

Feb. 14, 1956

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ELECTROLYTIC PREPARATION OF REDUCED
TITANIUM CHLORIDE COMPOSITION
Filed Nov. 20, 1951

2,734,855

Fig. 1.

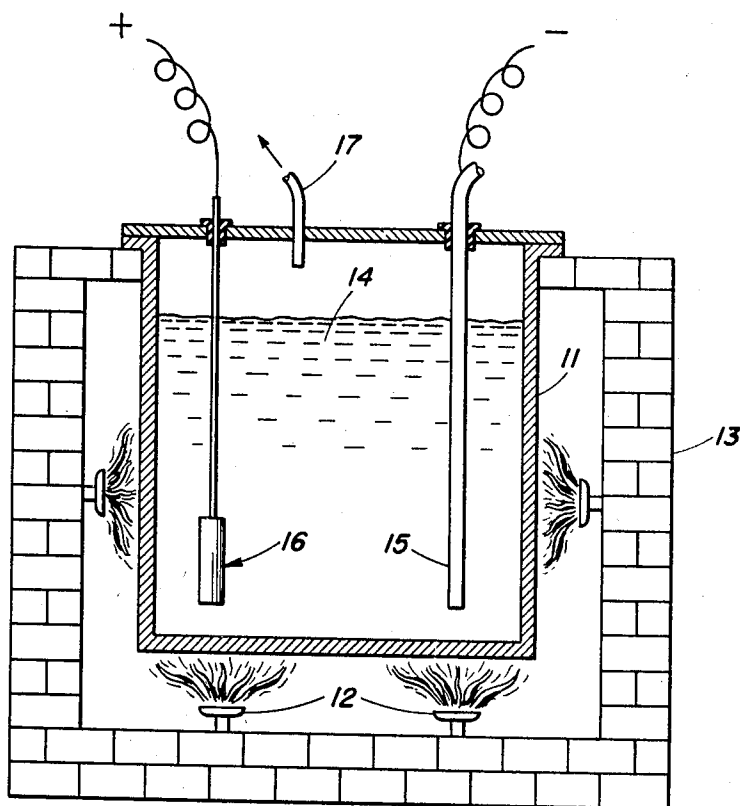
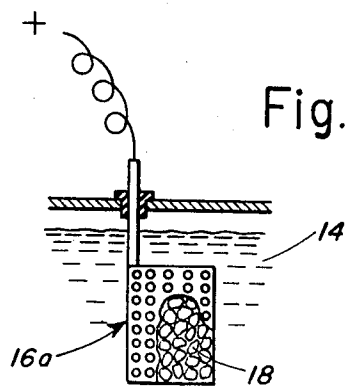


Fig. 2.



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ELECTROLYTIC PREPARATION OF REDUCED TITANIUM CHLORIDE COMPOSITION

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Application November 20, 1951, Serial No. 257,258

3 Claims. (Cl. 204—61)

This invention relates to a method for preparing reduced titanium chloride compositions. More specifically it relates to an electrolytic method for preparing reduced titanium chlorides.

Reduced titanium chlorides, that is, titanium dichloride and titanium trichloride are powerful reducing agents. Titanium dichloride in particular finds commercial use as a reducing agent in many non-aqueous organic and inorganic systems.

Several methods are known for preparing reduced titanium chlorides. For example, titanium tetrachloride may be reduced to titanium dichloride or titanium trichloride by reaction with a metallic reducing agent such as sodium or magnesium. Small amounts of titanium dichloride and titanium trichloride have also been produced by passing titanium tetrachloride over titanium metal. Apparently however, the titanium metal soon becomes coated with a portion of the reduced titanium chlorides and further reaction between the titanium tetrachloride and titanium metal is hindered.

An object of this invention, therefore, is to provide a direct method for preparing reduced titanium chloride compositions. A still further object of the instant invention is to provide an electrolytic process for the preparation of compositions containing titanium dichloride and titanium trichloride. Another object of this invention is to provide a simple and economical electrolytic method for the preparation of reduced titanium chloride compositions in which the compositions contain large amounts of titanium dichloride and small amounts of titanium trichloride. These and other objects will become apparent from the following more complete description of the instant invention.

Broadly this invention contemplates a method for preparing reduced titanium chloride composition which comprises employing, in an electrolytic cell having an anode, a cathode, and a molten salt electrolyte titanium metal as the anode in said cell, and introducing titanium tetrachloride into the cell, meanwhile concurrently passing electricity through said electrolytic cell in amount sufficient to convert all of the titanium tetrachloride to reduced titanium chloride, whereby an electrochemically equivalent amount of titanium metal from the anode is solubilized during the conversion of titanium tetrachloride to reduced titanium chloride.

In order to more clearly illustrate the type of apparatus which has been successfully used in preparing reduced titanium chloride compositions according to the instant invention, Fig. 1 and Fig. 2 are presented in which Fig. 1 shows in cross-section a type of electrolytic cell which is suitable for employment and Fig. 2 shows, also in cross-section, a type of anode which may also be used in place of the anode shown in Fig. 1.

Referring to Fig. 1, the electrolytic cell consists of container 11 which is heated externally by gas flames 12, in furnace 13. The halide salt electrolyte 14 is placed in the container 11 and a cathode 15 is inserted into the cell and extends down into the electrolyte. The cathode may

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be composed of any suitable material such as nickel. The anode 16 consists of titanium metal from which a portion of the reduced titanium chloride is obtained as the process progresses. In this particular instance the cathode is made up of a hollow nickel tube through which titanium tetrachloride may be introduced into the electrolytic cell. However, the titanium tetrachloride may be introduced into the electrolyte through a separate inlet port positioned adjacent to the cathode, and the cathode may possess other suitable form as for example, that of a solid rod or bar. The cell is further provided with a vent 17 through which any gaseous products may be removed.

The particular type of anode construction is unimportant and substantially any suitable means for supporting the anodic titanium metal may be utilized. For instance, the titanium metal may be consolidated such as by sintering or pressing into the form of a rod or bar which is then immersed into the fused salt bath as the anode. Another method of suspending the impure titanium metal in the fused salt bath is to provide a metallic container such as a basket, for example, one constructed of nickel or other suitable material in which the titanium metal may be placed. A suitable basket type anode 16A containing lumps of impure titanium metal 18 is shown in Fig. 2.

The amount of fused halide salt electrolyte originally present in the electrolytic cell is not critical and may be present in amount only to be sufficient to permit initiation of the electrolysis reaction. The starting halide salt electrolyte preferably is composed of at least one compound selected from the group consisting of the halide salts of the alkali metals, alkaline earth metals and magnesium. It is particularly desirable to employ the chlorides of said metals because of the economics involved. These halides may be employed singly or in combination. Mixtures of these halides which form low melting point eutectics are most convenient to employ, such as mixtures of sodium chloride and strontium chloride or sodium chloride and magnesium chloride.

The temperature of operation may also vary over a considerable range. Naturally it is necessary to employ temperatures sufficiently high to maintain the reduced titanium chloride composition in the molten state during electrolysis. The use of exceedingly high temperatures is undesirable because of the increased tendency toward corrosion and attack on the equipment involved. An atmosphere of argon or other inert gas is preferably maintained above the molten salt bath in order to prevent contamination of the titanium values by the outside atmosphere.

In order to carry out the process of the instant invention, the titanium metal employed as the anode is introduced into the fused salt bath. Titanium tetrachloride is then introduced into the fused salt bath in the vapor state and a sufficient quantity of electricity is concurrently passed through the electrolytic cell in order to reduce the titanium tetrachloride substantially immediately to titanium dichloride and titanium trichloride. At the same time an electrochemically equivalent amount of the titanium metal at the anode is dissolved to form an additional amount of reduced chlorides.

To prepare reduced titanium chloride compositions according to the instant invention, it is desirable theoretically to pass approximately from 1 to 2 faradays of electricity through the cell for each mol of titanium tetrachloride introduced. In actual practice a quantity of electricity slightly in excess of the theoretical amount is usually employed in order to overcome current losses due, for example, to side reactions and other effects occurring as a result of the particular cell design which is employed. If one desires to prepare reduced titanium chloride compositions containing a large proportion of titanium dichloride, it is preferred in theory to add electricity in a quantity

equivalent to approximately 2 faradays per mol of titanium tetrachloride introduced. In practice, high titanium dichloride concentrations have been obtained by passing through the cell from about 1.8 to 2.3 faradays per mol of titanium tetrachloride introduced. In actual practice the extended use of electricity in excess of 2.3 faradays per mol of titanium tetrachloride introduced, results in part of the titanium values depositing as titanium metal on the cathode. If one adds less than 1.8 faradays per mol of titanium tetrachloride introduced, the reduced chloride composition will contain larger proportions of titanium trichloride. As stated above for each mol of titanium tetrachloride converted to reduced titanium chlorides, it has been found that an electrochemically equivalent amount of titanium metal from the anode will also be converted to reduced titanium chlorides. Thus, in theory, when approximately 2 faradays of electricity per mol of titanium tetrachloride introduced are passed through the cell, substantially one mol of titanium metal will likewise be converted to reduced chloride. Obviously, if less than 2 faradays per mol of titanium tetrachloride introduced is used, a proportionally smaller amount of titanium metal from the anode will be solubilized.

In carrying out the process of the instant invention, titanium tetrachloride is introduced into a cell having a titanium metal anode, and concurrently a quantity of electricity in amount sufficient to reduce the titanium tetrachloride to reduced titanium chloride is passed through the cell, and as the process is continued the reduced titanium chloride composition is steadily enriched. At any concentration the reduced titanium chloride composition may be removed from the electrolytic cell and solidified as by cooling, and the resultant product will be in such form as to be conveniently handled or stored.

In order to illustrate further the process of the instant invention the following examples are presented:

Example 1

Using an electrolytic cell as described in Fig. 1, the following experiment was conducted in order to prepare a mixture of reduced titanium chloride composition.

10,000 grams of a chloride salt electrolyte consisting of 7,300 grams of strontium chloride and 2,700 grams of sodium chloride were placed in a cell and heated to 700° C., a hollow nickel cathode was inserted into the fused salt bath. An anode consisting of impure titanium metal was also inserted into the electrolyte. Titanium tetrachloride vapors were then added at the rate of 2.9 grams per minute through the hollow nickel cathode. Simultaneously electricity equivalent to 2 faradays per mol of titanium tetrachloride introduced was passed through the cell by employing a current of 50 amperes at an impressed voltage of approximately 1.3 volts. The anode current density was approximately 0.3 ampere per square centimeter, and a cathode current density of about 0.2 ampere per square centimeter was maintained. The titanium tetrachloride and a portion of the impure metal anode were converted to solubilized titanium dichloride and titanium trichloride. The process was continued for 9 hours, the fused salt bath was analyzed and found to contain concentrations equivalent to 1.2 molal titanium dichloride and 0.3 molal titanium trichloride. This product was used as the electrolytic medium in a process for electrolytically refining impure titanium metal.

Example 2

Another reduced titanium chloride composition was prepared in which higher concentration of the reduced titanium chlorides was obtained as titanium dichloride. 7300 grams of strontium chloride and 2700 grams of sodium chloride were placed in a cell similar in design to that described in Fig. 1 and heated to 700° C. Titanium metal was then inserted into the molten chloride electrolyte

as the anode, and a hollow nickel cathode was also placed in the electrolyte. Titanium tetrachloride vapors were then added at the rate of 2.7 grams per minute through the hollow cathode into the electrolyte. Simultaneously electricity in amount equivalent to 2 faradays per mol of titanium tetrachloride introduced was passed through the cell. The same conditions with respect to current and electrode current densities as reported in Example 1 were maintained in this example. The titanium tetrachloride and a portion of the impure titanium metal anode were converted to solubilized titanium dichloride and trichloride. The process was continued for 60 hours and the fused salt mixture then was removed from the electrolytic cell. The product was analyzed and found to contain concentrations equivalent to 8 molal titanium dichloride and 2 molal titanium trichloride.

It has clearly been shown by the description and examples presented above that reduced titanium chloride compositions may be directly prepared according to an electrolytic process in which titanium tetrachloride is introduced into an electrolytic cell having an impure titanium metal anode and a halide salt electrolyte and in which electricity is passed through the electrolytic cell whereby the titanium tetrachloride and a portion of the impure titanium metal anode are converted to reduced titanium chlorides. Furthermore, it has been shown that it is possible to provide an electrolytic method which is simple and economical to operate for the preparation of reduced titanium chloride compositions containing large proportions of titanium dichloride.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly limited thereto and other modifications and variations may be employed within the scope of the following claims.

We claim:

1. Method for the preparation of reduced titanium chloride composition which comprises employing, in an electrolytic cell having a titanium metal anode, a cathode and a molten salt electrolyte, said electrolyte being composed of at least one compound selected from the group consisting of the halide salts of alkali metals, alkaline earth metals and magnesium, and introducing titanium tetrachloride below the surface of said electrolyte adjacent to said cathode; meanwhile concurrently passing electricity through said cell, said electricity and said $TiCl_4$ being added in a faraday per mol ratio such as to convert all of the titanium tetrachloride to titanium trichloride and titanium dichloride, whereby an electrochemically equivalent amount of titanium metal from the anode is solubilized during the conversion of titanium tetrachloride to reduced titanium chloride.

2. Method according to claim 1 wherein the electricity is added in amount from 1.8 to 2.3 faradays for each mol of titanium tetrachloride introduced into said cell, whereby the titanium trichloride and titanium dichloride composition comprises predominantly titanium dichloride.

3. Method according to claim 1 wherein said cathode has a bore and wherein said titanium tetrachloride is introduced into said cell through said bore.

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