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R. H. SINGLETON ET AL
METHOD OF PRODUCING TITANIUM

2,783,142

Filed Aug. 14, 1952

2 Sheets-Sheet 1

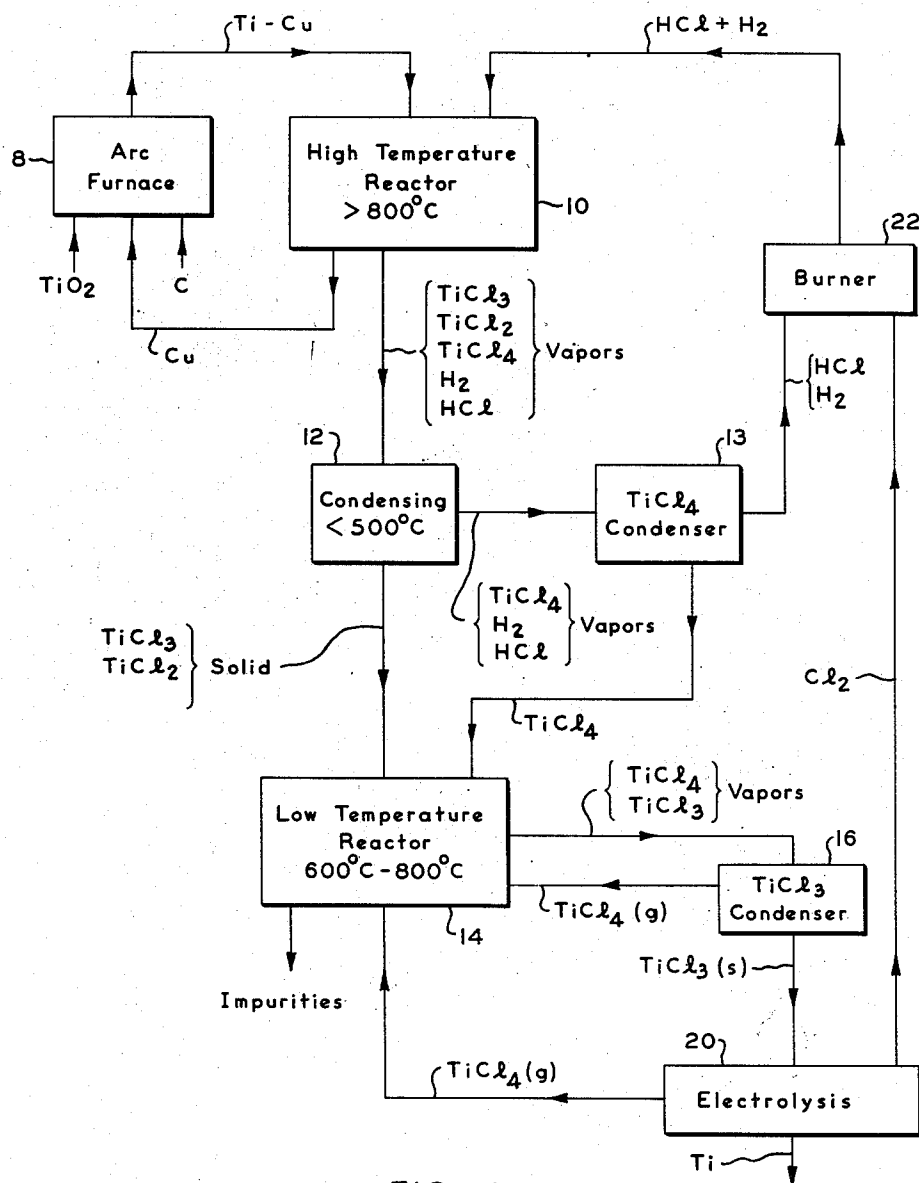


FIG. 1

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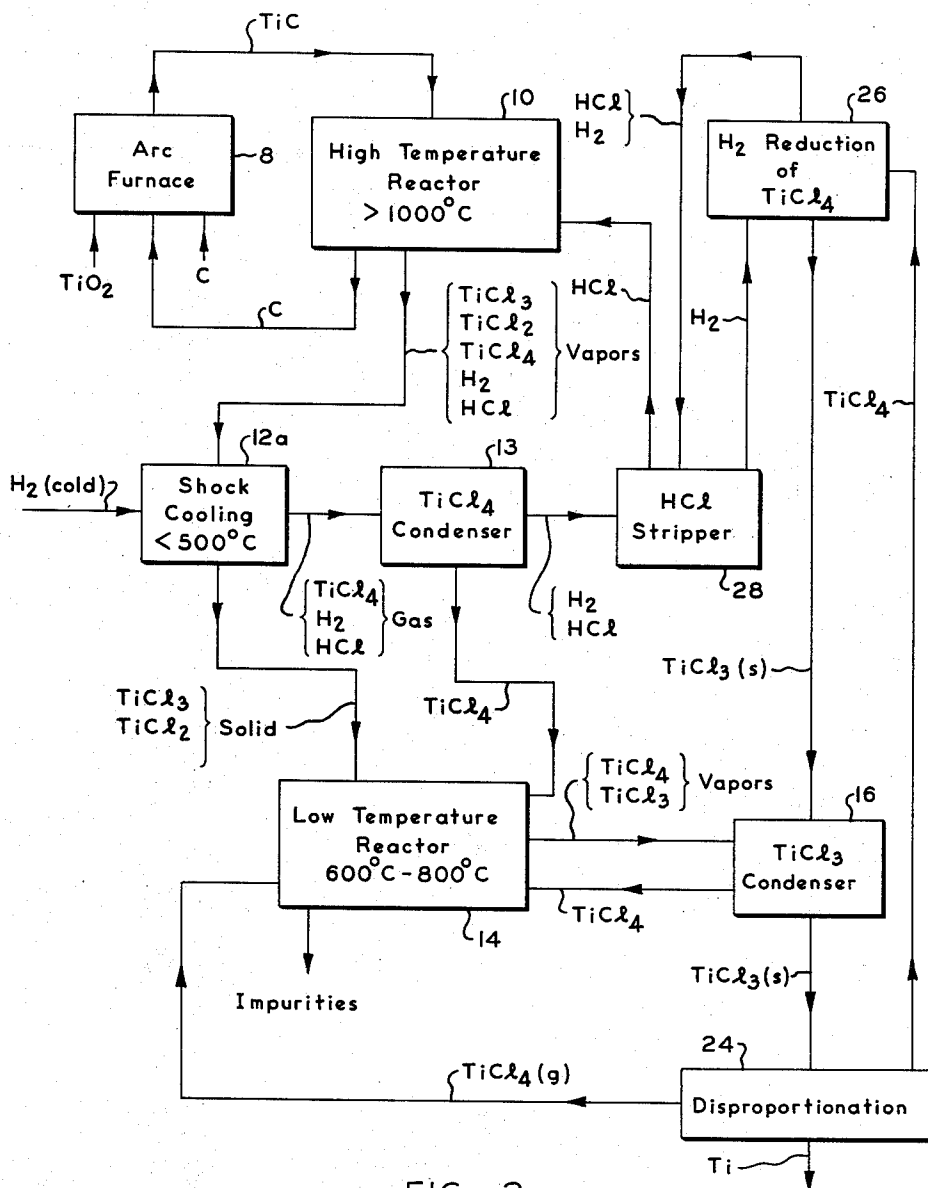
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METHOD OF PRODUCING TITANIUM

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6 Claims. (Cl. 75—84.5)

This invention relates to the production of titanium metal or lower chlorides of titanium, and more particularly to the production of pure titanium metal or pure titanium trichloride from titanium bearing materials.

It is a principal object of the present invention to provide an improved process for manufacturing titanium from titanium bearing materials so as to obtain the titanium in a form essentially uncontaminated by the original materials associated therewith.

Another object of the invention is to provide a relatively cheap process for obtaining relatively pure titanium trichloride from titanium bearing materials such as titanium carbide.

Still another object of the invention is to provide a process of the above type which is particularly adapted to the production of relatively pure titanium trichloride from titanium alloys.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description, taken in connection with the accompanying drawings, wherein:

Fig. 1 is a diagrammatic flow sheet illustrating one embodiment of the invention; and

Fig. 2 is a diagrammatic flow sheet illustrating another embodiment of the invention.

The present invention is primarily directed to the production of titanium or lower chlorides of titanium from titanium bearing materials. In particular, the present invention is concerned with the use as starting materials of titanium carbide and titanium alloys. Of the alloys, copper-titanium alloys are preferred, although other alloys such as the alloys of titanium with nickel can be employed. From the standpoint of cheapness and ease of operability of the process, the titanium-copper alloys are much preferred.

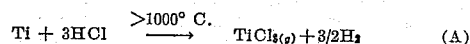
Titanium carbide and copper-titanium alloys can be relatively cheaply manufactured by electric furnace reduction of titanium dioxide in the presence of carbon. When the alloy is to be made, the alloying metal is also present in the electric furnace charge. The use of titanium-copper alloys as a starting material in the present process will be discussed first. This alloy may be made by the arc furnace reduction of ilmenite or the like with carbon in the presence of copper. Equally, it may be made by dissolving impure titanium in molten copper.

A titanium-copper alloy from an electric furnace 8 (Fig. 1) is fed to a first high temperature reactor 10 which is arranged to hold the molten titanium-copper alloy at a temperature above about 800° C. so as to provide a large surface area for contact with hydrogen chloride vapors. At high temperatures on the order of

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800° C. and above, the copper in the titanium alloy is relatively inert to hydrogen chloride. This is particularly true if the atmosphere in the high temperature reactor 10 contains at least one mole of hydrogen for each three moles of hydrogen chloride. Some of the hydrogen partial pressure is due to the oxidation of the titanium by the hydrogen chloride. Additional hydrogen is added to the reactor 10 as required, to maintain at least this ratio of 1 to 3.

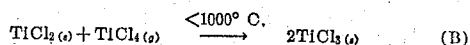
The titanium in the titanium-copper alloy will react with the hydrogen chloride to form gaseous titanium lower chlorides at temperatures on the order of 800° C. and above. However, it is preferred to operate at a temperature above the melting point of the titanium-copper alloy. This melting point will vary with the changing composition of the alloy. As a general proposition it is preferred to operate at a temperature of about 1000° C. or above so as to maintain the alloy molten at all times. The principal (and idealized) reaction between titanium and hydrogen chloride is expressed by the following equation:



The gaseous reaction products from Equation A are preferably removed from the high temperature reactor as gases, and the condensable gases are preferably condensed in a condenser 12, which may include a mechanical scraper for removing the condensed solids. The uncondensed gases in the condenser will consist of titanium tetrachloride, hydrogen and hydrogen chloride. These gases are passed through a condenser 13 and the titanium tetrachloride is separated therefrom. However, if the condenser 12 is operated below 136° C., the titanium tetrachloride can be condensed along with the titanium dichloride and titanium trichloride collected in the condenser. The unreacted hydrogen chloride and the hydrogen can be fed to a chlorine burner for converting most of the hydrogen to hydrogen chloride and the hydrogen chloride can then be recycled to the high temperature reactor. As will be apparent, some excess hydrogen is recycled so as to provide the adequate partial pressure of hydrogen in the high temperature reactor 10.

The condensed solids from condenser 12 are next reacted in low temperature reactor 14 with titanium tetrachloride to assure a high conversion of the condensed solid products to titanium trichloride. As a result of the condensing and the reaction with titanium tetrachloride, essentially all of the titanium is in the form of titanium trichloride. A number of reactions take place during the process of condensing and reaction with the titanium tetrachloride. Titanium trichloride leaving the high temperature reactor 10 may disproportionate to titanium dichloride during the condensing. Thus, the initially condensed products may comprise titanium trichloride, and titanium dichloride, gaseous titanium tetrachloride being given off during this condensing as a result of the disproportionation. While the condensing has been shown as the preferred cooling step at 12 in Fig. 1, this cooling may be achieved by shock-cooling as shown at 12a in Fig. 2 and discussed more fully hereinafter.

The titanium dichloride is converted to titanium trichloride by reaction with titanium tetrachloride in accordance with the following equation:



This reaction will take place quite rapidly at relatively low temperatures on the order of 300° C. Since some contaminating materials, such as oxides or carbides of titanium, may also be present in the condensed products in the low temperature reaction zone, it is preferred to re-sublime the titanium trichloride so as to obtain this

titanium trichloride in a state of high purity. This re-sublimation may be readily accomplished by heating the reaction products in the second reactor under an atmosphere of titanium tetrachloride to a temperature on the order of about 600° C. or higher. Although this temperature is well above the disproportionation temperature for titanium trichloride, the titanium trichloride will not disproportionate due to the atmosphere of titanium tetrachloride and may be transported to a suitable condenser 16 for condensing the titanium trichloride as a solid. While one reactor 14 has been shown for achieving conversion of the titanium dichloride to titanium trichloride and for subliming this trichloride this reactor may comprise two separate pieces of equipment. Equally, the conversion of titanium dichloride to titanium trichloride may be achieved at a higher temperature (on the order of 600° C. to 800° C.) during the sublimation of the titanium trichloride.

In Fig. 2 the titanium carbide is fed to the high temperature reactor 10 where it is reacted at a high temperature above about 1000° C. with hydrogen chloride vapor. The vapors leaving the high temperature reactor comprise unreacted hydrogen chloride, titanium trichloride, perhaps some titanium dichloride, some titanium tetrachloride and hydrogen. The condensable portions of these vapors may be condensed or shock-cooled (by use of cold hydrogen or argon) preferably to a temperature below 500° C. in a shock cooling zone 12a. The shock-cooled solid products (comprising primarily titanium trichloride, and titanium dichloride) are fed to the low temperature reactor 14 where they are reacted with titanium tetrachloride in a manner similar to that discussed in connection with the process of Fig. 1 to form titanium trichloride.

Both of the above processes result in high yields of essentially pure titanium trichloride. This titanium trichloride may be converted to titanium metal by a number of techniques, such as in an electrolysis cell 20 (Fig. 1) which may be of the type described more fully in the copending application of Benner and Chadsey, Serial No. 233, 204, filed June 23, 1951.

As can be seen from Fig. 1, the electrolysis of a solution of titanium trichloride will yield chlorine at the anode along with some titanium tetrachloride, the yield of titanium tetrachloride being dependent upon the amount of titanium trichloride in solution at the anode. At the cathode the titanium trichloride is electrolyzed to titanium metal. The chlorine generated in the electrolytic cell may, as shown, be combined in burner 22 with the hydrogen resulting from the high temperature reactor to form additional hydrogen chloride for recycling to the high temperature reactor. It is of course obvious that, depending upon economic considerations, it may be more desirable to sell the resultant hydrogen and chlorine separately than to recombine these materials to generate hydrogen chloride. This naturally will depend to a large extent on the relative cost of hydrogen, chlorine, and hydrogen chloride at any plant location.

The titanium tetrachloride resulting from the electrolysis of the titanium trichloride may be recycled to the low temperature reactor 14 or perhaps recycled to the high temperature reactor (along with the hydrogen chloride) depending upon how much excess titanium tetrachloride is obtained from the electrolytic cell. As mentioned previously, the production of titanium tetrachloride in the electrolytic cell is a function of the amount of titanium trichloride in solution in the vicinity of the anode. This quantity may be greatly reduced by the use of baffles, diaphragms, and the like in the electrolytic cell.

Equally, the titanium trichloride may be converted to titanium metal, such as by the use of a disproportionation apparatus 24 (Fig. 2) of the type described and claimed more fully in the copending application of

Singleton and van Arkel, Serial No. 285,975, filed May 3, 1952.

When disproportionation is used for converting the titanium trichloride to titanium, considerable quantities of titanium tetrachloride are generated. This titanium tetrachloride may be converted to titanium trichloride and hydrogen chloride in a suitable apparatus 26 (Fig. 2) therefor by passing titanium tetrachloride and hydrogen over a surface heated to approximately 1200° C. or higher. The titanium trichloride is recycled to the disproportionation apparatus 24, while the resultant hydrogen chloride is recycled to the high temperature reactor. Since the conversion of titanium tetrachloride to titanium trichloride is not quantitative it is necessary to employ recycle of the titanium tetrachloride and hydrogen leaving the reduction apparatus 26. This recycle of titanium tetrachloride is not shown on Fig. 2, but may be readily accomplished by condensing titanium tetrachloride in the outgasses.

It is also necessary to strip the hydrogen chloride from the hydrogen (at 28) before recycling the hydrogen through the hydrogen reduction apparatus. This may be readily achieved by low temperature refrigeration. The stripper 28 has been shown as a single step but will actually comprise several separate pieces of equipment, the condensed hydrogen chloride being revaporized for recycle into the high temperature reactor 10. In connection with the hydrogen reduction of titanium tetrachloride to titanium trichloride, it has been found that small amounts of aluminum trichloride vapors in the stream of titanium tetrachloride and hydrogen vapors greatly catalyzes the conversion of titanium tetrachloride to titanium trichloride.

In addition to the above techniques, the titanium trichloride may be thermally reduced to titanium metal by the use of reducing agents, such as sodium, magnesium and the like. Alternatively, the titanium trichloride may be chlorinated to produce pure titanium tetrachloride for use in thermal reduction processes, such as those shown in the Kroll patent No. 2,205,854, Maddex patent No. 2,556,763, or in the "torch" process described and claimed more fully in the copending application of Findlay, Serial No. 200,606.

When converting the titanium trichloride to titanium tetrachloride, it is preferred to operate at a temperature slightly above the boiling point of titanium tetrachloride (i. e., above 136° C.) so as to remove the titanium tetrachloride from the reaction zone as fast as it is formed. In this case it is also possible to eliminate the low temperature reactor since titanium dichloride is highly reactive with chlorine.

In the preferred form of apparatus employed with the above discussed invention, the various high temperature portions of the reactor are preferably formed of graphite or carbon. When carbon or graphite is used, the necessary heat input can be readily achieved by using the carbon or graphite as an electrical heating element in either an induction or resistance heating circuit. Where mechanical movement is required in the high-temperature portions, it is preferred to employ refractory metals, such as molybdenum, for those parts requiring high-temperature mechanical strength or wear resistance. Those portions of the apparatus which operate at temperatures of about 600° C. or lower can be formed of stainless steel, nickel or refractory metals, such as molybdenum and the like. Carbon and graphite can equally be used in the relatively low-temperature portions of the apparatus, but, for mechanical reasons, may be less preferred than the metals in many cases.

In general, the high temperature reactor may be a countercurrent still, similar to a zinc still, or a rotary kiln. Both of these arrangements furnish a large surface area for the titanium-copper alloy to be reacted with the hydrogen chloride. The still type of apparatus is pre-

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ferred with the molten alloy while the rotary kiln type is preferred with the solid titanium carbide. When shock cooling is employed it may take place in a portion of the high temperature reactor. In this case the shock-cooled products may be removed from the high temperature reactor as solids. Equally, the shock-cooling or condensing may take place outside of the high temperature reactor as illustrated on the attached flow sheets.

When a titanium-copper alloy is used, the percentage of titanium in the alloy is preferably in the range of 40% titanium to 60% titanium, the percent titanium being reduced to about 5% before the copper is recycled to the electric furnace for addition of more titanium.

In connection with the above discussed embodiments of the invention it should be pointed out that, on a recycle basis, there may be either an excess or shortage of titanium tetrachloride. If there is an excess of titanium tetrachloride, this may be reduced to titanium trichloride as shown at 26 in Fig. 2. If there is a shortage of titanium tetrachloride, which might result in an excess of titanium dichloride, this dichloride can be chlorinated to titanium trichloride.

In connection with the above discussion of the present invention, little emphasis has been placed on the shock-cooling requirements. It should be pointed out that the shock-cooling gases must be free of oxygen, nitrogen and compounds thereof such as water vapor, carbon monoxide and the like. This is due to the extreme reactivity of titanium and its chlorides with oxygen and the like. The great mass of cold hydrogen or argon required to shock-cool the hot reaction products necessitates high purity for these gases and, as a consequence, these gases are preferably used on a recycle basis with any necessary purification apparatus in the recycle system.

While resublimation of the product titanium trichloride in the low temperature reactor 14 has been set forth as a highly desirable step in the process it is not essential in all cases. This is particularly true where this titanium trichloride is essentially pure or sufficiently pure for its subsequent use. This purity will naturally depend upon the purity of the starting materials and the degree of carry-over of contaminants from the high temperature reactor to the cooling zone. The purity requirements of the titanium trichloride will vary considerably with the details of the further processing steps. For example, if disproportionation is to be employed, the titanium trichloride must have a very high purity. If the subsequent step is chlorination to titanium tetrachloride the titanium trichloride need not be particularly pure, provided the contaminants can be separated from titanium tetrachloride. With regard to electrolysis the purity requirements will be largely dependent upon the solubility of the impurities in the molten electrolyte.

Since certain changes may be made in the above process, without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description, or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of manufacturing titanium trichloride which comprises forming a crude alloy of titanium and copper, heating said alloy in a reaction zone to a temperature above about 800° C., contacting said hot alloy with hydrogen chloride to convert said titanium to gaseous titanium trichloride, maintaining in the reaction zone at least one mole of hydrogen for each three moles of hydrogen chloride, and removing gaseous titanium trichloride from the reaction zone.

2. The process of manufacturing titanium which comprises forming a crude alloy of titanium and a second metal selected from the class consisting of copper and nickel, heating said alloy in a reaction zone to a temperature above about 1000° C., contacting said hot alloy with hydrogen chloride to convert said titanium to a gaseous

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lower chloride of titanium and to convert said hydrogen chloride to hydrogen, passing the gaseous products from the reaction zone, cooling the gaseous products leaving the said reaction zone to a temperature below about 500° C., heating the cooled products to a temperature of about 600° C. in the presence of titanium tetrachloride to sublime titanium trichloride, condensing said sublimed titanium trichloride, and converting said titanium trichloride to titanium metal.

3. The process of manufacturing titanium trichloride which comprises heating a titanium bearing material in a reaction zone to a temperature above about 800° C., said titanium bearing material being selected from the class consisting of titanium carbide and a titanium alloy of a second metal selected from the class consisting of copper and nickel, contacting said hot titanium bearing material with hydrogen chloride to convert said titanium to a gaseous lower chloride of titanium and to convert said hydrogen chloride to hydrogen, passing the gaseous products from the reaction zone, cooling the gaseous products leaving said reaction zone to a temperature below about 500° C., heating the cooled products to a temperature of about 600° C. in the presence of titanium tetrachloride to sublime titanium trichloride, and condensing said sublimed titanium trichloride.

4. The process of claim 3 wherein the gaseous products leaving the high temperature reaction zone are shock-cooled to reduce the amount of disproportionation of titanium trichloride during cooling.

5. The process of manufacturing titanium trichloride which comprises heating titanium carbide in a reaction zone to a temperature above about 1000° C., contacting said hot titanium carbide with hydrogen chloride to convert said titanium carbide to a gaseous lower chloride of titanium and to convert said hydrogen chloride to hydrogen, passing the gaseous products from the reaction zone, cooling the gaseous products leaving said reaction zone to a temperature below about 500° C., heating the cooled products to a temperature of about 600° C. in the presence of titanium tetrachloride to sublime titanium trichloride, and condensing said sublimed titanium trichloride.

6. The process of manufacturing titanium trichloride which comprises heating titanium-copper alloy in a reaction zone to a temperature above about 800° C., contacting said hot titanium-copper alloy with hydrogen chloride to convert said titanium-copper alloy to a gaseous lower chloride of titanium and to convert said hydrogen chloride to hydrogen, maintaining in said reaction zone a ratio of partial pressures of hydrogen to hydrogen chloride of at least 1 to 3 to inhibit formation of copper chlorides, passing the gaseous products from the reaction zone, cooling the gaseous products leaving said reaction zone to a temperature below about 500° C., heating the cooled products to a temperature of about 600° C. in the presence of titanium tetrachloride to sublime titanium trichloride, and condensing said sublimed titanium trichloride.

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