCl_3 and most of the added chlorides, e.g. all the alkali metal chlorides, form double salts when dissolved in each other. The second group does not contain AlCl_3 except amounts which may represent unintentional contamination. Such electrolytes are, e.g. the ternary eutectic of LiCl, KCl, NaCl, or the binary eutectic of LiCl and KCl or of NaCl and BeCl_2 .

The first group of carriers has the advantage that it is molten at a temperature below the temperature at which the dissolved chlorides of the reducing metal and TiCl_3 would reverse the reaction, forming that metal and TiCl_4 . The solubility of TiCl_3 at this low temperature is rather low.

The use of carriers of the first group is limited to a range of temperatures, which are determined by the factors influencing the reversing of the reaction between TiCl_3 and the metal chloride. Since the formed TiCl_4 vaporizes away, the reverse reaction would proceed as soon as unfavorable conditions of temperature and concentration were established.

Carriers of the second group have been used before. They have higher solubility for TiCl_3 . The absence of AlCl_3 allows a larger range of voltage in the cell. Carriers of the second group, however, can only be used when chlorides of reducing metals are removed, since they would, at the higher melting temperature, destroy the TiCl_3 to reform TiCl_4 , which latter would vaporize out of the carrier.

The low melting point of a carrier of the first group allows it to be molten at a temperature at which $TiCl_3$ is but slightly soluble. At a temperature of $100^\circ C.$, using for example a carrier of 77% $AlCl_3$, 10% $NaCl$, 10% KCl , and 3% $LiCl$, the solubility of $TiCl_3$ is only about 0.03%, while the solubility of other metal chlorides, e. g. $HgCl_2$ or $FeCl_3$, is much higher. Another example is a carrier-melt consisting of 75% $AlCl_3$, 15% $NaCl$, and 10% KCl , in which the estimated solubility at $180^\circ C.$ is between .05 and .15% $TiCl_3$. The composition of the carrier, therefore, can be chosen within limits, in which most of the $TiCl_3$ stays undissolved, while the chloride of the reducing metal is dissolved and can be separated by filtering, e. g. through ceramic filters. Other means of separation, like decantation or centrifuging, may be substituted for or be combined with filtration.

If Al -powder is used for breaking down $TiCl_4$, often some particles remain unreacted or are covered with a crust of $TiCl_3$, thereby hindering complete reaction. The separated residue, therefore, may contain residual amounts of the carrier of the first group, unreacted metal, residual amounts of occluded chlorides of these metals, and $TiCl_3$.

$TiCl_3$ from this residue is dissolved in a carrier, of the second group. At higher melting temperature of this type of carrier residual amounts of $AlCl_3$ may vaporize. The minor part of the original amount of $AlCl_3$, being still present, is allowed to either vaporize or back-react with $TiCl_3$. Thus, a small part of $TiCl_3$ is lost during purification. The $TiCl_4$ formed is collected and recycled. $AlCl_3$ thus remains only in minor amounts as unintentional contamination. Metallic residues and metals formed by reversible reaction are filtered off and the carrier is then ready for electrolysis (see Fig. 2).

This method offers the advantage of combining the preparation of an electrolyte with purification of $TiCl_4$. The purification of $TiCl_4$ is difficult. The literature offers many suggestions, most of them involving fractional distillation combined with chemical steps of purification. The fractional distillation is difficult because the partial pressure of other chlorides commonly present in $TiCl_4$, is sufficiently high to cause trouble. Silicon tetrachloride, though boiling lower than $TiCl_4$, contains always large amounts of $TiCl_4$ upon removal. Repeated distillations are needed to eliminate $SiCl_4$ and to recover a satisfactory yield of $TiCl_4$. These difficulties are best illustrated by the fact that water-white $TiCl_4$ of a purity suitable for Ti -production is available on the U. S. market only at a price which is more than 50% higher than for crude yellow $TiCl_4$, which can be received without too much difficulty. The method described above offers simultaneously a method for purification of such crude $TiCl_4$. The problem of the partial pressure of $TiCl_4$ in relation to that of $SiCl_4$ does not matter after the $TiCl_4$ has been converted into $TiCl_3$. Other metallic chlorides dissolve readily in the carrier of the first group. Their solubility is much higher than that of $TiCl_3$. They are removed along with the chlorides of reducing metals. The carrier can be freed from them and adjusted by known means, like cementation, electrolysis, or vaporization of $AlCl_3$. Hydrates, if present in crude $TiCl_4$, form sludge and stay with the $TiCl_3$ residue which is filtered from the carrier of the first group. After this residue is dissolved in a carrier of the second group, this sludge is filtered off along with the metallic impurities.

Generally speaking, the low solubility of $TiCl_3$ at low temperature in a molten carrier of the first group is used to leach out and separate the metallic chlorides of metals used to break down $TiCl_4$ and soluble halides of impurities contained in the crude $TiCl_4$.

The following is one example of carrying out the method described above. $TiCl_4$ purified by common filtration and fractional distillation, or still containing other metallic chlorides and $SiCl_4$ as impurities, is intimately mixed

or contacted with mercury at about $100^\circ C.$ The mercury is used in excess, preferably in a column, the $TiCl_4$ being introduced from underneath its surface, preferably from the bottom of a reaction vessel with provisions that it has to travel slowly enough and with sufficient contact to react as completely as possible. On top of the mercury a melt is kept floating consisting of the ternary eutectic of $AlCl_3$, KCl , $NaCl$, or a similar mixture, e. g. 77% $AlCl_3$, 10% KCl , 10% $NaCl$, and 3% $LiCl$. Unreacted $TiCl_4$ is only slightly soluble in this mixture. Any excess will float atop of it and can be removed by overflow. Any vapors of $TiCl_4$, $SiCl_4$ and $AlCl_3$ are condensed. They may be purified by return to the crude $TiCl_4$ and passing them through the preliminary purification.

The products of the reaction, namely $TiCl_3$ and $HgCl$ rise to the surface because of their buoyancy, where they contact the carrier. $HgCl$ decomposes upon this contact and forms spontaneously $Hg+HgCl_2$. It seems that $AlCl_3$ has a catalytical influence in promoting this decomposition. The mercury reformed by this reaction reunites with the mercury stock. The amount of carrier is large enough to dissolve all of the $HgCl_2$, while only a small part of the $TiCl_3$ is dissolved. The remainder forms a suspension. By adding new or recycled carrier and moving the saturated carrier out of the vessel, circulation can be established, allowing the process to be carried out continuously.

This carrier is ready to be used as such, preferably in a two-step electrolysis, first plating out the mercury, and thereafter the titanium. This method is most useful if Ti is plated out against a mercury-cathode. The electrolysis can be done in two different cells. The first cell is charged with carrier filtered off the original carrier. This offers the advantage that impurities from the crude $TiCl_4$ may be deposited in the first cell and that different conditions of concentration, carriers, temperatures, cathodes, and electrical controls may be used in the cells.

The separated residue of $TiCl_3$ is dissolved in a carrier of the second group, it being first separated from the above described melt by mechanical means such as decantation, filtration, centrifuging, or such means in combination. In this case it is advisable first to form a coarser particle size for easy filtering. This can be done by allowing the solid products in the reducing apparatus to dwell preventing them by mechanical means from rising to the surface of the mercury.

The mechanical separation is done at a temperature range of low solubility of $TiCl_3$, e. g. about $100^\circ C.$ The amount of carrier of the first group is chosen large enough and the temperature should be low enough as to dissolve the chloride of the reducing metal, but not to dissolve substantial amounts of $TiCl_3$. The temperature should also not be so high as to endanger reformation of $TiCl_4$, e. g. not above $180^\circ C.$, in the case of the example.

The filtering may be done with ceramic filters, like alundum. Filtering aids, especially those based on diatomaceous silica, may be used to retain finer particles. The filtrate is readjusted by plating or depositing out the mercury and whatever impurities found in the filtrate. It is not necessary to deplete it, since it is recycled and reused. Thus it dissolves more $HgCl_2$ in subsequent cycles, while the dissolved amount of $TiCl_3$ remains unchanged. The more noble impurities and the mercury do not require as high a decomposition voltage as $TiCl_3$. Thus, losses of Ti can be minimized. The mercury is cleaned from co-deposited contaminating metals and is reused.

For use with a carrier of the second group, the filtered residue is heated in order to drive off $AlCl_3$ and whatever amounts of $TiCl_4$ or $SiCl_4$ may still be present. The temperature is raised above $180^\circ C.$ into the range of the reversed reaction between $HgCl_2$ and $TiCl_3$ in order to remove any occluded mercury-compound by reforming mercury and $TiCl_4$, which are driven off and collected by condensation. The heating is preferably done in a separate

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step before dissolving the $TiCl_3$ in a carrier of the second group, in order to avoid excessive formation of froth. A clean solution can be formed by a second filtering through ceramic filters before electrolyzing. (See Fig. 1.)

The following example shows the use of aluminum powder as reducing agent. Aluminum powder is reacted in the presence of some $AlCl_3$ with $TiCl_4$ at $130^\circ C.$, using reflux conditions. Excess $TiCl_4$ carries with it whatever amounts of $SiCl_4$ that may be present in the raw material. The reaction can be speeded up by the use of higher temperatures, e. g., higher than the boiling point of $TiCl_4$, and in a pressure vessel.

The mixture of $AlCl_3$ and $TiCl_3$ formed is dissolved in a carrier melt of the first group, containing only as much $AlCl_3$ as is necessary to dissolve more of it. In this example a melt is used containing 70% $AlCl_3$, 20% $NaCl$, and 10% KCl . The $AlCl_3$ simultaneously formed with the $TiCl_3$ is allowed to form a melt with the carrier, e. g. bringing the concentration from 70 to 80% $AlCl_3$. Impurities of chlorides of other metals may be dissolved in the carrier, and stay there, if they are less noble than Al . Nobler metals are deposited or cemented out by some of the Al -powder during the foregoing reducing reaction and form sludge.

For preparing an electrolyte of the second group, the $TiCl_3$ is separated by e. g. filtering from the first melt at about $100^\circ C.$

The $TiCl_3$ recovered by filtration is still contaminated with adherent carrier melt, unreacted Al -powder, and sludge. The contamination with adherent melt is compatible with the electrolyte of the second group, in which the residue is dissolved. It is, however, advisable to drive off $AlCl_3$ from the residue by distillation before dissolving it in the final carrier. In this example the eutectic of KCl and $LiCl$ is used as final carrier, and a temperature above $400^\circ C.$ is applied. The residue of unreacted Al -powder and sludge is filtered from the solution (see Fig. 2).

The preparation of an electrolyte for Ti , containing $TiCl_3$ dissolved in an inorganic salt melt, as known to the art, involved the costly steps of purifying $TiCl_4$, producing and purifying $TiCl_3$ therefrom, and finally dissolving the pure $TiCl_3$ chemical in a salt melt. This invention combines the action of reducing metals with the action and selective properties of suitable salt melts. The different electrolytical potentials in such melts allow selective electrolysis. The different solubility at a given temperature allows selective separation of $TiCl_3$ from different metallic compounds dissolved in such melts. These properties are not only used to reduce $TiCl_4$ but also to purify it, while preparing an electrolyte containing $TiCl_3$, thereby saving costly steps otherwise required. The invention, therefore, shows a method of producing inorganic electrolytes suitable for the electrolytical recovery of Ti with considerable economical advantage.

Though the carriers described above are based on $TiCl_3$ as the Ti -compound to be electrolyzed, some amounts of $TiCl_2$ or $TiCl_4$ may be simultaneously present. When, e. g. Al -powder is used as reducing metal, there is always some $TiCl_2$ formed along with $TiCl_3$. There may also be a small amount of $TiCl_4$ dissolved in the carrier. The scope of this invention is, therefore, not limited to $TiCl_3$ alone, though this compound is the main constituent, desired by the invention. The Ti -chlorides of lower or higher valency may, however, be left in the carrier without causing difficulties.

Having described my invention, what I claim and desire to secure by Letters Patent is as follows:

1. In a method of preparing an inorganic molten electrolyte for the purpose of electrolytically producing Ti , said electrolyte consisting substantially of a plurality of halides selected from the group of chlorides and fluorides of metals less noble than Ti and containing $TiCl_3$ being obtained by partial reduction of $TiCl_4$ by reaction with metallic Al , said $TiCl_3$ being therefore mixed with $AlCl_3$,

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the improvement which comprises mixing said $TiCl_3$ and $AlCl_3$ with a melt consisting essentially of $AlCl_3$ and at least one alkali chloride selected from the group consisting of $NaCl$, KCl , and $LiCl$, forming a melt in which the quantity by weight of $AlCl_3$ is larger than the quantity of said alkali chloride, applying a quantity of that melt sufficiently large and at a temperature sufficiently low so as to dissolve said $AlCl_3$ yet not to dissolve substantial amounts of $TiCl_3$, said temperature being also sufficiently low not to cause reformation of $TiCl_4$, separating the undissolved $TiCl_3$ from the melt, thereafter forming said electrolyte by mixing the $TiCl_3$ with said plurality of molten halides selected from the group of chlorides and fluorides of metals less noble than Ti , the amount of $AlCl_3$ present in said electrolyte being limited to a minor amount such as being introduced as contamination along with the $TiCl_3$.

2. In a method of preparing an inorganic molten electrolyte for the purpose of electrolytically producing Ti , said electrolyte consisting of a plurality of halides selected from the group of chlorides and fluorides of metals less noble than Ti and containing $TiCl_3$ being obtained by partial reduction of $TiCl_4$ by reaction with a metal selected from the group consisting of Al , and Hg , said $TiCl_3$ being therefore mixed with the corresponding chloride of the reducing metal, the improvement which comprises mixing said $TiCl_3$ and chloride of the reducing metal with a melt consisting essentially of $AlCl_3$ and at least one alkali chloride selected from the group consisting of $NaCl$, KCl , and $LiCl$, forming a melt in which the quantity by weight of $AlCl_3$ is larger than the quantity of said alkali chloride, applying a quantity of that melt sufficiently large and at a temperature sufficiently low so as to dissolve said chloride of reducing metal, yet not to dissolve substantial amounts of $TiCl_3$, said temperature being also sufficiently low not to cause reformation of $TiCl_4$, separating the undissolved $TiCl_3$ from the melt, thereafter forming said electrolyte by mixing the $TiCl_3$ with said plurality of molten halides selected from the group of chlorides and fluorides of metals less noble than Ti , the amount of $AlCl_3$ present in said electrolyte being limited to a minor amount such as being introduced as contamination along with the $TiCl_3$.

3. In a method of preparing an inorganic molten electrolyte for the purpose of electrolytically producing Ti , said electrolyte comprising substantially the eutectic mixture of $LiCl$ and KCl and containing $TiCl_3$, being obtained by partial reduction of $TiCl_4$ by reaction with metallic Al , said $TiCl_3$ therefore being originally contaminated with $AlCl_3$ in the molar relation of three moles $TiCl_3$ and one mole $AlCl_3$, the improvement which comprises substantially reducing the amount of said $AlCl_3$ contamination by mixing said $TiCl_3$ and $AlCl_3$ with a melt consisting essentially of $AlCl_3$ and at least one alkali chloride selected from the group consisting of $NaCl$, KCl , $LiCl$, forming a melt in which the quantity by weight of $AlCl_3$ is larger than the quantity of said alkali-chloride, applying a quantity of said melt sufficiently large and at a temperature sufficiently low so as to dissolve all of said $AlCl_3$ yet not to dissolve substantial amounts of $TiCl_3$, the temperature being also sufficiently low not to cause reformation of $TiCl_4$, separating the undissolved $TiCl_3$ from the melt, and thereafter forming said electrolyte by mixing the separated $TiCl_3$ with said molten eutectic mixture of $LiCl$ and KCl .

4. A method for separating $TiCl_3$ from the chloride of a reducing metal for the purpose of preparing said $TiCl_3$ suitable to be fed into a molten inorganic electrolyte, said reducing metal being selected from the group comprising Al and Hg , said $TiCl_3$ and chloride being simultaneously formed by reducing $TiCl_4$, which comprises dissolving the chloride of the reducing metal in a melt consisting essentially of a mixture of $AlCl_3$ and at least one alkali-chloride selected from the group consisting of $NaCl$, KCl and $LiCl$, thereby forming a melt in which

the quantity by weight of AlCl_3 is larger than the quantity of said alkali-chloride, employing a quantity of said melt sufficiently large and at a temperature sufficiently low, so as to dissolve all of said chloride of reducing metals, yet not to dissolve substantial amounts of TiCl_3 , and separating the undissolved TiCl_3 from the melt.

5. The method of separating TiCl_3 from at least the major part of AlCl_3 , said TiCl_3 being obtained by reducing TiCl_4 with aluminum, simultaneously forming a mixture having the proportion of 3 moles TiCl_3 to 1 AlCl_3 for the purpose of preparing TiCl_3 suitable to be fed into a molten inorganic electrolyte, which comprises dissolving the AlCl_3 by incorporating it into a melt consisting essentially of a mixture of AlCl_3 and at least one alkali-chloride selected from the group consisting of NaCl, KCl and LiCl, thereby forming a melt in which the quantity by weight of AlCl_3 is larger than the quantity of said alkali-chloride, employing a quantity of said melt sufficiently large and at a temperature sufficiently low so as to dissolve all of the AlCl_3 , yet not to dissolve substantial amounts of TiCl_3 , and separating the undissolved TiCl_3 from the melt.

6. In a method of preparing an inorganic molten electrolyte for the purpose of electrolytically producing titanium, said electrolyte consisting of a plurality of halides selected from the group of chlorides and fluorides of metals less noble than titanium and containing TiCl_3 being obtained by partial reduction of TiCl_4 by reaction with mercury, said TiCl_3 being therefore mixed with the corresponding chloride of the reducing metal, the improvement which comprises reacting mercury with TiCl_4 , forming TiCl_3 and HgCl_2 , while keeping floating on the top of the mercury a mixed melt consisting essentially of a major proportion by weight of AlCl_3 , and a minor proportion by weight of at least one alkali-chloride selected

from the group consisting of NaCl, KCl, and LiCl, said melt having a temperature above its melting point and below 180°C ., allowing the products of the reaction to rise and to be mixed into said melt, the HgCl_2 thereupon forming Hg and HgCl_2 , employing a quantity of said melt sufficiently large so as to dissolve all of the HgCl_2 yet not large enough to dissolve substantial amounts of TiCl_3 , said temperature being also sufficiently low not to cause reformation of TiCl_4 , separating the undissolved TiCl_3 from the melt, and thereafter forming said electrolyte by mixing the TiCl_3 with said plurality of molten halides selected from the group of chlorides and fluorides of metals less noble than Ti, the amount of AlCl_3 present in said electrolyte being limited to a minor amount such as being introduced as contamination along with the TiCl_3 .

7. In the method of claim 6 the additional step which comprises purifying the TiCl_3 after its separation from the melt in which the HgCl_2 has been dissolved, by heating it to a temperature above 180°C ., effecting the reversed reaction between TiCl_3 and any occluded HgCl_2 , vaporizing the reformed Hg and TiCl_4 , and thereafter mixing the purified residue consisting mainly of TiCl_3 with said plurality of molten halides.

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