

2,857,242

METHOD FOR THE PREPARATION OF
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Serial No. 552,227

12 Claims. (Cl. 23—87)

The present invention deals with the preparation of titanium tetrachloride of a sufficiently high degree of purity to be useful as a source for the recovery of metallic titanium.

Titanium metal, because of its strength characteristics, its ductility, and its resistance to corrosion, particularly when alloyed with various other metals, has become a very important metal commercially. Several types of processes have been devised for the production of the metal in substantially pure form, despite the difficulties due to the affinity of the metal for oxygen, nitrogen, carbon, and other contaminants all of which affect adversely the properties desired in the metallic titanium. Many of the processes presently being employed for the recovery of titanium metal make use of titanium tetrachloride as the starting material, the tetrachloride being reduced by suitable reducing agents down to the pure metal. An example of such a process is the process for making sponge titanium in which titanium tetrachloride is reacted with molten magnesium metal, resulting in the formation of the substantially pure titanium metal and magnesium chloride.

Theoretically the production of titanium tetrachloride by the chlorination of the readily available oxide ores of titanium should be a simple, economical process. However, it has been found that the temperatures required for the chlorination reaction, being on the order of 800 to 850° C., present corrosion problems which make the process difficult as well as expensive.

Titanium tetrachloride is usually obtained by the chlorination of briquettes or pellets of titanium dioxide or ilmenite in the presence of carbonaceous material as a reducing agent. One of the difficulties in this process arises from problems of corrosion in the furnace due to the high temperature chlorination and because of localized overheating of the solids, which, in turn, cause sintering and clinker formation in the furnace. In addition, the binders employed for the briquettes are a source of difficulty because such binders usually contain hydrogen resulting in chlorine losses in the furnace, due to the interaction of the hydrogen with the chlorine and the formation of hydrogen chloride. Accordingly, the briquettes must first be calcined to drive off the hydrogen. The facilities involved for briquetting and calcining require a sizable capital investment, and the removal of ash from the furnace calls for more special equipment.

The process of the present invention overcomes these difficulties by providing a source of titanium tetrachloride from readily available materials. In the process of the present invention, excessively high temperatures are not required, so that the problems of chlorine corrosion are minimized. Furthermore, the titanium tetrachloride is recovered in high yields, thus making this process considerably more economical than the conventional process of chlorination of oxide ores.

An object of the present invention is to provide an improved process for the recovery of titanium tetrachloride.

Still another object of the invention is to provide a process for the synthesis of titanium tetrachloride from readily available materials to give a high yield of titanium tetrachloride substantially uncontaminated with undesirable impurities.

Another object of the invention is to provide a process for the recovery of titanium tetrachloride which does not require expensive and elaborate apparatus.

Still another object of the invention is to provide an improved method for drying solid materials to reduce their moisture content, both as free moisture and as molecularly bound water.

In the process of the present invention, the starting material employed is an alkali chlorotitanate which can be produced by precipitation according to techniques well known in the art. While it is theoretically possible to produce some titanium tetrachloride by the thermal decomposition of an alkali chlorotitanate by merely heating the precipitate to an elevated temperature, I have discovered that the presence of even relatively small amounts of physically or chemically bonded oxygen compounds very seriously inhibits the progress of the reaction and substantially cuts down the amount of titanium tetrachloride which may be recovered. These oxygen compounds may take the form of physically absorbed water, water of hydration, or hydroxo compounds which combine with titanium atoms to form stable titanium oxygen compounds on heating. Accordingly, the process of the present invention provides a unique and highly effective drying process for reducing the content of physically or chemically bonded oxygen compounds in the chlorotitanate to the point where the content of these compounds is no longer a detrimental factor through the mechanism of hydrolysis in the subsequent pyrolytic decomposition.

The starting material according to the present invention may be an alkali chlorotitanate such as ammonium chlorotitanate, $(\text{NH}_4)_2\text{TiCl}_6$ or potassium chlorotitanate (K_2TiCl_6). These compounds can be prepared by precipitation from saturated acid solutions, particularly from solutions in hydrochloric acid or sulphuric acid in the presence of the appropriate alkali salt, followed by cooling to a temperature of about 0° C. or lower. Following the precipitation, the actual and potential moisture content of the precipitate is reduced substantially by treatment with dry hydrogen chloride gas, the details of which will be more fully developed in a succeeding portion of this specification. Following the drying, the resulting dehydrated chlorotitanate is then thermally decomposed at relatively low temperatures, such as between about 150° to 550° C., in an inert atmosphere to produce yields of titanium tetrachloride on the order of 90 to 95%.

A typical synthesis of the chlorotitanate involves providing a hydrochloric acid solution of a titanium compound of a concentration of about 100 grams of titanium per liter. The titanium solution is then cooled to 0° C. or below, and usually on the order of minus 20° C., and saturated with dry hydrogen chloride gas. An equivalent amount of ammonium chloride or potassium chloride is then added to form the corresponding alkali chlorotitanate. The precipitation on the chlorotitanate occurs almost immediately. The salt which results may be filtered on a cooled filter and washed with cooled, concentrated hydrochloric acid. For further purification the filter cake may be redissolved in a 1 to 1 hydrochloric acid solution and reprecipitated from the solution by cooling at minus 20° C. and saturating with hydrogen chloride gas.

To produce substantial yields of titanium tetrachloride, it has been found necessary to remove as much of the water remaining in the filter cake as possible. Ordinarily, the filter cake should be treated so that the moisture content, including both the free water and the molecularly bound water, should be no higher than about 1% by

weight prior to the thermal decomposition. It has been found that any moisture adherent to or occluded in the salt decreases the yield of titanium tetrachloride because of the hydrolysis of the titanium compounds to form titanium dioxide during the subsequent thermal decomposition. Attempts to dry the wet salt by processes such as heating, vacuum treatment, or azeotropic drying, to the desired level have been found to be ineffective, because of the partial hydrolysis which inevitably occurs.

One of the features of the present invention resides in drying the precipitate prior to thermal decomposition by means of a heated, dry hydrogen chloride gaseous atmosphere. Basically, this procedure involves introducing the wet material into a rotating kiln and passing dry hydrogen chloride gas over the material while tumbling the material in the kiln and maintaining a temperature of about 70° C. to about 300° C. in the kiln. During the removal of the water it is desirable slowly to increase the temperature in the kiln, starting at about 70° C. and raising the temperature up to about 250° C. to accelerate the drying process. With the described process, the total water content of the wet, precipitated alkali chlorotitanate can be reduced from a normal value of about 25% to about 1% or less by weight.

The drying time required can be further substantially reduced by preceding the treatment with dry hydrogen chloride gas by a washing of the wet cake with a non-aqueous liquid containing dissolved hydrogen chloride. This type of treatment is usually effective to reduce the water content of the filter cake down to the order of a few percent, usually about 2 to 3% by weight. As the non-aqueous liquid, I prefer to use dry organic solvents such as acetone and ethyl acetate, both of which can readily absorb hydrogen chloride. Other organic, relatively volatile liquids similarly capable of dissolving hydrogen chloride can also be used. In general, the solvent should be one capable of dissolving hydrogen chloride at least to the extent of 10% by weight. While this step of washing with a non-aqueous liquid containing dissolved dry hydrogen chloride can be omitted, it is preferred because it lessens the time required for drying in the subsequent dry hydrogen chloride gas treatment, and, furthermore, leaves the chlorotitanate in a non-caking discrete form particularly favorable to the HCl gas treatment and eliminates any milling or grinding step at any stage of the process.

After drying in the stream of dry hydrogen chloride gas, the chlorotitanate, which now has a moisture content not appreciably in excess of about 1% by weight, readily decomposes thermally. This decomposition is preferably carried out in a rotating kiln at temperatures between about 150° C. and 550° C. in the presence of an inert atmosphere such as argon, helium, nitrogen, or the like. The decomposition can be carried out in the same kiln as is used in the drying step, merely following the dry hydrogen chloride gas used in the drying step with an inert gas, heating the kiln at the same time to the higher temperatures indicated for the thermal decomposition step. Yields of titanium tetrachloride of 90 to 95% based upon the dehydrated material, are common in this reaction.

The following specific example will illustrate the process of the present invention and the results obtained:

Example

Potassium chlorotitanate was precipitated according to the usual process, and 864 parts by weight of the wet precipitate containing 190 parts by weight of liquid in the form of mother liquor were washed with 225 parts by weight of ethyl acetate solution containing 135 grams per liter of free hydrogen chloride. After filtration and vacuum treatment at 14 millimeters of mercury absolute pressure, the organic liquid content of the material was reduced to 75 parts by weight. It was then dry enough to break up upon being tumbled in a kiln into a fine

powder, which was further dried by heating in a rotating kiln in a stream of dry hydrogen chloride gas. The temperature of the kiln was raised from 150° C. to 220° C. in a period of about 2½ hours. At the end of this time, 677 parts by weight of potassium chlorotitanate material were obtained which were sufficiently dry for the thermal decomposition into titanium tetrachloride and potassium chloride. The material was decomposed immediately by passing it through the hot zone of a nitrogen filled kiln maintained at a temperature of about 425° C. A yield of 95% of the available titanium was obtained in the form of titanium tetrachloride (TiCl₄).

Instead of starting with potassium chlorotitanate, any of the other alkali metal chlorotitanates or ammonium chlorotitanate can be used in the above example and similar yields of available titanium obtained.

From the foregoing, it will be evident that the process of the present invention provides a convenient and economical means for the recovery of substantially pure titanium tetrachloride. The compacting and briquetting steps employed in the chlorination of oxide ores have been eliminated, and the temperatures required for the synthesis have been substantially reduced in this process. Furthermore, the material recovered is substantially uncontaminated with iron as is the case of the titanium tetrachloride recovered by the chlorination process. Furthermore, the process can use relatively impure ores and still produce titanium tetrachloride of high purity.

The term "alkali chlorotitanate" as used herein and in the claims is intended to include the ammonium and potassium chlorotitanates.

It will also be evident that various modifications can be made of the described embodiments without departing from the scope of the present invention.

I claim as my invention:

1. The method of converting an alkali chlorotitanate into substantial quantities of titanium tetrachloride, which comprises providing an alkali chlorotitanate mass including oxygen compounds which tend to hydrolyze said chlorotitanate, passing a stream of dry hydrogen chloride gas over said chlorotitanate until the amount of said oxygen compounds is reduced substantially, and thereafter thermally decomposing the dried chlorotitanate in an inert atmosphere to yield titanium tetrachloride.

2. The method of converting an alkali chlorotitanate into substantial quantities of titanium tetrachloride which comprises precipitating an alkali chlorotitanate from an aqueous acid solution, passing a stream of dry hydrogen chloride gas over the precipitated chlorotitanate until the water content of the precipitate has been substantially reduced, and thereafter thermally decomposing the dried chlorotitanate in an inert atmosphere to yield titanium tetrachloride.

3. The method of converting an alkali chlorotitanate into substantial quantities of titanium tetrachloride which comprises precipitating an alkali chlorotitanate from an aqueous acid solution, passing a stream of dry hydrogen chloride gas over the precipitated chlorotitanate until the water content of the precipitate has been substantially reduced, and thereafter thermally decomposing the dried chlorotitanate in an inert atmosphere at a temperature in the range from 150 degrees to 550 degrees C.

4. The method of converting an alkali chlorotitanate into substantial quantities of titanium tetrachloride which comprises precipitating an alkali chlorotitanate from an aqueous acid solution, passing a stream of dry hydrogen chloride gas over the precipitated chlorotitanate at a temperature in the range from about 70 degrees to about 300 degrees C. until the water content of the precipitate has been substantially reduced, and thereafter thermally decomposing the dried chlorotitanate in an inert atmosphere to yield titanium tetrachloride.

5. The method of claim 2 in which said alkali chlorotitanate is ammonium chlorotitanate.

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6. The method of claim 2 in which said alkali chlorotitanate is potassium chlorotitanate.

7. The method of converting an alkali chlorotitanate into substantial quantities of titanium tetrachloride, which comprises providing a moist alkali chlorotitanate mass, washing said mass with a mixture of a non-aqueous liquid containing dissolved hydrogen chloride to reduce the moisture content of said mass, treating the partly dehydrated mass with dry hydrogen chloride gas until the moisture content is further reduced, and thereafter thermally decomposing the resulting dried mass in an inert atmosphere to produce titanium tetrachloride.

8. The method of claim 7 in which said non-aqueous liquid is acetone.

9. The method of claim 7 in which said non-aqueous liquid is ethyl acetate.

10. The method of converting an alkali chlorotitanate into substantial quantities of titanium tetrachloride, which comprises providing a moist alkali chlorotitanate mass, washing said mass with a solution of a non-aqueous liquid containing dissolved hydrogen chloride to reduce the moisture content of said mass, treating the partly dehydrated mass with heated, dry hydrogen chloride gas until the moisture content is further reduced, and thereafter thermally decomposing the resulting dried mass in an inert atmosphere at a temperature in the range of about 150° to about 550° C.

11. The method of converting an alkali chlorotitanate into substantial quantities of titanium tetrachloride, which comprises providing a moist alkali chlorotitanate mass, washing said mass with a mixture of a non-aqueous liquid containing dissolved hydrogen chloride to reduce the moisture content of said mass, treating the partly dehydrated mass with dry hydrogen chloride gas at a temperature in the range from about 70° C. to about

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350° C. until the moisture content is further reduced and thereafter thermally decomposing the resulting dried mass in an inert atmosphere at a temperature within the range of 150° to about 550° C.

12. The method of converting an alkali chlorotitanate into substantial quantities of titanium tetrachloride, which comprises providing a moist alkali chlorotitanate mass, washing said mass with a mixture of a non-aqueous liquid containing dissolved hydrogen chloride until the total moisture content is on the order of a few percent, treating the partly dehydrated mass with dry hydrogen chloride gas until the total moisture content is reduced to a value on the order of 1% by weight, and thereafter thermally decomposing the resulting dried mass in an inert atmosphere to yield titanium tetrachloride.

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