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SEPARATION OF IRON FROM TITANIFEROUS IRON ORES

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The present invention relates in general to the manufacture of metal halides, especially titanium tetrachloride, and more particularly to an improved method for separating iron from titaniferous materials or titaniferous iron ores to produce a substantially iron-free titaniferous product for use in the manufacture of titanium tetrachloride, titanium metal and analogous products. As used herein the term titaniferous iron ore shall be understood to include titaniferous iron ores, rutile ore and ore-like materials such as processed ores which have been chemically or physically treated to produce titaniferous iron concentrates, slags and other beneficiated products.

One of the customary processes for separating titanium values from titaniferous material has been by chlorinating comminuted titaniferous materials at relatively low temperatures and in the presence of carbon or other reducing agents to produce a gaseous mixture of titanium tetrachloride and iron chlorides, i. e. ferric and ferrous chlorides; and subsequently separating the gaseous mixture into its components to obtain a relatively pure form of titanium tetrachloride.

This and similar procedures entail various difficulties not the least of which is that of separating the iron chlorides from the gaseous mixture of iron and titanium chlorides. Some degree of separation of these gaseous components of the mixture may be effected by fractional condensation due to the normal tendency of ferric chloride to condense from the vapor state directly to the solid state while the ferrous chloride condenses to form a liquid. However, since the liquid ferrous chloride tends to coat the solid reactants and thus cause objectionable plugging and low operation efficiencies, it is highly desirable to convert all of the iron values to the volatile ferric chloride state.

Other methods have been proposed for separating iron from titaniferous materials in the absence of a reducing agent in an effort to form volatile iron chlorides which may be removed as vapor without effecting volatilization of the titanium chloride, but as far as is known there is no commercial application of these processes.

The present invention is based, in part, upon the discovery that titanium tetrachloride may be used successfully to separate iron from the titanium values of titaniferous iron ore. Accordingly, an object of the invention is to provide an improved method for separating iron from titaniferous materials. A further object of the invention is to provide an improved method for separating iron from titaniferous materials so as to produce efficiently, substantially pure titanium values conveniently and on a commercial scale. A further object of the invention is to provide an improved method for treating titaniferous iron ore whereby the iron in the ore may be separated from the titanium values without the difficulties attending the use of a carbonaceous reducing agent and in a manner to insure the production of a granular titanium residue susceptible to chlorination for the production of titanium tetrachloride. A still further object of the invention is to provide an improved method for the commercial

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production of substantially pure titanium dioxide wherein a gaseous oxidizing agent and titanium tetrachloride are reacted with a titaniferous iron ore in the absence of a reducing agent.

Other objects and advantages of the invention will be evident from the following description thereof.

The present invention in its broadest aspects contemplates a unitary process for separating iron from titaniferous iron ore by treating it with a gaseous oxidizing agent and titanium tetrachloride so as to form vaporous ferric chloride and a substantially pure titanium dioxide residue which is susceptible to additional chlorination for the production of titanium tetrachloride. More specifically, the improved and integrated process of this invention comprises the oxidation and chlorination of a titaniferous iron ore by a mixture of titanium tetrachloride and chlorine to form a titanium residue substantially free of iron.

The term "oxidation" as used herein shall be understood to mean a process in which the positive valence of an atom is increased and hence is comprehensive of processes wherein the positive valence of an atom is increased by reaction with air, chlorine or other oxidizing agents.

Separation of iron by treatment with titanium tetrachloride and chlorine

In a preferred embodiment of the invention, the separation of the iron from the titanium values in the ore is accomplished by treating raw (unoxidized) ore with a mixture of volatilized titanium tetrachloride and chlorine in the absence of carbon or equivalent reducing agent. Although the exact nature of the reaction of volatilized titanium tetrachloride and chlorine with the ore is not exactly known, two possible explanations of the reaction are offered; the one being that the chlorine serves as an oxidizing agent for converting some of the ferrous oxide values to ferric chloride and ferric oxide while the titanium tetrachloride reacts with the ferric oxide values thus formed and with the original ferric oxide values in the ore to convert these iron values to volatile ferric chloride, the titanium tetrachloride also reacting with any remaining ferrous oxide to form ferrous chloride which, in turn, is acted upon by the free chlorine to form volatile ferric chloride. The second proposed explanation is that the titanium tetrachloride converts the iron oxide values of the ore to ferric and ferrous chlorides and that the chlorine oxidizes the ferrous chloride values to form ferric chloride. In any event, substantially all of the iron values escape from the reactor as volatile ferric chloride thereby leaving a residue of substantially pure granular titanium dioxide. In this connection experiments have shown that when volatilized titanium tetrachloride alone is used to chlorinate the iron or raw ore, i. e. unoxidized ore, the reaction soon slows down, the bed becomes frozen and the gas flow is reduced to channeling through the bed. It is important, therefore, that a mixture of titanium tetrachloride and chlorine be used with raw ore to insure the commercial success of the process. The term "granular" as applied to the titanium dioxide product of the reaction is used to connote a material consisting of separate and distinct particles of appreciable size such as may be susceptible to chlorination; and to distinguish over an amorphous product which may not be chlorinated at all or only with relatively great difficulty.

The titaniferous ore to be treated is a raw ore comprising a mixture of iron and titanium compounds in subdivided form, and is preferably treated in a fluid-solid system by a mixture of titanium tetrachloride and chlorine gases in the absence of a reducing agent and at an elevated temperature.

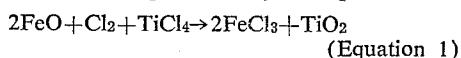
One convenient method for carrying out the reaction is to initially form a bed of ore in a reactor by charging the reactor with a predetermined amount of subdivided

titaniferous iron ore which has been beneficiated by the removal of siliceous gangue including iron oxides. To initiate the reaction, volatilized titanium tetrachloride, mixed with chlorine is preheated to a temperature between about 250° C. and about 350° C. and introduced into the reactor beneath the bed to flow upwardly therethrough and form a fluidized bed, that is to say, a bed of ore in which the individual particles of ore are held in a state of dynamic suspension, the suspension being maintained preferably by a regulated upward flow of the gases. In forming the fluidized bed in the reactor the velocity of the gases flowing upwardly through the bed must be sufficient to hold the particles of ore, or equivalent material, in dynamic suspension, but not so great as to force these particles upwardly out of the reaction zone of the reactor. Satisfactory dynamic suspensions have been obtained with space gas velocities from about 0.3 foot per second to about 1.0 foot per second using ores the particles of which fall within the size range of an average ilmenite beach sand which may be of the order of 20-200 mesh.

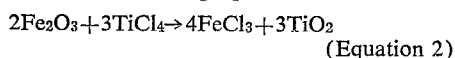
Although the fluid solid system described is satisfactory, it will be understood that other methods of carrying out gas phase-solid phase reactions are contemplated within the purview of the invention; and that while a static bed system is generally slower and subject to channeling, the process of this invention may, nevertheless, be carried out by this method.

To the aforementioned fluidized or dynamic bed is added additional raw titaniferous ore, which has been preheated to between about 300° C. and about 400° C. in order to prevent lowering of the temperature of the reaction zone and condensation of the volatile ferric chloride as the raw ore is fed downwardly into the fluidized bed.

Although the exact mechanism of the reaction between FeO, Cl₂ and TiCl₄ is not known, the overall results of these reactions may be represented by the equation:



In this reaction the TiCl₄ reacts with the ferric oxide values according to the following equation:



The chlorine reacts with the ferrous oxide values in the ore and with the ferrous chloride values formed by reaction of the TiCl₄ with the ferrous oxide values in the ore to form ferric chloride. The conversion of the iron values in the ore to volatile ferric chloride may be 90% or higher while substantially all of the volatilized ferric chloride escapes from the fluidized bed of the reactor thereby leaving a substantially pure titanium dioxide residue.

In accordance with these two equations 0.494 part of chlorine and 1.32 parts of titanium tetrachloride will be required for each part of ferrous oxide present in the ore; and, in addition, 1.78 parts of titanium tetrachloride will be required for each part of ferric oxide in the ore.

The amount of titanium tetrachloride used is preferably the theoretical amount required to react with the iron in the raw material and although a slight excess of titanium tetrachloride could be employed to insure high conversion of the iron to ferric chloride, large excesses of titanium tetrachloride are to be avoided, since this procedure involves loss of titanium tetrachloride and concurrent contamination of the volatile ferric chloride product with titanium tetrachloride.

The amount of chlorine used should be sufficient to oxidize the ferrous oxide values in the ore as well as any ferrous chloride produced by reaction of the titanium tetrachloride with the ferrous oxide, and satisfactory results have been obtained when the stoichiometric amount of chlorine has been used. In actual practice, however, it seems desirable, when oxidizing said chlorine to employ at least 10% excess chlorine over the stoichiometric proportions to secure rapid and complete reaction. Any

unreacted chlorine may be subsequently collected and recirculated through the dynamic bed of the reactor for oxidizing additional ore. On the basis of the preferred molar ratios of titanium tetrachloride to chlorine being from 1:1 to 1:3 then from 2.7 to 0.9 parts titanium tetrachloride are used with 1 part chlorine by weight depending upon the amount of ferrous oxide present in the titaniferous ore.

In general the reactions by which the iron values in the titaniferous iron materials are converted from oxides to chlorides occur over a temperature range from about 500° C. to 1200° C. For titaniferous materials of the order of less than 325 mesh and in which substantially all of the iron values are in a reduced or ferrous state, the conversion of the oxides by oxidation and chlorination to ferric chlorides occurs at the lower end of the temperature range, the preferred reaction temperature from the standpoint of high efficiencies being in the range from about 700° C. to 900° C. On the other hand, where the titaniferous materials contain both ferrous and ferric iron values, generally higher temperatures are used for an efficient conversion of the oxides by the process of this invention, the preferred range being from about 850° C. to 1050° C.

It has been discovered that when maintaining a fluidized bed of granulated ore by an upward flow of gas at a rate of between 0.3 foot and 1.0 foot per second the titanium dioxide is not carried up out of the reactor with the volatilized ferric chloride but accumulates as a residue in the fluidized bed. This unexpected phenomenon may be attributed to the fact that the particle size of the chlorinated ore remains substantially unchanged, or at most, suffers but slight decrease in size. Apparently the displaced iron atoms of the ore are replaced by titanium atoms with the result that the lattice structure remains substantially unchanged. Hence, while the ferric chloride formed by chlorination of the ferric oxide is volatilized from the bed, the titanium dioxide, being non-volatile and occluded in the residue remains in the bed and may be subsequently chlorinated in the same reactor or transferred to a separate zone where the titanium dioxide particles may be suspended in the presence of a mixture of carbon and chlorine gases to produce titanium tetrachloride. Chlorination of the residue, i. e. enriched titanium dioxide, by either the batch process or continuous reaction process has established that the enriched titanium dioxide may be chlorinated with at least equal and even greater facility than natural rutile ore.

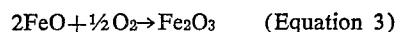
The volatilized ferric chloride may be removed from the reactor by collecting the chloride in a separate zone and decomposing the chloride by the introduction of oxygen to form iron oxide and chlorine gas.

Although the foregoing description relates, in particular, to the oxidation and chlorination of a raw (unoxidized) ore, the process of this invention is applicable also to titaniferous materials in which substantially all of the iron values are in the reduced or ferrous oxide state.

Separation of iron by oxidation and subsequent treatment with titanium tetrachloride

While the treatment of raw (unoxidized) titaniferous ore by an admixture of titanium tetrachloride and chlorine is preferred, it is within the purview of the invention to treat a titaniferous ore by preliminarily oxidizing the raw ore and thereafter chlorinating the oxidized ore.

The oxidation of the raw ore may be effected in any one of several accepted ways, such as, for example, by roasting the ore in the presence of air. Where air or other oxygeniferous gas is used, the amount used must be sufficient to convert substantially all of the ferrous iron present in the ore to ferric iron according to the following equation:



Thus a minimum of 0.111 part of O₂ must be supplied for each part of FeO present in the ore. In actual prac-

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tice it may be desirable to depart from the exact stoichiometric proportions and to use a large excess of air to secure rapid and complete reaction.

The ferric iron already in the ore, as well as that produced by the oxidation of the ferrous iron react with titanium tetrachloride according to Equation 2, supra, from which it is apparent that 1.78 parts of titanium tetrachloride are required for the conversion of 1 part of ferric oxide in the oxidized ore to ferric chloride; or differently expressed, 1.32 parts of titanium tetrachloride will be necessary to convert each part of ferrous oxide and 1.78 parts of titanium tetrachloride for each part of ferric oxide in the original ore.

Treatment of the oxidized ore by titanium tetrachloride gas is preferably carried out by forming a fluidized bed of the oxidized ore in a reactor by passing titanium tetrachloride gas, which may be mixed with an inert non-reducing gas such as nitrogen, upwardly through the ore at a space gas velocity of between 0.3 foot per second and 1.0 foot per second. To this fluidized bed additional oxidized ore is added as the reaction goes forward at an elevated temperature to produce volatilized ferric chloride and substantially pure titanium dioxide.

The amount of titanium tetrachloride used for efficient and economical operation is preferably the theoretical amount required to react with the oxygen values of the iron in the ore although a slight excess of the stoichiometric amount of titanium tetrachloride will insure high conversions of the iron values.

An inert gas such as, for example, nitrogen may be mixed with the titanium tetrachloride in the ratio of about 1 part of titanium tetrachloride to about 1 part of nitrogen which is used primarily to help sustain the fluidized bed, and to facilitate regulation of the ratio of titanium tetrachloride to ore being fed to the reactor. However, where such considerations are not paramount, the titanium tetrachloride alone may be used successfully. The temperature for chlorination of the iron values by the titanium tetrachloride (and nitrogen) is preferably between about 850° C. and about 1050° C. at which temperatures and, in particular, the higher temperatures the efficiency of the reaction may be expected to be as high as 98.5%.

In this connection, the heat necessary to maintain the hereinabove described reactions at their most efficient operating temperatures may, for small installations such as pilot plant installations, be supplied by electric resistance elements wrapped around or otherwise intimately associated with the reactor of the apparatus. In the case of large commercial installations, heat generated by an exothermic reaction within the reactor may be relied upon, in large measure, to maintain the reaction for continuous operation.

Thus by the improved and economical method of this invention, titaniferous iron ores may be treated by oxidation and chlorination to separate out volatile ferric chloride from the ore and leave a residue of substantially pure titanium dioxide.

The following examples are presented to explain more fully the details of a preferred embodiment of this invention.

Example I

5,529 parts, more or less, of finely divided raw titaniferous iron ore analyzed as comprising 58.6 parts of titanium dioxide, 22.4 parts ferric oxide and 13.5 parts ferrous oxide and having particle sizes of the order of 48-150 mesh were preheated to substantially 300° C. and added at the rate of substantially 34 parts, more or less, per minute into the upper portion of a reaction chamber in which a fluidized bed, between about 25 to 36 inches in height, and containing substantially 1,805 parts, more or less, of beneficiated titaniferous ore was maintained. The beneficiated titaniferous ore of the fluid bed had a particle size of the order of 48-150 mesh. The fluidized bed was maintained by passing a gaseous mixture in the ratio of between about 2.7 to 0.9 parts titanium tetra-

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chloride to about 1 part chlorine in an upward flow through the constituents of the fluidized bed at the rate of substantially 0.35 foot per second and preheated to substantially 300° C. The temperature of the bed was maintained at about 1050° C. The titaniferous residue was withdrawn from the reactor at the rate of between about 23 parts to about 30 parts per minute and contained substantially 90% titanium dioxide and 6.6% iron oxide, the balance being siliceous gangue and the like. The reaction was continued for a period of 2½ hours under substantially steady state conditions and a total of substantially 4,622 parts, more or less, of titanium residue was obtained.

The efficiency of the reaction was computed on the basis of the number of parts of titanium tetrachloride required theoretically to replace all the chlorinatable elements per 100 parts of ore. On this basis the calculated required titanium tetrachloride was substantially 2,795 parts while the actual titanium tetrachloride used in the experiment was substantially 2,873 parts. The overall efficiency of the reaction was therefore 97.5%.

Example II

The procedure used in Example I was repeated except that the raw ilmenite ore added to the reactor was replaced by an ilmenite ore which contained substantially 25.9% iron and which had been oxidized by roasting in the presence of air until substantially all of the iron was converted to the ferric state, the percentage of iron remaining in the ferrous state being as low as about 1.67%. A beneficiated titaniferous iron ore bed was maintained by passing a mixture of titanium tetrachloride and nitrogen in the ratio of about 1 part of titanium tetrachloride to about 1 part nitrogen at the rate of substantially 0.35 foot per second and preheated to substantially 300° C. in an upward flow through the bed, the temperature of which was held at substantially 1050° C. Additional oxidized ore preheated to about 300° C. was added at the rate of about 42 parts per minute, more or less, and the titaniferous residue was withdrawn from the reactor at the rate of about 30 parts per minute, more or less. The residue contained substantially 87.5% titanium dioxide and 6.02% iron oxide, the balance being siliceous gangue and the like.

The reaction proceeded smoothly throughout the run with no evidence of the formation of ferrous chloride, nor was there any evidence of plugging or sintering of the fluid bed.

Example III

2,260 parts, more or less, of finely divided reduced titaniferous iron ore analyzed as comprising 74.1 parts of titanium dioxide, 5.8 parts ferric oxide, and 20.9 parts ferrous oxide was added at the rate of substantially 35 parts per minute to a fluidized bed at a temperature of substantially 875° C. The gas space velocity of the fluidized bed was substantially 0.31 foot per second and was maintained by adding gaseous titanium tetrachloride at the rate of substantially 13.2 parts per minute and gaseous chlorine at the rate of substantially 5 parts per minute, the mixture of gaseous titanium tetrachloride and chlorine being the theoretical amount to react with the given quantity of ore to yield vaporous ferric chloride and titanium dioxide. The run was continued for substantially one hour and twenty minutes under substantially steady state conditions. The titanium residue contained substantially 97.8% titanium dioxide and 3.2 iron oxide, the overall efficiency of the titanium tetrachloride reaction based on iron and other chlorinatable products removed from the reduced ore being substantially 98.2%. It was noted that the reaction could be run successfully at lower temperatures than 875° C. and conversions have been obtained at temperatures as low as 500° C.

By use of the improved and integrated process of this invention, an unusually high conversion of the iron, in a titaniferous iron material, to volatile ferric chloride has

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been obtained with substantially no contamination by titanium values, while the resulting titanium dioxide product has been substantially pure and in a granular form susceptible to chlorination. Moreover, by using the improved and integrated ore treating process of this invention, iron may be separated from raw titaniferous iron ore on a commercial scale with a high degree of efficiency to produce a volatile substantially uncontaminated ferric chloride which is substantially free of carbon or carbon-containing gases and which may be subsequently oxidized, if desired, to produce chlorine for recirculation through additional raw ore; and a stable titanium residue which is substantially pure titanium dioxide and which may be subsequently chlorinated to produce titanium tetrachloride. Furthermore, by the improved process of this invention, titaniferous iron materials in which substantially all of the iron values are in, or have been converted to, the ferric state may be directly chlorinated to form volatile ferric chloride, the constituents being used to their full advantage and with a minimum of handling with the result that the process is characterized by high yields which are substantially free of the unrecoverable losses inherent in processes heretofore known and used.

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 limits of the following claims.

We claim:

1. A method for separating the iron values from the titanium values in a titaniferous iron ore containing both ferrous and ferric iron which comprises treating said ore with an oxidizing agent and titanium tetrachloride in the absence of a reducing agent at a temperature of at least 500° C. to form volatilized ferric chloride and titanium dioxide, said titanium tetrachloride being added in substantially the stoichiometric amount to react with the iron values to form iron chloride and titanium dioxide,

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said oxidizing agent being added in amount to oxidize the ferrous iron values to ferric iron.

2. A method according to claim 1 in which the temperature is from about 850° C. to about 1050° C.

3. Method according to claim 2 in which said oxidizing agent employed is chlorine gas.

4. A method for separating the iron values from the titanium values in a titaniferous iron ore containing both ferrous and ferric iron which comprises forming a fluidized bed of said ore, treating said ore with chlorine gas and titanium tetrachloride in the absence of a reducing agent at a temperature of at least 500° C. to form volatilized ferric chloride and titanium dioxide, said titanium tetrachloride being added through said bed in substantially stoichiometric amount to react with the iron values to form iron chloride and titanium dioxide, said chlorine being added through said bed in an amount to oxidize the ferrous iron values to ferric iron.

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