This invention relates to the preparation of titanium oxide concentrates from titaniferous ores. More particularly, it relates to a process for removing iron from titaniferous ores and for the preparation of a substantially iron-free titanium dioxide concentrate. In a more specific sense, the invention contemplates effecting iron removal from titaniferous ores by volatilization and through employment of gaseous hydrogen chloride.

Previously, the removal of iron from ilmenite ores by employment of chlorine gas or phosgene has been proposed. Such processes are unsatisfactory and commercially non-adaptable for the purpose, because these types of chlorinating agents require excessively high consumption of elementary chlorine, and the chlorine or phosgene so employed cannot be readily and economically regenerated to permit of its reuse in the system. As a consequence, these processes are excessively costly and economically prohibitive.

Likewise, iron removal from ilmenite by digesting ilmenite ore with aqueous hydrochloric acid has been proposed, but this type of process possesses the disadvantage of being applicable to and operative upon only highly reactive ilmenite ores, and has the further undesirable feature of converting the hydrochloric acid employed to waste ferrous chloride solution which is entirely unsuitable for acid recovery and for which there is no commercial demand. Furthermore, such type of process requires that relatively large amounts of hydrochloric acid be readily available at all times, while disposal of the waste ferrous chloride formed constitutes a serious and costly economic item.

It has been found that these and other disadvantages of prior methods of iron removal from titaniferous ores by employment of chlorine compounds can be effectively overcome, and it is among the objects of this invention to provide a novel type of process for obtaining such results. An additional object is to provide a novel type of process for the preparation of desirable titanium dioxide concentrates which are substantially free from compounds of iron. A further object is the provision of a process from which powdered titanium oxide, in substantially rutile crystalline form, can be obtained. An additional object is to provide an improved method for removing iron from titaniferous ores by efficient volatilization.

These and other objects are obtainable in the present invention, which broadly comprises effecting iron removal from ferric iron-containing titaniferous ores by subjecting the ore to treatment at an elevated temperature in the presence of gaseous hydrogen chloride.

In a more restricted and preferred embodiment, the invention comprises oxidizing a titaniferous ore, such as ilmenite, to convert its iron values to substantially complete ferric state, and then subjecting the oxidized ore to the action of gaseous hydrogen chloride at elevated temperatures within the range of substantially 750° C. to 1000° C.

In one preferred adaptation of the invention to practice, ilmenite ore (usually considered to be ferrous titanate, FeTiO3), if coarser than relatively fine sand, is subjected to grinding to reduce its particles to a relatively fine state of subdivision. The finely-divided ore is then subjected to oxidation, whereby its iron content becomes converted to the ferric condition, such oxidation being effected by roasting in a suitable internally or externally fired rotary furnace, operating in a continuous manner and in the presence of an oxidizing medium such as oxygen or air, while maintaining the mass at a relatively high temperature, preferably within the range of about 750° C. to 1000° C. As a result of this operation, and as stated, the ferrous iron of the ilmenite becomes converted to the ferric condition, and the product comprises ferric iron and titanium dioxide. For convenience, the ore so treated is designated herein and in the appended claims as oxidized titaniferous ore.

The oxidized ore thus obtained is then preferably subjected to a stream of hydrogen chloride gas, malainted at an elevated temperature and preferably within the range of substantially 600 to 800° C. Treatment of the oxidized, ferric iron-containing ore with the hydrogen chloride gas effects conversion of its ferric iron content to ferric chloride, which readily volatilizes under prevailing conditions, and thus reduces or eliminates entirely the ferric oxide present in said ore, depending upon the extent of hydrogen chloride gas treatment. The titanium concentrate remaining comprises substantially grayish powdered titanium dioxide of rutile crystalline structure, which may be used in ceramics, welding rods, paints, and other fields where titanium oxide finds use because of its chemical or physical characteristics.

In order that the invention may be more clearly understood, the following examples are given, each of which is merely illustrative in character:

**Example I**

An ore analyzing 60% TiO2, the remaining 40%
being ferrous oxide, ferric oxide, silica in small amounts and other impurities, was placed in a revolving furnace and heated to 750° C. It was maintained at this temperature for one hour and in contact with a stream of air. The product was found by analysis to have been oxidized during this time and to have decreased in TiO₂ content due to the oxidation to the iron oxide. The oxidation was almost complete as the product contained less than 1% ferrous oxide at this time. This oxidized ore was then placed in an acid resisting rotating cylinder and a stream of dry hydrogen chloride gas was passed through the cylinder for one hour while maintaining the temperature at above 750° C. The exit gases were cooled and the ferric chloride and hydrogen chloride content determined after absorption in water. Analysis showed that 14.9% of the HCl was converted to FeCl₃ on the single passage of the HCl through the furnace.

**Example II**

The operations of Example I were repeated and the passage of the HCl continued for four hours. During this time, 5.25 parts by weight of hydrogen chloride were passed through the furnace per part of ore used. The product analyzed 78.6% TiO₂ and contained less than 5% of iron. The exit gases were chilled to below 10° C. and were found to consist of almost pure HCl which is useful for recycling to the volatilization furnace.

**Example III**

The operation of Example I was repeated while holding the temperature of the volatilization at 800° C. The analysis of the exit gases for the first hour of operation showed that 71.0% of the HCl was used in the volatilization of the iron on its passage through the furnace.

**Example IV**

The operation of Example I was again repeated but at a volatilization furnace temperature of 700° C. In this case the percentage of the HCl consumed in the formation of FeCl₃ on its one passage through the furnace was found to be 12.7% during the first hour of operation.

As will be apparent, a method is provided by the present invention for treating oxidized, ferric iron-containing titaniferous ores with gaseous hydrogen chloride at elevated temperatures, wherein wet reactions are at no time employed and the titaniferous material under treatment remains in relatively dry condition throughout the process. As a result, a dry, powdered concentrate, rich in relatively pure titanium dioxide, is obtained. This concentrate will be found to be substantially free from iron, or if any iron oxides are present, will only be to the extent of negligible quantities or traces, not exceeding substantially 5% and usually less than 2%, depending upon the extent of oxidation and gaseous hydrogen chloride treatment employed to induce iron volatilization and removal. Any iron oxide produced as a by-product in the process will also be in a relatively high state of purity and readily available for various commercial usages. The titanium dioxide present in the resultant concentrate will be in substantially rutile modification, as a result of the conversion of the titanium dioxide in the ilmenite (present as the titanate) by reason of its treatment at elevated temperatures with gaseous hydrogen chloride and ferric chloride. Thus, a novel method for producing rutile TiO₂ pigment is afforded.

It will be obvious the invention is not limited to ilmenite treatment, and that all types of titaniferous ores may also be subjected to treatment in the process. Thus, titaniferous ores containing more or less iron than is present in ilmenite, such as rutile bearing ilmenite having a content of TiO₂ ranging from about 55-90%, will be found to be quite useful in the invention, since by the instant process the TiO₂ content can be easily increased to 95% or higher. Similarly, titaniferous magnetite, a very common mineral available at very low cost, is also advantageous for use in the invention.

While roasting or oxidizing temperatures of the order of 750° C. to 1000° C. have been indicated as preferable for converting the iron content of titaniferous ores to the ferric state, in order to obtain optimum benefits in the invention, it will be understood that the invention is not limited to temperatures of such order, and that temperatures as low as 500° C. will also be found useful to effect oxidation. Similarly, temperatures in excess of 1000° C. may also be employed, although it has been found that more beneficial effects result when temperatures not to exceed 1000° C. are utilized. Previous to subjecting the titaniferous ore to the process, the ore is preferably ground to a relatively fine state of subdivision, since in such condition oxidation is more readily and effectively accomplished. Best results accrue in the invention when the titaniferous ore is in such finely-divided condition that substantially all of its particles are finer than about 200 mesh. While a finely-divided condition of ore will be found preferable for use during the roasting operation, in order to promote the efficiency of the process, it is obvious that ore in a relatively coarse condition, such as when the particles are as coarse as 40 mesh, may also be employed, and with reasonably good results.

While treatment of the oxidized ore with a stream of hydrogen chloride gas, maintained at an elevated temperature within the range of about 688-800° C., has been indicated, it is to be understood that such range of temperature is not necessarily critical to the invention, and that higher or lower temperatures, i. e., to as low as 400° C. or as high as 1000° C. are also contemplated as useful in the invention. Similarly, while the foregoing examples are illustrative of batch volatilization furnace operations, processes of the continuous type may also be employed. Thus, continuous passage of the oxidized titaniferous ore through a furnace or series of furnaces and countercurrent to hydrochloric acid gas passage through said furnace, is also contemplated and in fact preferred in large scale operations. In such instances, the fresh gas comes first in contact with the ore which has been previously treated, and from which practically all of the iron has been removed, passing on towards the feed end of the furnace where the iron content of the ore is relatively high, thereby insuring maximum conversion of the hydrogen chloride to ferric chloride.

As stated, the volatilized ferric chloride may then be removed from the furnace with the exit gases which are subjected to cooling to effect removal and recovery of their ferric chloride content. Although the ferric chloride thus recovered forms a valuable by-product, in the instant process it is preferably subjected to reaction with...
steam at elevated temperatures to produce iron oxide and hydrogen chloride. After drying, the recovered hydrogen chloride is again passed over the oxidized titaniferous ore to effect iron removal. By this recovery treatment, conversion of hydrogen chloride to ferric chloride becomes almost complete, and thus, an attractive and highly economical and successful process is achieved. By this means, the consumed hydrogen chloride is regenerated for reuse in the system, rendering the process cyclic. Since no hydrogen chloride is actually consumed in the process, purchases of this commodity will be found limited to the small amount used arising by reason of cyclic operation losses. Gaseous hydrogen chloride is available as a cheap by-product from many organic and other chlorination operations. If desired, of course, the recovered ferric chloride, instead of being employed to regenerate hydrogen chloride, may be sold as a by-product of the process since it finds relatively wide use as a coagulant in sewage and water treatments, which economic considerations justify the operation of the instant process in localities where the demand for ferric chloride is large and where titaniferous ores running as low as 25% TiO₂ are available.

I claim as my invention:

1. A process for producing substantially iron-free titanium dioxide concentrates, comprising heating a titaniferous ore in the presence of a gaseous oxidizing medium maintained at a temperature ranging from substantially 500-1000° C., and then subjecting the oxidized ore to treatment with gaseous hydrogen chloride, maintained at a temperature ranging from substantially 600-800° C., whereby said ferric values are converted to ferric chloride and volatilized for removal.

2. A process for producing substantially iron-free titanium dioxide concentrates, comprising heating a titaniferous ore in the presence of a gaseous oxidizing medium to a temperature within the range of substantially 500-1000° C. to convert iron values in said ore to substantially ferric state, and then subjecting the oxidized ore to treatment with gaseous hydrogen chloride, maintained at a temperature ranging from substantially 600-800° C., whereby said ferric values are converted to ferric chloride and volatilized for removal.

3. A process for producing substantially iron-free titanium dioxide concentrates, comprising heating ilmenite ore in the presence of a gaseous oxidizing medium to temperatures within the range of substantially 750-1000° C. to convert iron values in said ore to the substantial ferric condition, and then subjecting said oxidized ore to reaction with gaseous hydrogen chloride, maintained at a temperature ranging from 600-800° C., whereby said ferric values in said ore become converted to ferric chloride, and are volatilized for removal.

4. A process for producing substantially iron-free titanium dioxide concentrates, comprising heating a titaniferous ore in the presence of a gaseous oxidizing medium to temperatures within the range of substantially 500-1000° C., to convert iron values present in said ore to substantial ferric condition, and converting said ferric iron to volatilized ferric chloride by subjecting said ore to treatment with gaseous hydrogen chloride passed countercurrent to said ore, and maintained at a temperature ranging from 600-800° C.

5. A dry process for removing iron values from titaniferous ores to produce relatively pure rutile titanium oxide concentrate, comprising subjecting a titaniferous ore to heat treatment in the presence of a gaseous oxidizing medium, at temperatures ranging from substantially 750-1000° C., and thereafter subjecting said oxidized ore to treatment with gaseous hydrogen chloride maintained at a temperature of substantially 600-800° C., whereby said ferric values become converted to volatilized ferric chloride for removal from the system.

6. A process for producing substantially iron-free titanium dioxide concentrates, comprising heating a titaniferous ore to an elevated temperature in the presence of a gaseous oxidizing medium, and then subjecting the oxidized ore to the action of gaseous hydrogen chloride, also maintained at an elevated temperature.

7. A process for producing substantially iron-free titanium dioxide concentrates, comprising heating a titaniferous ore to an elevated temperature in the presence of a gaseous oxidizing medium, subjecting the resultant oxidized ore to treatment at an elevated temperature with gaseous hydrogen chloride, whereby volatilized ferric chloride is formed, condensing and treating the ferric chloride thus formed to recover hydrogen chloride therefrom, and recycling the recovered hydrogen chloride for reaction with the titaniferous ore under treatment.

8. A process for producing substantially iron-free titanium dioxide concentrates comprising heating a titaniferous ore to an elevated temperature, in the presence of a gaseous oxidizing medium, subjecting the resultant oxidized ore to treatment with gaseous hydrogen chloride, also maintained at an elevated temperature, whereby volatilized ferric chloride is formed and recovered, subjecting said ferric chloride to reaction with steam at an elevated temperature, whereby hydrogen chloride is recovered, and recycling the gaseous hydrogen chloride thus obtained for reaction with the oxidized ore under treatment.

9. A process for treating titaniferous ores to obtain valuable oxide concentrates therefrom, comprising oxidizing a titaniferous ore to convert its iron values to substantially the ferric condition, and then subjecting the oxidized ore to the action of hydrogen chloride gas while maintaining the reactants at an elevated temperature.

10. A process for treating titaniferous ores to obtain valuable titanium oxide concentrates therefrom, comprising oxidizing a titaniferous ore to convert the iron values thereof to the ferric condition, and then subjecting said oxidized ore to the action of gaseous hydrogen chloride, maintained at a temperature ranging from about 400° C. to 1000° C.
CERTIFICATE OF CORRECTION.


JAMES ELIOT BOOGE.

It is hereby certified that an error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 47, for "688-800° C." read 600-800° C.; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of January, A. D. 1910.

Henry Van Arsdale,
(Seal)
Acting Commissioner of Patents.