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68690/87

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COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION ACCEPTED AND ~~AMENDMENTS~~

ALLOWED 3-4-90

CONVENTION APPLICATION FOR A PATENT

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Melbourne

We, E.I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, 19898, United States of America, hereby apply for the grant of a patent for an invention entitled, "SELECTIVE CHLORINATION OF IRON VALUES IN TITANIFEROUS ORES", which is described in the accompanying complete specification.

This application is a Convention Application and is based on the application for a patent or similar protection made in the United States of America on 14 February 1986 numbered 829,231.

Our address for service is: Care of JAMES M. LAWRIE & CO., Patent Attorneys of 72 Willsmere Road, Kew, 3101, Victoria, Australia.

DATED this 20 day of January 1987.

JAMES M. LAWRIE & CO

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11 FEB 1987
Melbourne

By Jeffrey A. Ryder

Patent Attorneys for
E.I. DU PONT DE NEMOURS
AND COMPANY

Forms 7 and 8

CH-1377

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1977

Declaration in Support of an Application for a Patent

(Combined Form – Convention [illegible])

* Strike out for non-convention

In support of the *Convention* application made for a patent [illegible] for an invention entitled SELECTIVE CHLORINATION OF IRON VALUES IN TITANIFEROUS ORES

Insert full name and address of declarant

I, Donald Allen Hoes, Asst. Secretary of the Patent Board of E. I. DU PONT DE NEMOURS AND COMPANY, 2718-A Montchanin Bldg., Wilmington, Delaware 19898, United States of America

do solemnly and sincerely declare as follows:–

1. [illegible]

1. I am authorised by E. I. DU PONT DE NEMOURS AND COMPANY the applicant for the patent [illegible] to make this declaration on its behalf.

Strike out Para. 2. for non-convention

2. The basic application~~(s)~~ as defined by section 141 of the Act was ~~were~~ made in the United States of America

on the 14th day of February 19 86, No. 829,231,

by Hans Hellmut GLAESER and James William REEVES, and

on the .... day of .... 19 ...., No. ....,

by ...., and

on the .... day of .... 19 ...., No. ....,

by ....

3. [illegible]

Insert full name(s) and address(es) of inventor(s)

3. Hans Hellmut GLAESER and James William REEVES

of 11 Meadows Lane, Wilmington, Delaware 19807 and 8 Wollaston Road, Wilmington, Delaware 19803, respectively, United States of America

~~is~~ are the actual inventor(s) of the invention and the facts upon which [illegible] the said Corporation is entitled to make the application are as follows:– **E. I. DU PONT DE NEMOURS AND COMPANY is the assignee of the invention and of the priority right from the said actual inventor(s)**

Strike out Para. 4 for non-convention

4. The basic application~~(s)~~ referred to in paragraph 2 of this Declaration was ~~were~~ the first application~~(s)~~ made in a Convention country in respect of the invention the subject of the application.

DECLARED AT Wilmington, Delaware, U.S.A.

this 7th day of January 19 87.

(12) PATENT ABRIDGMENT **(11)** Document No. **AU-B-68690/87**
(19) AUSTRALIAN PATENT OFFICE **(10)** Acceptance No. **597935**

(54) Title
SELECTIVE CHLORINATION OF IRON VALUES IN TITANIFEROUS ORES

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(56) Prior Art Documents
AU 261207 20507/62 15.6 07.9

(57) Claim

1. A process for removing iron values from titaniferous ores, comprising:

(a) contacting ore to be treated with a reducing atmosphere generated by partial oxidation of a hydrocarbon fuel, at a temperature from 700°C to 1100°C, in a reducing reactor;

(b) continuously cycling a part of the ore being treated from the reducing reactor to a chlorinating reactor, and from the chlorinating reactor to the reducing reactor;

(c) contacting ore in the chlorinating reactor with a molar excess of Cl_2, at a temperature from 600°C to 1000°C, in an atmosphere substantially free of carbon, thereby producing $FeCl_3$ vapor and a TiO_2 beneficiate;

(d) withdrawing the $FeCl_3$ vapor from the chlorinating reactor and

. . . /2

contacting it with oxygen, at a temperature from 500°C to 1200°C, to produce Cl_2 gas and a Fe_2O_3 waste stream;

(e) recycling the Cl_2 gas to the chlorinating reactor; and

(f) withdrawing the resulting TiO_2 beneficiate from the chlorinating reactor.

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Form 10

PATENTS ACT 1952–1973

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

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68690/87

Complete Specification—Lodged:
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Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

TO BE COMPLETED BY APPLICANT

Name of Applicant: E.I. DU PONT DE NEMOURS AND COMPANY., a corporation organised and existing under the laws of the State

Address of Applicant: of Delaware, of Wilmington, Delaware 19898, United States of America.

Actual Inventor: Hans Hellmut Glaeser & James William Reeves

Address for Service: Care of JAMES M. LAWRIE & CO., Patent Attorneys of
72 Willsmere Road, Kew, 3101, Victoria, Australia

Complete Specification for the invention entitled: SELECTIVE CHLORINATION OF IRON VALUES IN TITANIFEROUS ORES

The following statement is a full description of this invention, including the best method of performing it known to me:—*

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*Note: The description is to be typed in double spacing, pica type face, in an area not exceeding 250 mm in depth and 160 mm in width, on tough white paper of good quality and it is to be inserted inside this form.

11710/76-L

C. J. Thompson, Commonwealth Government Printer, Canberra

CH-1377

TITLE

Selective Chlorination of Iron Values in Titaniferous Ores

BACKGROUND OF THE INVENTION

1. Technical Field

The present invention relates to processes for preparing titaniferous ore beneficiates. In particular, the present invention relates to processes for selectively chlorinating iron values in titaniferous ores to provide ferric chloride, which is then oxidized to provide chlorine for recycle and ferric oxide for disposal.

2. Description of the Prior Art

Significant quantities of pigmentary titanium dioxide are produced by chlorination of titaniferous ores, e.g., rutile or ilmenite, to produce titanium tetrachloride ($TiCl_4$), which is subsequently oxidized. In this reaction, coke, chlorine, and a titanium-containing ore are reacted at temperatures ranging from 700° to 1200°C, typically in a fluidized bed reactor. The hot chlorination gases resulting from this reaction contain primarily titanium tetrachloride and iron chloride impurities, namely ferric chloride and ferrous chloride. Generally, iron chlorides are removed from the product stream by condensation.

Removal of iron chlorides from the chlorination gases is a significant problem in production of substantially pure titanium tetrachloride from certain ore feedstocks. Of the most common ore feedstocks, rutile contains about 90-96% titanium dioxide and 1 to 7% iron oxide. Ilmenite and mechanical concentrates of anatase, preferred feedstocks due to cost, contain 40-70% titanium dioxide and 20-60% iron oxide. Thus, iron chlorides make up a considerable portion of chlorination gases in ilmenite-based or anatase-based processes.

Although a portion of this iron chloride by-product stream can be diverted to other uses, a significant proportion must be disposed of by neutralization followed by landfilling or deep-well injection. The costs associated with safe disposal of iron chloride wastes are rising. Moreover, a significant quantity of potentially recoverable chlorine is lost when iron chloride wastes are discarded. These considerations have led to a search for alternative methods of separating iron from titaniferous ores.

Considerable effort has been expended in the development of ore enrichment, or beneficiation, processes, which have the common objective of removing iron values from titaniferous materials prior to the titanium tetrachloride production step.

Since iron reacts more readily with chlorine than titanium, iron values can be removed by selective chlorination followed by ferric chloride volatilization, leaving a titanium-enriched residue. Under appropriate conditions, substantially all iron can be removed before $TiCl_4$ production begins. The resulting beneficiate can then be further chlorinated to produce $TiCl_4$. Optionally, the ore can be oxidized with air at high temperature to convert substantially all iron to Fe_2O_3 prior to carbon-free selective iron chlorination. The processes disclosed by Australian Patent No. 242,474 and Ketteridge, "Chlorination of Ilmenite," <u>Aust. J. Appl. Sci.</u> <u>15</u>:90 (1964) are examples of this approach.

One variation on the selective chlorination approach is disclosed by Australian Patent Specification 10957/53 (Hoechst). In this process, titanium oxide-containing material is fluidized inside a reaction zone heated to 800°C-1300°C with chlorine gas containing at most 30 volume percent inert gas, and the resulting ferric chloride is volatilized and removed, leaving a residue consisting essentially of titanium dioxide. A further variation, disclosed by German Offenlegungsschrift 3,210,729 (Hoechst), involves calcining the titanium oxide-containing material at 870°C to 1300°C, prior to the carbon-free selective chlorination step.

Alternative beneficiation processes involve solid-state reduction of ferric iron (+3) to the ferrous (+2) state, followed by hydrochloric or sulfuric acid leaching. Kahn, "Non-Rutile Feedstocks for the Production of Titanium," J. Metals, July 1984, p. 33, and Chen, U. S. Patent 3,825,419, (Benelite Corporation), disclose use of such processes in preparation of synthetic rutile ore concentrates.

Finally, several references are directed to beneficiation processes which include various combinations of solid state iron reduction and partial chlorination. Daubenspeck, U. S. Patent 2,852,362 (National Lead Company), describes a process in which iron values in titaniferous ores are first reduced to the ferrous state by reaction with a solid or gaseous reducing agent such as finely ground coke or carbon monoxide, at temperatures from 650°C to 1000°C. Second, additional carbon-containing material, for example, finely ground coke or carbon monoxide, is added to the reduced ore product, and the resulting mixture is chlorinated at a temperature from 600°C to 900°C.

Dunn, U. S. Patent 3,699,206, discloses a single-reactor reduction/chlorination process wherein ore is alternately contacted, for short intervals under fluidizing conditions, with carbon monoxide and chlorine in a gas-solids reactor. Dunn, U. S. Patent 3,713,781, discloses a cross-flow fluid bed reactor for ore beneficiation, which permits alternate contacting of a moving fluid bed with carbon monoxide and chlorine.

Fukushima, "Mitsubishi Process for Upgrading Ilmenite and Chlorine Recirculation," in TMS-AIME Publication No. A74-48 (1974) describes an ore beneficiation process involving the following steps. First, ilmenite ore is heated under oxidizing conditions, producing rutile and pseudobrookite. Second, coke is added to the pre-oxidized ore in a fluidized bed, and reacted with chlorine at a temperature of at least 900°C, selectively chlorinating iron values to ferric chloride, which is removed as vapor. The resulting beneficiate material can then be subjected to magnetic separation and flotation processes to recover synthetic rutile for further processing. Ferric chloride produced in the selective chlorination step is reacted with oxygen at high temperatures. Ferric oxide and an off-gas mixture of chlorine and carbon dioxide result, from which chlorine can be recovered for recycle via a liquefaction step. U. S. Patent 3,803,287, U. K. Patent 1,471,198, and Japanese Patent Publication 58-39895 (all Mitsubishi Metals K.K.) are directed to various aspects of the foregoing process.

Technical difficulties such as bed defluidization, loss of $TiCl_4$, incomplete Cl_2 conversion, and unfavorable thermal balance associated with carbon-free chlorination have prevented commercialization of the above-described chlorination processes. Moreover, facilities for liquefaction of chlorine or condensation and revaporization of ferric chloride involve high levels of capital investment. Although reduction/acid leaching processes have been commercialized, their economies of operation are largely dependent upon inexpensive sources of acid for leaching. Furthermore, the foregoing processes largely do not address environmental considerations relating to disposal of ferric chloride or acid leachates.

SUMMARY OF THE INVENTION

The present invention provides a process for removing iron values from titaniferous ores, comprising:

(a) contacting ore to be treated with a reducing atmosphere generated by partial oxidation of a hydrocarbon fuel, at a temperature from about 700°C to about 1100°C, in a reducing reactor;

(b) continuously cycling a part of the ore being treated from the reducing reactor to a chlorinating reactor, and from the chlorinating reactor to the reducing reactor;

(c) contacting ore in the chlorinating reactor with a molar excess of Cl_2, at a temperature from about 600°C to about 1000°C, in an atmosphere substantially free of carbon, thereby producing $FeCl_3$ vapor and a TiO_2 beneficiate;

(d) withdrawing the $FeCl_3$ vapor from the chlorinating reactor and contacting it with oxygen, at a temperature from about 500°C to about 1200°C, to produce Cl_2 gas and a Fe_2O_3 waste stream;

(e) recycling Cl_2 gas to the chlorinating reactor; and

(f) withdrawing the resulting TiO_2 beneficiate from the chlorinating reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram depicting process flows involved in a preferred embodiment of the present invention.

FIGS. 2-4 are provided as an aid in understanding the disclosure of Examples 1 and 2 and comparison A. FIG. 2 illustrates process flows involved a process of the present invention wherein iron is prereduced to ferrous iron prior to selective chlorination, while FIG. 3 illustrates flows where iron is prereduced to 50% elemental iron prior to selective chlorination. FIG. 4 illustrates flows involved in a comparison process wherein ore is heated but not reduced prior to selective chlorination.

Each drawing is discussed in additional detail below.

DETAILED DESCRIPTION OF THE INVENTION

In a generalized aspect, the present invention provides a process involving selective chlorination of ferrous iron in ilmenite or anatase. The process is characterized by the elimination of carbon from the reaction wherein the reduced ore is chlorinated. In this process, iron in the ferric, or Fe^{3+}, state, in titaniferous ores is first reduced to the ferrous, or Fe^{2+}, state, with gaseous reductants (i.e., hydrocarbons, H_2, and CO), and then selectively chlorinated in a second reaction vessel, providing essentially complete Cl_2 conversion and negligible loss of titanium values. The resulting carbon-free $FeCl_3$ stream is then oxidized to recyclable Cl_2 without prior condensation of $FeCl_3$ or subsequent liquefaction of Cl_2. A continuous recycle stream between the ore reduction and chlorination stages is maintained to allow essentially complete iron removal.

Reduction of ferric iron in ilmenite to ferrous iron is accomplished by contacting ore with a reducing atmosphere comprising one or more constituents selected from the group consisting of hydrocarbons, CO, and H_2, at a temperature from about 700°C to about 1100°C. Preferably, reduction temperatures are maintained from about 800°C to about 1000°C. In a preferred aspect, the reducing atmosphere is generated from combustion of fuel oil in the presence of air, since this method also serves to heat the ore being treated to reduction temperature. Alternatively, methane or natural gas combustion can supply the required reducing atmosphere. Preferably, reduction is carried out using ore of a particle size which allows fluidization (e.g., < 500 microns diameter).

The present invention contemplates two modes of prereduction. In the first, or preferred mode, substantially all iron values are prereduced to the ferrous state. In this mode, exit gases from the reduction reactor (or zone) are monitored and flows of hydrocarbons and air controlled to provide an exit gas mixture having a molar ratio of CO_2 and H_2O to other constituents within the range 0.1 to 0.95. This exit gas molar ratio is calculated as follows:

$$\frac{[CO_2] + [H_2O]}{[CO_2] + [H_2O] + [CO] + [H_2].}$$

In the second comtemplated prereduction mode, the recycle rate between the chlorinating and reducing reactors (or zones) ~~zones~~ is set to remove all oxygen during reduction, rather than by displacement with chlorine, in order to provide a prereduced product comprising iron in the ferrous state and iron in the metallic state.

The resulting reduced ore is then fed into a second fluidized bed reactor, where exothermic chlorination occurs with essentially complete Cl_2 conversion, in accordance with the following equation:

I: $3\ FeO + xTiO_2 + 1\text{-}1/2\ Cl_2 \rightarrow FeCl_3 + Fe_2O_3 + xTiO_2$

The foregoing chlorination reaction provides superior results to the following endothermic reaction which is known to be incomplete, providing less than 30 per cent Cl_2 conversion at 1000°C, and diminishing conversion with decreasing temperature:

II: $Fe_2O_3 + xTiO_2 + 3\ Cl_2 \rightleftarrows 2\ FeCl_3 + xTiO_2 + 1\text{-}1/2\ O_2$

Chlorination is conducted at temperatures from about 600°C to about 1000°C, preferably from about 700°C to about 900°C. Most preferably, ore is selectively chlorinated at about 750°C to about 850°C. Chlorination is most effectively accomplished under fluidizing conditions. Carbon-containing materials are substantially excluded from the chlorination reactor to prevent loss of $TiCl_4$.

Since the reaction of equation (I), above, removes only about one-third of the iron in ilmenite as volatile $FeCl_3$, and since it generates Fe_2O_3, this is recycled to the reduction stage for additional oxygen removal. The size of the recycle stream must be sufficiently large to maintain a low iron content so that a TiO_2 beneficiate with low iron content can tbe withdrawn from the chlorination stage. Techniques for recycling of fluidizable solids between two fluidized beds, without mechanical valving, are known.

The resulting stream of ferric chloride vapor exiting the chlorinator is contacted with oxygen at a temperature from about 500°C to about 1200°C, preferably from about 900°C to about 1100°C, to provide a gas/solids stream containing Cl_2 and Fe_2O_3. This stream is flue-cooled, optionally with added scrub solids in the form of sand, and then separated in cyclone separators to provide a waste stream of solid Fe_2O_3, which is environmentally suitable for landfilling. The remaining stream of Cl_2 can then be recycled to the chlorinator.

Optionally, this ferric chloride oxidation step can be conducted according to the process disclosed by Reeves et al., U. S. Patent 4,174,381 (Du Pont).

The cyclic process of the present invention overcomes inefficient Cl_2 conversion and the requirement for external heating necessitated by chlorination of iron in unreduced ore. In contrast to selective iron chlorination with coke as a reductant, the process of the present invention provides a $FeCl_3$ vapor stream containing substantially no carbon oxide. Hence the

$FeCl_3$ can be oxidized to recyclable Cl_2 without condensation of $FeCl_3$ prior to its oxidation and also without subsequent Cl_2 liquefaction for removal of carbon oxide from the recycle stream. In addition, coke-free iron chlorination is extremely selective, avoiding essentially all $TiCl_4$ loss.

The process of the present invention results in production of essentially all $FeCl_3$. Therefore, process control problems attributable to $FeCl_2$ formation are avoided. $FeCl_2$ is higher boiling than $FeCl_3$, and therefore tends to condense in liquid form, interfering with fluidization.

Selective chlorination can be carried out at temperatures below those required for selective chlorination processes requiring in situ reduction with coke. This aspect of the present invention is particularly important in chlorination of Brazilian anatase, which contains significant concentrations of both iron and calcium. The process of this invention permits chlorination at temperatures below 781°C, the melting point of $CaCl_2$. Thus, waste $CaCl_2$ forms a fluidizable solid which can be removed from beneficiates by water leaching.

Referring now to FIG. 1, a flowchart is provided which depicts process flows involved in one embodiment of the present invention.

Titaniferous ore, which can be, for example, ilmenite or a titanium-bearing carbonatite such as Brazilian anatase, is comminuted to a particle size suitable for fluidization and introduced to fluidization reactor 4 via inlet 1. Air is introduced via manifold 3, to reactor 4, where it is mixed with heavy fuel oil, which is introduced into reactor 4 via inlet 2. This fuel/air mixture is ignited, and the resulting combustion reaction is balanced by regulation of fuel and air inputs to provide an internal temperature in reactor 4 of about 900°C.

Within reactor 4, ore to be treated is contacted with a mixture of CO_2 and CO that exits reactor 4 in a molar ratio of about 10:1. Excess gases are vented from reactor 4 by outlet 5. An exit stream 6 of reduced ore, comprising FeO and TiO_2, is continuously cycled from reduction reactor 4 to chlorinator 7, where it is contacted with Cl_2 gas at a temperature from about 700°C to about 800°C. A recycle stream 10 of partially chlorinated material is continously fed back to reduction reactor 4, where it is again contacted with a reducing atmosphere. A product stream of beneficiated ore is removed from chlorinator 7 via outlet 19.

A vapor flow 9 of $FeCl_3$ gas exits chlorinator 7 and is routed to oxidizer 12, where it is contacted at about 700°C to about 800°C with oxygen provided to oxidizer 12 via inlet 11. The resulting stream of Fe_2O_3 and Cl_2 exiting oxidizer 12 is mixed with scrub solids, for example, sand, provided from mixer 13, and then cooled in flue network 14 before gas/solids separation in cyclones 15. The resulting stream of cooled, inert Fe_2O_3 is discharged from cyclones 15 at outlet 16 and landfilled. The flow of Cl_2 gas exiting cyclones 15 is routed via conduit 17 to recycle blower 18, from which it is recycled to chlorinator 7 via inlet 8.

The following examples illustrate particular aspects of the present invention.

Examples 1 and 2 illustrate pilot plant-scale operation of processes involving preduction to ferrous iron or, in the case of Example 2, a mixture of ferrous and metallic iron, followed by chlorination. Comparison A illustrates a comparative process in which ferric iron is chlorinated. The following advantages are illustrated by comparison of Examples 1 and 2 with

Comparison A. First, 100% Cl_2 conversions are possible. Second, recycle of large quantities of ore heated nearly to a "sticking" temperature are avoided. Third, costly, high temperature reduction to elemental iron is avoided. Fourth, high reducing gas conversion is possible, avoiding recycle. Fifth, a single-stage reducer-preheater can be employed. Finally, direct $FeCl_3$ feed to oxidation is feasible, avoiding the need for costly condensation and revaporization apparatus.

Example 3 provides calculated equilibrium conversions for chlorination of reduced and unreduced ilmenite ore. Examples 4-7 report the results of laboratory-scale chlorination experiments involving reduced and unreduced samples of Florida ilmenite and Brazilian anatase.

In the examples, all degrees reported are Celsius (°C), and all parts and percentages are by weight unless otherwise indicated.

Example 1

Referring now to FIG. 2, a flowsheet is provided which indicates material flows involved in a process wherein ilmenite or other ore is preheated and iron values reduced to the ferrous state prior to selective chlorination.

Ore provided via inlet 1 is preheated and prereduced in a single stage fluid bed 10, by contact with combustion products derived from partial oxidation of a hydrocarbon fuel (fuel oil and CH_4 are contemplated). The resulting reduced ore, at a temperature of 1000°, is standpipe fed via stream 5 to a fluid bed chlorinator 11 at 1000°, where it is contacted with Cl_2 provided via inlet 7. Approximately 90% of iron values are removed as $FeCl_3$ vapor via outlet 9, and beneficiated ore concentrate is constantly withdrawn at outlet 8. A portion of the fluid bed is continuously recycled to preheater/reducer 10 via lift line 6. This recycle stream contains ferric iron that is again reduced. This recycle stream should be approximately 17 times the magnitude of the ore feed rate in order to remove all oxygen in the reduction step and achieve 90% iron chlorination.

A material balance for the numbered process streams indicated in FIG. 2 appears below. All indicated values refer to units of lb.-mols/hr.

Stream:	1	2	3	4	5	6	7	8	9
TiO_2	0.75				13.50	12.75		0.75	
Fe_2O_3	0.231					0.391		0.023	
FeO					1.244				
CH_4		0.450							
O_2			0.577						
CO				0.041					
CO_2				0.409					
H_2O				0.918					
H_2				0.082					
N_2			2.308						
Cl_2							0.624		
$FeCl_3$									0.416
Temp.($^{\circ}$)	25	25	25	500	1000	1000	25	1000	1000

Example 2

In FIG. 3, a flowsheet is provided which indicates material flows involved in a process wherein ilmenite or other ore is preheated and iron values reduced to a mixture of 50% elemental iron and 50% ferrous iron with H_2 prior to selective chlorination.

Ore is preheated to 500° in a preheat furnace (not shown) and fed via inlet 1 to a three-stage counter-current H_2 reduction fluid bed reactor 10. Iron is reduced to 50% ferrous iron and 50% elemental iron. Full reduction to elemental iron is not shown because recycle between the chlorinator 11 and reducer 10 is necessary for an adequate thermal balance. This allows all oxygen removal in prereduction even in the iron is not all metallized. Equilibrium H_2 conversion in the 800° reducer 10 is estimated at 10%. Gas exiting via outlet 4 is heat-exchanged with inlet gas (2) in exchanger 12, is cooled to remove water at 13, recompressed at 14 and reheated via heat exchanger 12 and preheater 15 prior to recycle to reducer 10.

The recycle ore rate (6) is estimated at 3.5 times the feed rate in order to exchange heat from the exothermic chlorination and the endothermic reduction. The chlorinator 11 operates at 1000° with 100% Cl_2 conversion and 90% iron conversion, analogous to the process of Example 1.

A material balance for the numbered process streams indicated in FIG. 3 appears below. All indicated values refer to units of lb.-mols/hr.

Stream:	1	2	3	4	5	6	7	8	9
TiO_2	0.75				3.33	2.58		0.75	
Fe_2O_3	0.231					0.079		0.023	
FeO					0.31				
Fe					0.31				
N_2									
CO									
CO_2									
Cl_2							0.624		
$FeCl_3$									0.416
H_2		0.621		5.59					
H_2O			0.621	0.621					
Temp(°):	500	800	5	800	800	1000	25	1000	1000

Comparison A

In FIG. 4, a flowsheet is provided indicating material flows involved in a conventional process wherein ilmenite or other ore is preheated without reduction of iron values prior to selective chlorination.

Ore provided to fluid bed roaster 10 via inlet 1 is preheated by combustion of a hydrocarbon fuel (2) in air (3). The preheated ore is fed via line 5 to a fluid bed chlorinator 11 at 1000°, where 90% iron conversion is achieved at an estimated Cl_2 conversion of 20%. A recycle 6 of 45 times the ore feed rate is necessary to maintain the 1000° chlorinator temperature while operating the preheater at the 1100° maximum temperature. This case requires condensation of iron chloride for Cl_2 separation before ferric chloride oxidation. Liquefaction of Cl_2 would be necessary to remove O_2. In contrast, pure $FeCl_3$ can be fed directly to an oxidizer in the processes described in Examples 1 and 2.

A material balance for the numbered process streams indicated in FIG. 4 appears below. All indicated values refer to units of lb.-mols/hr.

Stream:	1	2	3	4	5	6	7	8	9
TiO_2	0.75				34.8	33.6		0.75	
Fe_2O_3	0.231				1.26	1.24		0.023	
O_2			1.04						0.31
N_2			4.16	4.16					
CO_2				0.52					
Cl_2							3.12		2.50
$FeCl_3$									0.416
H_2O				1.04					
CH_4		0.52							
Temp(°):	25	25	25	1100	1100	1000	25	1000	1000

Example 3

Table 1, below, provides molar equilibrium concentrations calculated for the reaction between chlorine and prereduced ilmenite ore ($FeO \cdot TiO_2$), as well as the reaction between chlorine and unreduced ilmenite ore ($Fe_2O_3 \cdot TiO_2$). Reduction of $FeO \cdot TiO_2$ can occur, for example, at 800-1000°, over a wide range of CO and CO_2 concentrations, in a suitable reactor.

The results presented in Table 1 indicate that reaction of prereduced ilmenite with Cl_2 results in essentially complete Cl_2 conversion; no unreacted Cl_2 needs to be recycled. All Cl_2 is converted to iron chloride and only negligible concentrations of $TiCl_4$ are formed. In contrast, where unreduced ilmenite ore is reacted with Cl_2, Cl_2 conversion is limited and highly temperature-dependent. At 600°, essentially no conversion is predicted, while 20% conversion is predicted at 1000°. Chlorination of unreduced ilmenite ore is hindered not only by incomplete Cl_2 conversion, but also by a highly endothermic heat of reaction when compared to chlorination of prereduced ilmenite. Therefore, superheating of reactant Cl_2 or external heating of the reaction vessel is required to chlorinate unreduced ore. These additional energy inputs are not required to chlorinate prereduced ilmenite.

Chlorine conversion with reduced ilmenite ore is essentially complete according to the following equation:

$$3\ FeO + xTiO_2 + 1\ 1/2\ Cl_2 \text{ --> } FeCl_3 + Fe_2O_3 + xTiO_2.$$

However, only about one-third of the FeO in the reduced ilmenite ore is converted to $FeCl_3$ during the first reaction path since about two-thirds of the FeO is converted into Fe_2O_3 which is difficult to react with Cl_2. Recirculation of $Fe_2O_3 \cdot TiO_2$ to the reduction stage results in continuing reduction and chlorination until essentially all iron values are removed as $FeCl_3$ and a rutile beneficiate is obtained.

Table 1: Calculated Equilibrium Conversion of Cl_2 with Prereduced and Unreduced Ilmenite

(Products in mols at reaction temperature)

Reaction	$3\ FeO \cdot TiO_2 + 1.5\ Cl_2$			$Fe_2O_3 \cdot TiO_2 + 3.0\ Cl_2$		
Temp.:	600°	800°	1000°	600°	800°	1000°
Products:						
$Fe_2O_3 \cdot TiO_2$	1.00	1.00	1.00	0.994	0.950	0.796
TiO_2	2.00	1.99	1.99	0.01	0.05	0.20
$FeCl_3(g)$	0.088	0.445	0.740	0.009	0.093	0.377
$Fe_2Cl_6(g)$	0.450	0.260	0.524	0.001	0.003	0.005
$FeCl_2(s)$	0.010	0.00	0.00	0.00	0.00	0.00
$FeCl_2(g)$	<0.001	0.023	0.134	<0.001	<0.001	0.21
$TiCl_4$	<0.001	0.003	0.003	<0.001	<0.001	0.001
Cl_2	0.005	0.015	0.075	2.98	2.85	2.40
O_2	0.00	0.00	0.00	0.008	0.075	0.306
Cl_2 Conversion (%):	99.7	99.0	95.0	0.67	5.00	20.0

Example 4

A laboratory scale fluidization reactor was constructed, consisting of a silica tube fitted with a fritted silica disc, gas inlet and exit orifices, heating means, and means for introducing N_2 and Cl_2 gas to the tube at measured rates. The exit orifice was connected in gas-tight relation to a cold trap, which was connected in series to two Cl_2 gas traps, each containing a measured quantity of 12.5% KI solution.

100 g Florida ilmenite, analyzing 64.8% TiO_2, 27.7% Fe_2O_3, and 2.1% FeO, were placed in the reactor and heated to 800^{o} in a stream of flowing N_2 gas. When the sample reached reaction temperature, gas flow to the reactor was switched to Cl_2 at 0.92 L/min. The silica tube was mechanically vibrated to ensure mixing of the solid reactor charge. Unreacted Cl_2 in the exit gas was

adsorbed in the KI traps, and unreacted, adsorbed Cl_2 was then determined by titration with 0.1N $Na_2S_2O_3$.

The foregoing procedure was repeated with the same ore following reduction at 900° in a stream of 2.3 L/min CO and 0.2 L/min CO_2. Under the latter conditions, Fe_2O_3 in ilmenite is reduced to $FeO \cdot TiO_2$, but not to metallic iron. As with the unreduced ore sample, unreacted Cl_2 in the exit gas was adsorbed in KI solution and subsequently titrated with 0.1N $Na_2S_2O_3$ solution.

The results obtained were dependent upon the oxidation state of the iron values in each sample. After 10 minutes reaction time with prereduced ore, 0.016 mols unreacted Cl_2 were detected in the gas adsorbers. Moreover, at the onset of each reaction, the flow of residual N_2 gas out of the reaction vessel (which was monitored using a gas bubbler at the reactor exit) ceased for at least 4 minutes. In addition, reduced pressure inside the reactor was observed upon contact with Cl_2, and copious amounts of $FeCl_3$ condensed on cold surfaces at the reactor outlet and in an empty trap located ahead of the gas adsorber.

When unreduced ore was tested under substantially similar conditions, 0.191 mols Cl_2 were detected in the gas adsorbers. In contrast to the experiments involving prereduced ore, gas flow did not stop upon switchover to Cl_2, and observed amounts of condensed $FeCl_3$ were minor.

The difference of 0.175 mols unreacted Cl_2 between experiments approximates the stoichimetric amount of Cl_2 required to convert 100 g prereduced ilmenite according to the following equation:

(1) $3\ FeO \cdot TiO_2 + 1\ 1/2\ Cl_2 \text{ --> } Fe_2O_3 \cdot 3\ TiO_2 + FeCl_3$.

After the initial reaction period of 10 minutes, unreacted Cl_2 was equal to 5-10% of the Cl_2 reactant with both unreduced and reduced Florida ilmenite. This relatively minor Cl_2 conversion can be explained by the following incomplete reaction:

(2) $Fe_2O_3 \cdot 3TiO_2 + 3\ Cl_2 \rightarrow 3\ TiO_2 + 2\ FeCl_3$

This experiment indicates that Cl_2 conversion with prereduced ilmenite is complete until essentially all $FeO \cdot TiO_2$ is consumed.

Example 5

In this experiment, ilmenite ore was added to a preheated silica tube in a continuous stream of Cl_2. 100 g Florida ilmenite, having the same composition as the sample described in Example 4, was air-roasted for 1 hour at 800°. A silica tube reactor similar to that described in Example 4 was heated to 800°, and the reactor and exit gas line were filled with Cl_2 gas by feeding Cl_2 at a flow rate of about 0.5 L/min. The air-roasted ilmenite sample was then added to the reactor. As in Example 4, the tube was mechanically vibrated, and KI traps were employed to permit observation of the initial flow-through of unreacted Cl_2 and subsequent determination of the quantity of unreacted Cl_2. This procedure was repeated using 100 g Florida ilmenite ore which had been prereduced by heating to 900° for 1 hour in a stream of 2.3 L/min CO and 0.2 L/min CO_2. The prereduced ilmenite was employed in two trials. In one experiment, it was fed into the Cl_2-filled silica reactor after preheating it to 600°; in a second experiment, it was first preheated to 800°.

Upon addition of unreduced ilmenite at 800°, Cl_2 flow did not cease, but was reduced by about 5-10% due to the presumed reaction between Cl_2 and Fe_2O_3 as described in equation (2) of Example 4, above. When prereduced ilmenite was added to the reactor at 600°, Cl_2 flow completely ceased for about 8 minutes; at 800°, Cl_2 flow ceased for about 10 minutes. After this initial period, Cl_2 flow rapidly increased to a level approximating the feed rate. At 600°, Cl_2 flow was 1-3% below the feed rate. At 800°, Cl_2 flow was 5-10% below the feed rate, similar to the result obtained using unreduced ilmenite.

Cl_2 consumption with prereduced ilmenite at 600° or at 800°, during the initial period when no unreacted Cl_2 was observed, approximated stoichiometrically calculated consumption, within allowances for experimental error. Such error can be attributed to slight variations in Cl_2 feed rate, Cl_2 escape from the reaction apparatus when ilmenite samples were added, and/or possible Cl_2 consumption in reactions involving minor ore constituents, e.g., alkali earth elements. The results obtained indicated that Cl_2 conversion with prereduced ilmenite was complete in less than 4 seconds at temperatures as low as 600°, while Cl_2 conversion was highly incomplete at 800° with unreduced air-roasted ilmenite.

Example 6

In a series of experiments similar to those described in Example 5, above, samples of reduced and unreduced Brazilian anatase ore were reacted with flowing Cl_2 in a silica tube reactor. The Brazilian anatase sample employed analyzed as 55.4% TiO_2, 24.3% Fe_2O_3, 4.8% P_2O_5, 4.4% Al_2O_3, 1.6% CaO, and lesser quantities of minor constituents.

100 g of unreduced Brazilian ore was fed to a mechanically vibrated silica tube preheated to 600°, while a continuous flow of Cl_2 was maintained at about 0.28 L/min. As previously described, unreacted Cl_2 exiting the reactor was assayed by KI adsorption and titration with 0.1N $Na_2S_2O_3$. This procedure was repeated using ore prereduced by reaction for one hour at 900° in a stream of 2.3 L/min CO and 0.2 L/min CO_2.

Essentially no cessation of gas flow was observed when unreduced ore was added to the reactor. Cl_2 flow was initially reduced about 14%, but gradually increased to within 2-5% of the feed rate. In contrast, when reduced ore was fed to the reactor under similar conditions, Cl_2 flow essentially ceased for about 10 minutes before increasing to less than 2% of feed rate after 15 minutes. Again, calculation indicated that Cl_2 consumption approximated stoichiometric amounts when prereduced ore was reacted.

The efficient low temperature (600^{o}) iron chlorination observed suggests that this process is particularly useful for exploitation of Brazilian anatase, which contains sufficient CaO to interfere with TiO_2 chlorination at higher temperatures due to formation of liquid $CaCl_2$. Previous studies have indicated formation of solid $CaCl_2$ at 600^{o}, well below the melting point of $CaCl_2$ at 781^{o}. Thus, $CaCl_2$ can be removed from anatase-derived TiO_2 beneficiates after selective iron chlorination by simple water leaching.

The claims defining the invention are as follows:-

1. A process for removing iron values from titaniferous ores, comprising:

(a) contacting ore to be treated with a reducing atmosphere generated by partial oxidation of a hydrocarbon fuel, at a temperature from 700°C to 1100°C, in a reducing reactor;

(b) continuously cycling a part of the ore being treated from the reducing reactor to a chlorinating reactor, and from the chlorinating reactor to the reducing reactor;

(c) contacting ore in the chlorinating reactor with a molar excess of Cl_2, at a temperature from 600°C to 1000°C, in an atmosphere substantially free of carbon, thereby producing $FeCl_3$ vapor and a TiO_2 beneficiate;

(d) withdrawing the $FeCl_3$ vapor from the chlorinating reactor and contacting it with oxygen, at a temperature from 500°C to 1200°C, to produce Cl_2 gas and a Fe_2O_3 waste stream;

(e) recycling the Cl_2 gas to the chlorinating reactor; and

(f) withdrawing the resulting TiO_2 beneficiate from the chlorinating reactor.

2. A process according to claim 1, wherein the reducing reactor and chlorinating reactor are maintained under fluidizing conditions.

3. A process according to claim 2, wherein the reducing atmosphere contains CO, CO_2, H_2, and hydrocarbons provided to the reducing reactor by combustion of fuel oil and air.

4. A process according to claim 2, wherein contains CO, CO_2, H_2, and hydrocarbons provided to the reducing reactor by combustion of methane or natural gas and air.

5. A process according to claim 2, wherein ore is contacted with the

reducing atmosphere at a temperature from 800°C to 1000°C.

6. A process according to claim 2, wherein substantially all iron values are reduced to the ferrous state prior to chlorination.

7. A process according to claim 4, wherein reducing conditions are controlled to provide an exit gas mixture having of molar ratio of CO_2 and H_2O to CO_2, H_2O, CO, and H_2 from 0.10 to 0.95.

8. A process according to claim 2, wherein iron values are reduced to a mixture of metallic iron and ferrous iron.

9. A process according to claim 8, wherein substantially all oxygen is removed from ore in gases exiting the reducing reactor.

10. A process according to claim 2, wherein ore is contacted with chlorine at a temperature from 700°C to 1000°C.

11. A process according to claim 2, wherein the ore to be treated is ilmenite.

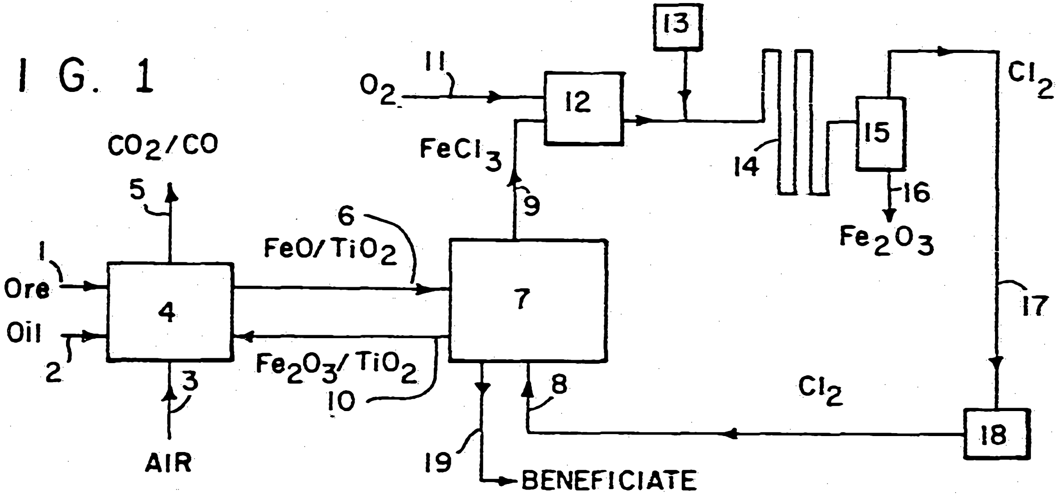
12. A process according to claim 2, wherein the ore to be treated is anatase.

13. Titanium oxide whenever prepared by a process as claimed in any one of the preceding claims.

DATED this 26 day of March 1990.

E.I. DU PONT DE NEMOURS & COMPANY
By Their Patent Attorneys:
CALLINAN LAWRIE

F I G. 1



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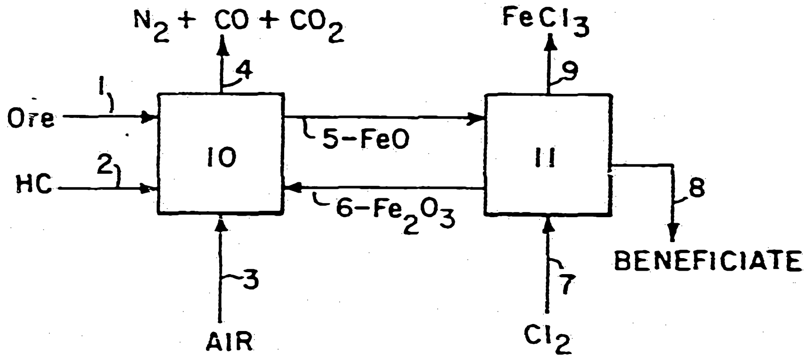

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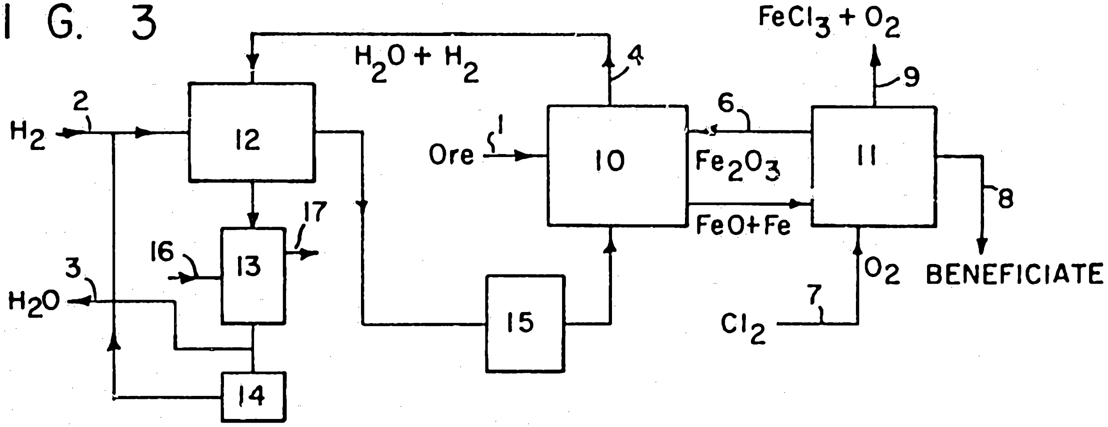
F I G. 3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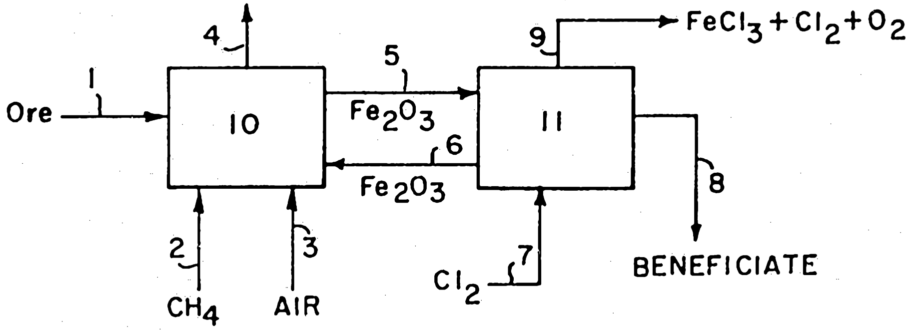
F I G. 4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Cl2
BENEFICIATE
CH4
AIR