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ALKALI TITANIUM HALIDE COMPOSITIONS

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The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to us of any royalty thereon in accordance with the provisions of the Act of March 3, 1883, as amended (45 Stat. 467; 35 U. S. C. 45).

This invention relates to the preparation of a series of materials produced by the reaction of an alkali metal with a tetrahalide of titanium, and in particular to the preparation of a reducing agent, which material may also be used in the electrodeposition of titanium.

At the present time titanium trichloride in aqueous solution is an important reducing agent in the chemical industry. The end product of the industrial process for the preparation of titanium trichloride is an aqueous solution from which anhydrous titanium trichloride cannot be isolated. Hence it is necessary to pay shipping charges on a relatively large amount of water when the material is transported.

There is at present no commercially operated process for the electrodeposition of titanium metal. Because titanium has many desirable characteristics, much research has been carried out in an effort to find such a process.

The electrodeposition of titanium is difficult and impracticable from a commercial standpoint at the present time. By employing electroplating methods of deposition, for example, only thicknesses of from 0.001"-0.002" have so far been obtained. In order to apply electrowinning methods to obtain titanium metal it would be necessary to start with an ore or compound of titanium and then electrodeposit the metal. It is a known fact, however, that molten titanium is extremely reactive and cannot therefore be employed as the melt in such process since no known receptacle will contain molten titanium without destruction. Therefore it is necessary to use a titanium salt as a basic source material in the electrowinning of titanium.

It is well known that the lower valent salts of compounds require lower current densities than the higher valent compounds for electrodeposition: For example, a tetravalent titanium compound such as K_2TiF_6 could be employed in an electrowinning process but a trivalent salt of titanium would be more economical and practicable especially from a commercial standpoint.

However, there is at present no known source of a sufficiently economical trivalent titanium compound which can be employed in a practicable process for electrowinning titanium.

The above referred-to titanium trichloride ($TiCl_3$) for example, is commercially unobtainable in the anhydrous form necessary for use in an electrowinning process.

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Anhydrous $TiCl_3$ is not only extremely expensive but is virtually unobtainable except as a laboratory oddity. Aqueous $TiCl_3$ is available but the anhydrous form cannot be separated therefrom so far as is known.

The present invention provides an economical and practicable source of trivalent titanium compound which offers possibilities toward the attainment of a practicable and commercially feasible electrodeposition process for the winning of titanium.

An object of the present invention is to produce a reducing agent that may be stored and shipped in the dry state.

Another object of this invention is to provide a chemical composition from which titanium metal may be electrodeposited.

The series of materials produced by the present invention have not been definitely proven to be chemical compounds as contrasted with mixtures, and therefore will be referred to as chemical compositions or complexes. The end product of the reaction is a water soluble crystalline solid of varying colors depending upon the alkali metal and titanium tetrahalide used. The compositions according to the invention conform to the empirical formula $M_aTi_bX_c$, in which M is an alkali metal and may be lithium, sodium, potassium, rubidium, or cesium. The X in the empirical formula is a halide and may be chlorine, bromine, or iodine. The atomic ratios of the different elements in the complex may vary. For example, M:Ti:X may be between 1:1:4 and 3:2:8. However, the ratio of the titanium to the halide must always be 1 to 4. Another way of stating this is that the ratio of a to b to c is 1-1.5:1:4.

In the preparation of these materials the titanium tetrahalide and the alkali metal are brought into contact, and to insure complete reaction between the two materials it is preferable that a grinding action be maintained in the reaction chamber. To obtain maximum purity the reaction is carried out in an inert atmosphere; that is, an atmosphere that is free of oxygen and water vapor. The reaction can be carried out by four different methods, the choice depending on such factors as the melting point and reactivity of the alkali metal, the boiling point and reactivity of the titanium tetrahalide, the reaction vessel, and economic factors.

In the first of these the alkali metal is immersed in (or suspended by) an inert diluent which is maintained at a temperature which is above the melting point of the alkali metal and below the boiling point of the titanium tetrahalide. It is convenient from the standpoint of temperature control if a diluent is chosen which has a boiling point in this range. Then the titanium tetrahalide is added slowly to the reaction mixture while it is subjected to a grinding action. Carrying out the reaction in the indicated temperature range is advantageous in two respects. First, the grinding action needs to be much less vigorous if the alkali metal is maintained in a molten state. Second, the temperature of the reaction mixture is maintained at a temperature below the boiling point of the titanium tetrahalide so that any desired concentration of tetrahalide can be maintained.

The second method for producing these materials is essentially the same as the first, except that the reaction is carried out at room temperature. In this method the need for heating the reaction mixture is eliminated, but the grinding action must be more vigorous or last for a

much longer time so as to insure completion of the reaction. In this connection it should be noted that cesium and rubidium are molten at room temperature or slightly above.

The third method for producing these materials is similar to the first and second except that the diluent is eliminated. Lithium and titanium tetraiodide, for example, do not require a diluent even though the reaction is carried out at a temperature which is above the melting point of lithium metal, since this reaction is not vigorous. The diluent is useful as a moderator of the reaction in combinations such as sodium and titanium tetrachloride where the reaction is very vigorous and would be difficult to control. This is particularly true if the sodium is molten.

In the fourth method of preparation no diluent is used and the alkali metal and titanium halide are heated to above the melting point of the reactants. In this method no grinding is required and great care must be exercised to insure against the reaction proceeding too rapidly.

Detailed examples of the preferred method of preparation of several of the complexes follow:

(a) $\text{Na}_a\text{TibCl}_c$.

This preparation is carried out in a flask with a reflux condenser and so equipped that it can be constantly flushed with dry nitrogen to exclude air from the system. The flask is supported by a device which can move it in such a way that three 1½ inch glass balls inside the flask constantly stir and grind the reactants and product.

About 200 milliliters of dry toluene and 11.5 grams (0.5 mole) of pure sodium metal are introduced and the toluene refluxed gently. The agitation of the flask is then started and a solution of 190 grams of titanium tetrachloride in 100 milliliters of dry toluene is added dropwise. Agitation and heating are continued for several hours after all the solution has been added. The product is then washed several times with dry toluene and dried under vacuum at about 150 degrees C. In all the above processes every effort should be made to exclude moisture and oxygen.

(b) $\text{Li}_a\text{TibCl}_c$.

0.14 gram (0.02 mole) of lithium metal and 5.7 grams (0.03 mole) titanium tetrachloride are sealed into a strong glass vessel along with a sufficient number of nickel balls (about ½ inch in diameter) to cover the reactants. This is placed in a shaking device for from several hours to several days depending on the vigor of the shaking. When the reaction is complete the vessel is opened and the product washed and dried as described under the preparation of $\text{Na}_a\text{TibCl}_c$.

(c) Li_aTibI_c .

0.14 gram (0.02 mole) lithium metal and 16.6 grams (0.03 mole) titanium tetraiodide are sealed into a strong glass tube and the whole heated overnight at 200 degrees C. The end containing the product is then held at 200 degrees C. while the other end is cooled to room temperature. When all the excess titanium tetraiodide has distilled into the cold end the product is isolated by drawing out the tube at its middle and sealing.

It is advantageous in these reactions to use an excess of titanium tetrahalide to insure complete reaction of the alkali metal. The product of the reaction can be isolated from the reaction mixture by evaporation of the inert diluent, if used, and excess titanium tetrahalide at atmospheric or reduced pressure, or by washing out these contaminants with a volatile inert solvent followed by evaporation of the residual volatile solvent.

The use of an excess of titanium halide in this manner results in the obtainment of a product of fairly reproducible composition even though it is not sufficiently constant insofar as chemical composition is concerned to be listed as a true compound. The use of an excess of titanium

halide also insures against the presence of free alkali metal in the final product.

It will be apparent that the embodiments shown are only exemplary and that various modifications can be made within the scope of our invention as defined in the appended claims.

We claim:

1. A composition of matter consisting of a mixture of alkali titanium halides consisting essentially of a substance having the empirical formula M_aTibX_c in which M is an alkali metal and X is a halogen selected from the group consisting of chlorine, bromine, and iodine, and in which the ratio of a to b to c is 1-1.5:1.4.

2. A process for the preparation of a low-valent alkali titanium halide consisting essentially of a substance having the empirical formula M_aTibX_c in which M is an alkali metal and X is a halogen selected from the group consisting of chlorine, bromine and iodine and in which the ratio of a to b to c is 1-1.5:1.4 which comprises the steps of mixing an excess of titanium tetrahalide selected from the group consisting of, titanium tetrachloride, titanium tetrabromide and titanium tetraiodide, with an alkali metal in an air-and-moisture-free atmosphere, and subjecting said mixture to a grinding action at a temperature which is above the melting point of the alkali metal and below the boiling point at atmospheric pressure of the titanium tetrahalide employed for a time sufficient to produce complete reaction of said titanium tetrahalide with said alkali metal, and isolating the alkali titanium halide composition from the reaction mixture.

3. A process for the preparation of a low-valent alkali titanium halide consisting essentially of a substance having the empirical formula M_aTibX_c in which M is an alkali metal and X is a halogen selected from the group consisting of chlorine, bromine and iodine and in which the ratio of a to b to c is 1-1.5:1.4 comprising, the steps of adding an excess of titanium tetrahalide selected from the group consisting of, titanium tetrachloride, titanium tetrabromide, and titanium tetraiodide to a mixture of dry inert organic solvent for the titanium tetrahalide and an alkali metal in an inert air-and-moisture-free atmosphere and subjecting the resulting mixture to a grinding action at a temperature which is above the melting point of the alkali metal employed and below the boiling point at atmospheric pressure of the titanium tetrahalide for a time sufficient to produce complete reaction of said titanium tetrahalide with said alkali metal.

4. A process for the preparation of a low-valent sodium titanium chloride comprising the steps of, mixing sodium metal with a dry, inert organic solvent for titanium tetrachloride in a reaction chamber which provides an inert air-and-moisture-free atmosphere, gently refluxing said solvent, adding titanium tetrachloride to said mixture in small increments until an excess of said titanium tetrachloride is present, and subjecting said reactants to a continuous grinding action during and after the addition of said titanium tetrachloride at a temperature corresponding to the boiling point at atmospheric pressure of said solvent for a time sufficient to produce complete reaction of said titanium tetrachloride with said sodium metal.

5. A process for the preparation of a low-valent lithium titanium chloride comprising the steps of, adding titanium tetrachloride to lithium metal in small increments until an excess of titanium tetrachloride is present, said mixing taking place in a reaction chamber which provides an inert air-and-moisture-free atmosphere, and subjecting said reactants to a continuous grinding action during and after the addition of said titanium tetrachloride at room temperature for a time sufficient to produce complete reaction between said titanium tetrachloride and lithium metal.

6. A process for the preparation of a low-valent alkali titanium iodide comprising the steps of mixing lithium metal with an excess of titanium tetraiodide, grinding the resulting mixture in an inert air-and-moisture-free atmosphere at a temperature of approximately 200° C. for a

period sufficient to produce complete reaction between said titanium tetraiodide and lithium metal and distilling out said excess titanium tetraiodide.

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