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METHOD FOR THE PRODUCTION OF TITANIUM

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This invention relates to a method of producing titanium from titanium bearing ores and other titanium bearing materials. More particularly it relates to such method whereby such ores and materials are first converted to dry alkali chlorotitanates which are then reduced to metallic titanium. Alkaline earth metal reducing agents are utilized for the latter reduction. Specifically my invention encompasses a novel procedure whereby solutions of titanium as derived from such titanium bearing materials are conveniently converted to titanium metal.

In recent years the need for titanium has greatly increased because of its unique properties and those of its alloys. Because of its comparatively low weight, corrosion-resistance and high-strength the uses of titanium are being multiplied daily. One great drawback to the use of titanium up to the present time has been the difficulty with which it is produced in commercial form with a consequent high price. Such high price has been a deterrent to the wide-spread use of the metal.

Although many disclosures have been made showing how to produce titanium, to my knowledge all these disclosures either contemplate improvements to the basic Kroll process, shown in U. S. Patent No. 2,205,854, a process which is primarily the magnesium reduction of titanium tetrachloride in a bomb-like container, or the Van Arkle "iodide" process. All such processes developed until the advent of the instant invention are limited to titanium production in a discontinuous batch manner. The raw materials are placed in a batch reactor, the process is carried out, and the metal is then separated from the receptacle. In many cases because of local overheating such separation is tedious and expensive. Although these aforementioned procedures could satisfy the limited demands for titanium of the past, our present stage of technological development and readily foreseeable demands of the future make it essential that a simple, relatively inexpensive and continuous process for titanium production be developed and it is to this end that the instant invention is directed.

In the past titanium has been produced primarily from titanium tetrachloride and said tetrachloride has in turn been made from high-grade, expensive rutile ores. The use of rutile was necessary because of the complexities and high cost of removing the impurities resulting from use of lower quality ores. In my invention, on the other hand, although rutile may be used, the cheaper titanium ores such as ilmenite ($FeTiO_3$), iron containing titanium slags or any other titanium bearing materials are readily converted into pure titanium metal. Thus, as will be shown below, not only is my process continuous but also less expensive in terms of raw materials and manufacturing costs.

Underlying the instant invention is my discovery that moist potassium chlorotitanate, specifically, and other alkali chlorotitanates more generally, may be dried to a fine powder by treatment with hydrogen chloride gas while heated in the temperature range from about 20° C. to about 300° C. This removes all but a minute fraction of the water or mother liquor present in the solid chlorotitanate particles. In accordance with the procedure set out fully below, once dry alkali chlorotitanate is obtained it is readily reduced to metallic titanium while salts of other elements originally present in the starting material are produced. The metal obtained by reduction of such dry alkali chlorotitanate is quite acceptable for industrial uses and is at least as pure as the standard commercial titanium presently available.

An object of the instant invention is to provide a continuous method producing titanium.

Another object of the instant invention is to provide a method of producing titanium from all available sources thereof, and particularly ilmenite.

Still another object of the instant invention is to provide a method of producing titanium from titanium solutions.

Yet another object of the instant invention is to produce titanium of commercial quality by the reduction of dry potassium chlorotitanate, and dry alkali chlorotitanates more generally with alkaline earth metal reducing agents.

A further object of the instant invention is to produce titanium under far less severe operating conditions of temperature and pressure than hithertofore known.

Before entering upon a detailed explanation of my process it should be understood that such process consists of two primary steps, first the production of dry alkali chlorotitanates from titanium bearing materials and second the reduction of such alkali chlorotitanates to yield titanium. In step one the raw material is dissolved in an acid solution, converted to a halide, precipitated, and dried. In step two reduction of the chlorotitanate and separation of the end products are accomplished.

It is well known that titanium ores and many other titanium bearing materials may be dissolved in sulfuric acid or a combination of sulfuric and hydrochloric acids as the initial step in the recovery of titanium compounds from such materials. After such solution has been made the novel features of my invention may be utilized to recover pure titanium metal.

It should be understood that my invention is operable with substantially all titanium solutions. Since the making of such solutions for the manufacture of titanium dioxide pigments is old in the art, reference will be had only to those factors in the prior art necessary to place the instant invention in proper perspective. Thus to be more exact while a complete procedure is disclosed herein only the concepts deemed novel are elaborated upon and fully considered.

In order that my invention may be fully understood the following example of the process is presented.

Ilmenite ore is first ground to 250 mesh and the particles mixed with sulfuric acid (66 Baumé). The ilmenite acid mixture is heated rapidly to from approximately 80° to 120° C. This heating initiates an exothermic reaction which maintains the temperature at the above range until solidification or caking of the reaction product occurs. The solidified mass is next leached with either dilute sulfuric acid or a mixture of sulfuric and hydrochloric acids. Such acid mixture may be obtained by the recycling of acidic solutions from other steps in the process. The leaching step produces an acid solution of titanium and iron having additional insoluble material suspended therein, which insoluble material is readily separated from the titanium-iron solution by filtration or a like procedure.

It is now necessary to remove the iron from the solution. Approximately 70% of such iron present may be crystallized out in the form of iron sulfate merely by cooling the solution to a point where iron sulfate crystals

precipitate. Usually such precipitation occurs at a temperature range between 5° and 15° C. The crystals are then separated from the supernatant solution.

The next step is to saturate the now partially iron-free solution with hydrogen chloride gas. Such saturation is accomplished at low temperature, preferably at −10° to −20° C., for at this temperature almost all of the iron remaining precipitates in the form of iron chloride which is then separated from the remaining titanium solution.

Solid potassium chloride is now added to the cooled titanium solution. This causes the precipitation of potassium chlorotitanate. Such precipitation should take place at a temperature of about 0° C. or at temperatures slightly above that at which the iron chloride was made to precipitate. About 95% of the titanium formerly in solution has now been converted into solid potassium chlorotitanate. The potassium chlorotitanate is filtered and the precipitate dissolved in hydrochloric acid at room temperature. Subsequent cooling of the solution and the addition of gaseous hydrogen chloride thereto results in the recrystallization and reprecipitation of such potassium chlorotitanate.

The above recrystallizing step is not absolutely essential to the success of my process but such step does constitute part of the preferred embodiment thereof. Other methods such as an acid wash are also available to purify the chlorotitanate crystals, but the recrystallization step assures adequate purity for most purposes. This latter step of recrystallizing the alkali chlorotitanate makes the material especially well suited for the filtration and subsequent drying processes because larger crystals are obtained from the hydrochloric acid solution than those present after the first precipitation of the salt from a mixture of sulfuric and hydrochloric acids. It should be understood of course that the recrystallization and/or purification of the crystals is not absolutely essential to my process. However without such steps titanium of lower quality may be produced.

The precipitate is now centrifuged to separate if from the supernatant liquid. At this point the centrifugate contains somewhat in the order of 2 to 3% moisture in the form of concentrated hydrochloric acid solution. If such moisture is permitted to remain in and around the potassium chlorotitanate crystals a marked decrease in the net yield of titanium and a lowering of its quality will result.

The next step of the instant process is directed to the removal of such moisture without hydrolyzing the titanium compound. I have found that the rather tenaciously bound mother liquor may be efficiently and readily removed by passing a stream of dry hydrogen chloride gas through the partially dried alkali chlorotitanate, such procedure being carried out at a temperature of from 20° to 300° C. By this treatment a solid product with a water content in the order of 0.01% may be obtained.

The hydrochloric acid necessary for several steps in my process may be recovered, recycled and reused, a fact which I think is quite important from an economic standpoint.

The quantitative production of dry potassium chlorotitanate may be seen from the following example: 362 parts of ilmenite containing 50.0% TiO_2 were mixed with 724 parts of 66 Baume sulfuric acid and the mixture rapidly heated to a temperature of 95° C. until the mass solidified. Such mass product was leached with sulfuric acid to obtain a titanium solution containing 133 grams of iron per liter. Upon cooling of this solution to 5° C. 79% of dissolved iron was precipitated in the form of iron sulfate. Subsequent to filtration the solution analyzed as follows:

	Grams per liter
Titanium	100
H_2SO_4	440
Iron	28

Further cooling of the solution to −17° C. accompanied by saturation with hydrogen chloride gas precipitated most of the remainder of the iron as ferrous chloride. After removal of such iron, 290.4 parts of solid potassium chloride were added to the solution to form small particles of solid potassium chlorotitanate. The latter material was separated from the supernatant solution by centrifuging. Following this, the wet solid was redissolved in concentrated hydrochloric acid at 30° C. Large crystals of K_2TiCl_6 were recrystallized and reprecipitated by saturating the hydrochloric acid solution with hydrogen chloride gas while maintaining said solution at −5° to −15° C. The recrystallized material was centrifuged and then dried in a rotary kiln at 220° C. for 3 hours under an atmosphere of hydrogen chloride gas. At the end of this time 660 parts of dried potassium chlorotitanate was obtained.

To the best of my knowledge potassium chlorotitanate has never before been dried to a utilizable state of dryness without destroying its usefulness for the instant invention. My earlier attempts to remove the physically and chemically bound water and other oxide bearing substances from alkali chlorotitanates have given rise to various forms of hydrated titanium oxides. My discovery that the treatment of potassium chlorotitanate with dry hydrogen chloride gas effectively removes practically all of the water originally contained therein has thus given rise to this application. In the instant invention the dry potassium chlorotitanate is reduced to the free metal.

The reduction process of the instant invention is shown by the following equation:

$$A_2TiCl_6 + 2M \xrightarrow[\text{Heat}]{} Ti + 2ACl + 2MCl_2$$

where M is an alkaline earth metal such as magnesium or calcium and as will be obvious to those skilled in the art acts as a reducing agent, and A is an alkali metal.

In the reduction of the potassium chlorotitanate to titanium I have found that an intimate mixture with the reducing agent is quite important for as will be readily understood the reactive surfaces of the two materials must be such that reduction readily occurs. It is for this reason that powdered alkali chlorotitanate and finely ground reducing metal is preferred. Although the exact particle size is not critical it should be understood that both types of reactant particles should have a high surface area/volume ratio. Present particle size ranges from 1 to about 10 microns and good results are obtained when both types of particles are substantially the same size.

Although it is not absolutely essential to the utility of the instant invention I have found that the briqueting or pelletizing of the reduction mixture simplifies the material handling procedures required in these processes and also produces an end product of perhaps more desirable form than mere granules. Compression of the chlorotitanate reducing agent mixture may be used to produce a variety of shapes, the particular shape dependent upon the equipment available to the operator for the reduction operation and the equipment used to place the crude titanium in condition for final fabrication. After reduction the titanium metal will be in substantially the same physical form as was the original pellet or briquet.

I have found that if briquets are the form in which the materials are reduced the operator must prevent the inclusion of the air in the briquet mass. Apparently air inclusion induces a variety of side-reactions which are detrimental to the production of titanium. For example, the oxygen of the air may unite with the magnesium reducing agent to form magnesium oxide which of course is not useful as a reducing agent or the oxygen may directly unite with the titanium as it is formed to yield brittle titanium metal. Since titanium metal may also combine with the nitrogen present in air it is I think evident that several side reaction products may be produced. Thus not only may the air increase the cost of my process by increasing the amount of necessary

reducing agent but of greater importance it may detract from the titanium pureness. The production of titanium-nitrogen and titanium-oxygen compounds must be prevented to as great an extent possible.

It should be mentioned, at least parenthetically, that even if briquets or pellets are not used, and reduction is only between for example granular magnesium and granular alkali chlorotitanate, the air effect problem must still be prevented. As the dry alkali chlorotitanate is produced it may be stored in an inert atmosphere and then reduced in such atmosphere. The reducing agent alkali chlorotitanate briquets should also be formed in an inert gas atmosphere. Most simply this entails formation by a press in such atmosphere. Either the die portions of the press may be enclosed in a container of argon or the like, or the mixture per se may be placed in a separate air-proof pliable container which has air excluded by flushing with argon and then forming the briquet while retaining the mass in the container. It is of course possible to form a briquet in a vacuum but of the alternatives possible this would probably be the most expensive in the terms of equipment and procedure; however where the manufacturer has the vacuum equipment available vacuum means surrounding the press die may be more convenient.

Because of the affinity of titanium for gases normally present in the atmosphere and because many of these gases either diminish or completely destroy the desirable properties of the metal, as above mentioned, it is also essential that the reduction stage of the instant invention be carried out in either a vacuum or in an inert gas atmosphere (such as helium or argon). I consider the noble gas atmosphere to be preferable.

After the material is placed in the inert gas atmosphere the reduction may be commenced. Somewhat of an excess of reducing agent (up to 15%) over and above the amounts stoichiometrically calculated may be utilized to insure the completeness of the reducing reaction. The reducing agents that can be used include magnesium, calcium, strontium and barium; however for the purpose of the instant example the reduction using magnesium is discussed. The equation representing this reduction is as follows:

$$K_2TiCl_6 + 2Mg \xrightarrow[\text{Heat}]{} Ti + 2KCl + 2MgCl_2$$

The KCl and $MgCl_2$ are produced in the form of occluded crystals and their removal to yield purified usable titanium is discussed below.

The potassium chlorotitanate-magnesium metal mixture is heated to a temperature of from 325° to 600° C. in the above mentioned inert gas atmosphere. The time required for the reduction will of course somewhat depend on the temperature which is used. At a temperature of approximately 500° C. approximately 3 hours are required to complete the reduction. The time-heat requirements may be readily determined by the individual operator in accordance with the rate of production required and the equipment at his disposal.

When the reduction process has been completed, the titanium has occluded therein the salts produced during the process. Alhough there are several ways to remove the by-products I prefer leaching with dilute hydrochloric acid. It is also possible to remove the reaction end products from the titanium metal by a vacuum distillation procedure, a procedure well-known to those skilled in this art.

The following examples are given to illustrate the reduction phase of my invention:

Example I

340 grams of dry K_2TiCl_6 (0.01% maximum oxygen content) was thoroughly mixed with 53 grams of powdered magnesium and the mixture was then formed into small briquets in an argon atmosphere. The briquets were heated in an argon atmosphere for 3 hours at a temperature of 500° C. After heating the resultant reduced material was leached with 5 successive 1 liter portions of hydrochloric acid (approximately 15% HCl).

Example II

307 lbs. of dry Na_2TiCl_6 (0.03% maximum oxygen content) was thoroughly mixed with 54 lbs. of powdered magnesium and the mixture was then formed into briquets in an argon atmosphere. The briquets were heated in an argon atmosphere for 1 hour at 600° C. After heating the resultant titanium metal was freed from other reaction products by a vacuum distillation process between 600° and 850° at a vacuum of 10^{-2} mm.

It is readily seen how the instant invention is utilized to produce titanium in a continuous manner. After its reprecipitation or upon its initial precipitation and subsequent separation from the mother liquor the moist chlorotitanate is conveyed in an atmosphere of hydrogen chloride. The dried material is then mixed with the reducing agent and formed into briquets. Following this the briquets are passed through the heating chamber where reduction takes place. Briquets are continuously fed onto a belt at one end of the reduction chamber and the reduced briquets drop off at the opposite end.

It will also be readily seen by those skilled in this art that a convenient low temperature operation is herein disclosed. Although reduction may take place with temperatures ranging from 325° to 600° C. it is not essential to use the higher extreme of this range.

It should be understood that although reduction in the briquet form is not essential to the instant invention this is the preferred embodiment.

The chlorotitanates of the other alkali metals namely sodium, rubidium, and cesium may also be used for the reduction to titanium. These other chlorotitanates are dried by hydrogen chloride gas treatment and the instant process is carried out in the same manner as the reduction of the potassium chlorotitanate.

As above stated the fact that precipitated alkali chlorotitanates may be almost completely dried by heating in an atmosphere of hydrogen chloride gases is of the utmost importance to the instant invention. I know of three British patents, namely number 645,152, 651,729 and 652,268 which issued to a nationalized Czechoslovakian corporation, Spolek Pro Chemickou Vyrobu, Narodni Podnik, which concern the production of titanium oxide pigments and show the very first steps of my process. There is no indication however as to the method of removing the moisture from the alkali chlorotitanate for obviously this moisture is of no importance for pigment production. In my process on the other hand moisture is quite detrimental to the net yield of titanium and the physical properties thereof and thus the drying step assumes the importance conceded to it. These three British patents illustrate the use of an acid titanium ore solution followed by precipitation of the halogenotitanates. Beyond this these cases do not go and nowhere do they indicate how titanium may be produced.

In U. S. Patent 1,437,984 issued to John W. Marden a process is described for the production of refractory metals, primarily zirconium, although titanium is also mentioned. Marden specifies the use of non-volatile salts (e. g. K_2ZrF_6) of the metal to be reduced, "which does not melt or volatilize appreciably in any way at the temperature of reaction, together with a volatile metal, obtaining a product which is non-volatile or sublimable at the temperature of the reaction" (pages 1, 11, 66–73 of Marden). One suggested reaction uses K_2ZrF_6 and sodium at 600° to 700° F., such sodium being molten at 700° F. No actual disclosure of other solid salts such as salts of titanium or other reducing agents such as magnesium is made by Marden.

It is thus apparent that Marden teaches specifically the use of a reaction involving a liquid metallic reducing

agent and a solid non-volatile salt of a refractory metal. In contrast, the instant reaction is a reaction between two solids, namely a solid alkaline earth metal reducing agent and solid alkali chlorotitanate. The claimed reaction has a distinct advantage that starting and end products are all solids, and that in spite of the fact that solids are always present much lower reaction temperature may be used. Such lower reaction temperatures are of particular industrial advantage.

It will be understood that modification and variation may be effected without departing from the spirit and scope of the instant invention.

I claim as my invention:

1. In the method of producing titanium from titanium-bearing materials whereby such materials are first converted into alkali metal chlorotitanates having physically and chemically bound water therein, the steps comprising: removing such water by subjecting said moist alkali metal chlorotitanate to hydrogen chloride gas while maintaining said chlorotitanate within the temperature range of from 20° to 300° C.; reducing said substantially anhydrous alkali metal chlorotitanate to titanium and other reaction end products with an alkaline earth metal reducing agent in an inert atmosphere at a temperature within the range from 250° C. to that which said reducing agent remains in the solid state, and separating the titanium from such other reaction products.

2. In the method of producing titanium from ilmenite wherein such ilmenite is first converted into potassium chlorotitanate having physically and chemically bound water therein, the steps comprising: removing such water by subjecting said moist potassium chlorotitanate to dry hydrogen chloride gas while maintaining said chlorotitanate within the temperature range of from 20° to 300° C.; reducing said substantially anhydrous potassium chlorotitanate to titanium and other reaction products with magnesium metal in an atmosphere of helium at a temperature within the range of from 350° to 600° C., and separating the titanium from such other reaction products.

3. The method of producing titanium from titanium-bearing material comprising the steps of: making an acidic titanium solution from such titanium-bearing material, such acidic solution being made from acids in the group consisting of sulfuric and mixtures of sulfuric and hydrochloric acids; saturating such solution with gaseous hydrogen chloride; adding to such acidic titanium solution an alkali metal chloride whereby an alkali metal chlorotitanate precipitates therein; drying said alkali metal chlorotitanate by passing hydrogen chloride gas therethrough while maintaining said chlorotitanate at a temperature of from 20° to 300° C.; reducing said alkali metal chlorotitanate with an alkaline earth metal reducing agent in an inert atmosphere at a temperature of from 250° C. to that at which said reducing agent remains in the solid state to produce titanium and other reaction end products, and separating the titanium from such reaction products.

4. The method of producing titanium from ilmenite comprising the steps of: making an acidic titanium solution from such ilmenite, such acidic solution being made from acids in the group consisting of sulfuric and mixtures of sulfuric and hydrochloric acids; saturating such acidic titanium solution with gaseous hydrogen chloride; adding to such acidic titanium solution potassium chloride whereby potassium chlorotitanate precipitates therein; drying said potassium chlorotitanate by subjecting it to dry hydrogen chloride gas while maintaining said potassium chlorotitanate at a temperature of from 20° to 300° C.; reducing said substantially anhydrous potassium chlorotitanate with an alkaline earth metal reducing agent in a helium atmosphere at a temperature of from 250° C. to that at which said reducing agent remains in the solid state to produce titanium and other reaction end products, and separating the titanium from such reaction products.

5. The method of claim 4 wherein said alkaline earth metal reducing agent is magnesium.

6. The method of producing titanium from titanium-bearing material comprising the steps of: making an acidic titanium solution from such titanium-bearing materials, such acidic solution being made from acids in the group consisting of sulfuric and mixtures of sulfuric and hydrochloric acids; saturating such acidic solution with gaseous hydrogen chloride; adding to such acidic titanium solution an alkali metal chloride whereby an alkali metal chlorotitanate precipitates therein; dissolving said alkali metal chlorotitanate in hydrochloric acid; reprecipitating said alkali metal chlorotitanate by treating said hydrochloric acid solution with hydrogen chloride gas; drying said reprecipitated alkali metal chlorotitanate by subjecting it to dry hydrogen chloride gas while maintaining said alkali metal chlorotitanate at a temperature of from 20° to 300° C.; reducing said substantially anhydrous alkali metal chlorotitanate with an alkaline earth metal reducing agent in an inert gas atmosphere at a temperature from 250° C. to that at which said reducing agent remains in the solid state to produce titanium and other reaction end products, and separating the titanium from such reaction products.

7. The method of producing titanium from ilmenite comprising the steps of: making an acidic titanium solution from such ilmenite, such acidic solution being made from acids in the group consisting of sulfuric and mixtures of sulfuric and hydrochloric acids; saturating such acidic titanium solution with hydrogen chloride gas; adding to such acidic titanium solution potassium chloride whereby potassium chlorotitanate precipitates therein; dissolving the said potassium chlorotitanate precipitate in hydrochloric acid; reprecipitating said potassium chlorotitanate by treating said hydrochloric acid solution with hydrogen chloride; drying said potassium chlorotitanate by subjecting it to dry hydrogen chloride gas, while maintaining said potassium chlorotitanate at a temperature of from 20° to 300° C.; reducing said substantially dry potassium chlorotitanate with an alkaline earth metal reducing agent in an inert atmosphere at a temperature of from 250° C. to that at which said reducing agent remains in the solid state to produce titanium and other reaction end products, and separating the titanium from such reaction products.

8. The method of producing titanium from titanium-bearing material comprising the steps of: making an acidic titanium solution from such titanium-bearing material, such acidic solution being made from acids in the group consisting of sulfuric and mixtures of sulfuric and hydrochloric acids; saturating such solution with gaseous hydrogen chloride; adding to such acidic titanium solution an alkali metal chloride whereby an alkali metal chlorotitanate precipitates therein; dissolving and recrystallizing said alkali metal chlorotitanate; mechanically drying said alkali metal chlorotitanate whereby a portion of its water content is removed; completing the drying of said alkali metal chlorotitanate by subjecting it to dry hydrogen chloride gas while maintaining said alkali metal chlorotitanate at a temperature of from 20° to 300° C.; reducing said substantially dry alkali metal chlorotitanate with an alkaline earth metal reducing agent in an inert gas atmosphere at a temperature of from 250° C. to that at which said reducing agent remains in the solid state to produce titanium and other reaction end products, and separating the titanium from such reaction products.

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