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(54) **Chlorination of titaniferous ore using porous carbon.**

(57) A process for chlorinating titaniferous materials using a treated porous carbon preferably derived from anthracite coal is described. Substantial chlorination can be achieved at temperatures as low as 600°C. In addition, other embodiments provide an effective method for removing vanadium impurities from the chlorinated product.

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CHLORINATION OF TITANIFEROUS ORE USING POROUS CARBON

BACKGROUND OF THE INVENTION

This invention relates to the chlorination of titaniferous materials using porous carbon reductants.

Titaniferous materials are often subjected to chlorination as chlorination is an efficient and economical way to obtain a high purity source of titanium for making titanium alloys, titanium compounds, and especially pigmentary titanium dioxide. Several processes have been described in the art for the chlorination of titaniferous materials. Such processes generally react a titanium-containing raw material such as rutile ore or ilmenite ore, with a chlorine-providing material and a carbon reductant at an elevated temperature according to one or both of the following equations:

$$TiO_2 + 2Cl_2(g) + C(s) \rightarrow TiCl_4(g) + CO_2(g)$$

$$TiO_2 + 2Cl_2(g) + 2C(s) \rightarrow TiCl_4(g) + 2CO(g)$$

Conventional chlorination reactions are generally carried out at about 1000°C., but can be carried out at any temperature in the range from about 800°C. to about 2000°C., using various carbon reductants and chlorine sources. Low-temperature chlorination, i.e., at a temperature below 800°C., has also been suggested. To achieve chlorination at the lower temperatures, a very reactive chlorine source, pre-agglomeration of reactants or other techniques have been suggested. Other chlorination processes have also been suggested to reduce or eliminate the chlorination of impurities commonly found in titaniferous raw materials and thereby improve the efficiency or economy of the process.

The carbon reductants utilized by the various processes are from divergent sources such as coal, coke, charcoal, and carbon-containing gases, and the particle size of the carbon typically is determined by other process parameters or desired economic conditions. However, contrary to the teachings of the prior art which place little emphasis on the carbon reductant, it has now been found that the carbon used in the chlorination of a titaniferous material can have a substantial effect on the completeness of said chlorination reaction and under some conditions render the vanadium impurities readily separable from the chlorinated product. Further, it has now been found that fluidized bed techniques can be effectively used in low temperature chlorination of granular titaniferous materials without the use of heretofore required fine grinding, preagglomeration of titaniferous material and carbon reductant, or resorting to highly reactive chlorine sources such as NOCl. Additionally it has been found that powdered titaniferous materials can be chlorinated in economic fashion in a downflow reactor and still further that other chlorination processes such as the laminar flow chlorination process described in U.S. Patent 4,138,899 can be greatly enhanced by using a porous carbon having micropores with a pore diameter of less than 20 Å as the carbon reductant in such processes.

One embodiment of the present invention is to chlorinate titanium-containing materials and ores in a fluid bed at a temperature of at least about 600°C. using a porous carbon reductant.

A second embodiment of the present invention is to chlorinate powdered titanium-containing materials and ores in a down-flow chlorination reactor.

A third embodiment of the present invention is to chlorinate titanium- and iron-containing materials and ores producing titanium chlorides and by-products metallic iron in a laminar flow process.

Additionally, an object and advantage of the present invention is that the present chlorination process can be more selective relative to impurity oxides in the materials and ores being chlorinated resulting in greater reactor efficiency and ease of operation due to the absence of normally liquid or sticky chlorides produced during high-temperature chlorination processes which adhere to reactor surfaces.

A still further object and advantage of the present invention is that vanadium impurities in the titanium-containing reactants can be rendered readily separable from the titanium-containing products if the reaction temperature is maintained at greater than about 800°C.

These and other objects and advantages of the present invention will become more apparent from the detailed description of the invention.

SUMMARY OF THE INVENTION

The present invention is a process for the chlorination of titaniferous materials. A mixture of titaniferous material and porous carbon reductant having internal surface due to micropores of less than 20 Å is reacted with a chlorine-providing material in a chlorination reaction zone at a temperature of at least about 600°C. The present process has been found effective and efficient for substantially chlorinating the titanium values of most titanium-bearing ores. Additionally, at temperatures greater than about 800°C. vanadium impurities in the titanium-containing materials can be rendered readily separable from the titanium-containing products.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is a chlorination process.

Porous carbon reductants useful in the present invention contain micropores having a pore diameter of less than about 20 Å. Typically such porous carbon reductants will have at least about $10 m^2/g$. of surface area in such micropores, advantageously at least about $100 m^2/g$. of surface area in such micropores and preferably about $500 m^2/g$. of such internal surface. Non-porous carbons and carbons having exclusively large pores, e.g. charcoal, are not useful in the present process. In addition the preferred carbons used in the present invention have less than about $1500m^2/g$ internal surface area and preferably less than about $1000m^2/g$ of internal surface area in said micropores.

The carbon particles can be any size useful in a chlorination process. For example, in a fluidized bed process such particles must be small enough to be fluidized by the fluidizing gas and yet be large enough such that they are not carried out of the fluid bed by the off-gas stream. Granular materials of about -8 mesh are typical. However, the average particle size can range from about 4 mesh to about 200 mesh and be useful in a fluid-bed process. Preferably the carbon particles will have an average particle size greater than about 100 mesh and will be substantially retained on a 140-mesh screen. In a down-flow process the carbon particles must be small enough to fall at a rate similar to the titaniferous material particles, such rate of fall being sufficiently slow to allow an adequate time within the reactor for chlorination to take place. Powdered materials of about -200 mesh are generally adequate here; however, various sizes, generally -140 mesh and finer, may be useful. In a laminar flow process the carbon particles must also be appropriately sized; however, in this case they must be so sized as to pass through the chlorination reactor in substantially laminar flow with the titaniferous material. Suitable materials are predominantly less than about 40 microns and substantially all will pass through a 325-mesh sieve.

A preferred high surface area carbon is a appropriately sized coal treated to increase its internal surface area by making it porous. Coal is an inexpensive source of carbon and can be obtained relatively free of undesirable impurities. It is readily available in various sizes and size distribution useful in the present invention. Coal is also an amorphous form or carbon and this attribute has been found to be advantageous in the present invention.

The titaniferous material useful in the present invention can be any titanium-containing compound or raw material such as rutile ore, ilmenite ore, or other. A particularly advantageous embodiment of the present invention is that the present chlorination process can be carried out at low temperature in a fluid-bed utilizing naturally occurring titanium-bearing sand such as naturally occurring sand-size rutile ore exemplified by certain Australian beach sands. Such sand-sized rutile ore is typically -40 mesh and +140 mesh. However, titaniferous materials having various particle sizes can be used in this and other embodiments of the present invention. Typically the titaniferous material will be similarly sized to the carbon reductant with which it reacts. Various sizes from about -4 mesh to about -325 mesh can be useful. In addition, the titaniferous material can be substantially pure or contain a wide variety of impurities.

For practical and economic operation of the fluid-bed embodiments of the present invention the titaniferous material should contain at least about 90% TiO_2; however, other embodiments will operate with lesser amounts of TiO_2 in the titaniferous material. For example, in the laminar flow embodiment of the present invention, the titaniferous material must contain a substantial proportion of iron for practical commercial scale operation, most often utilizing an Fe/Ti ratio of about 0.5 to 1.5. Impurities present in the titaniferous raw materials will chlorinate along with titanium values; however, the problem created by such impurity chlorination can be minimized by operating certain embodiments of the present process within preselected temperature ranges as described herein.

The chlorine-providing material can be chlorine gas, HCl, an organo-chloride and mixture thereof. In the fluid-bed embodiment of the present chlorination process the chlorine-providing material is used as the fluidizing gas in the process. As such, it is preferred that the gas contain a high percentage of chlorine such that a minimum volume of fluidizing gas can be used and maximum reaction rates obtained. Chlorine gas (Cl_2) is preferred; however, other organo-chlorides can be used. Highly reactive chlorine sources such as NOCl and selective chlorination agents such as $FeCl_2$ are not within the scope of the present invention.

The titaniferous material and the porous carbon reductant are intimately mixed within the chlorination reaction zone. Discrete particles of titaniferous material and carbon reductant are utilized in the present invention. Preagglomeration of titaniferous material and carbon together into larger granules is not practiced; however, some preagglomeration of titaniferous fines into larger titaniferous material granules or of carbon fines into larger carbon granules, may be practiced within the scope of the present invention. Such agglomerates of titaniferous materials or of carbon reductant are considered to be discrete particles for present purposes so long as any given agglomerate contains only titaniferous material or only carbon reductant and not both.

During the reaction process, the temperature is maintained greater than about 600°C. The off-gas stream is then collected and cooled to condense the products and facilitate collection.

According to the fluid-bed embodiment of the present invention, granular porous carbon reductant and granular titaniferous material are blended together and charged into the fluid-bed reactor. The reactor temperature is raised to a chlorination reaction temperature of at least about 600°C. and chlorine-providing gas is introduced into the bottom of the reactor to fluidize the bed and an off-gas product stream is withdrawn from the top of the bed.

According to the down-flow embodiment of the present invention, powdered porous carbon and powdered titaniferous material are entrained in a stream of chlorine-providing gas and introduced into a chlorination reaction zone wherein they proceed in a substantially downward path. The chlorination reaction temperature is maintained at a temperature from about 800°C. to about 1200°C. and the reaction zone is sufficiently long so that the falling carbon and titaniferous material experience a retention time of between about 1 and 10 seconds within the chlorination reaction zone.

According to the laminar flow embodiment of the present invention, a mixture of powdered porous carbon reductant and titaniferous material is passed in substantially laminar flow through a chlorination reaction zone maintained at about 1350°C. to about 1950°C., the atomic ratio of carbon in said mixture to the oxygen content in said mixture being greater than 1:1 for formation of CO, the ratio of the moles of chlorine in said chlorinating agent to said titanium in said titaniferous materials being not substantially above about 2 and the ratio of iron to titanium (Fe/Ti) in the titaniferous material passed into said zone being not substantially above 2.

When operated at low temperatures of less than about 800°C., the present process increases the selectivity of the chlorination reaction for titanium values over impurities such as aluminum, zirconium, and silicon oxides. This is beneficial because the chlorination of aluminum produces $AlCl_3$, which is very corrosive toward the collection chambers used in the chlorination processes. Also, $AlCl_3$ and $ZrCl_4$ tend to condense on the titanium chloride condensation chamber surfaces which results in eventual plugging and shutdown. Furthermore, the production of impurity chlorides consumes chlorine and thereby reduces the overall efficiency of the process and also creates a pollution and disposal problem for such impurity chlorides.

A further benefit of low-temperature fluid-bed operation of the present process is that no liquid metal chloride impurities are formed in the fluid bed itself. For example, at 600° to 670°C. the fluidized bed and the off-gas products would be below the melting points of normally troublesome calcium, magnesium, and iron chlorides. At conventional operating temperatures of greater than about 800°C., liquid chlorides of calcium and magnesium tend to cause bed defluidization.

Similarly, when operating at conventional temperatures, $FeCl_2$ vapor tends to condense on the off-gas product pipeline wall as a liquid and cause dusty solids in the off-gas to stick. This collection of liquid and dusty materials will eventually plug the apparatus and cause a shutdown. At low operating temperatures these troublesome impurity chlorides are solid and are removed from the bed as a fine dust in the off-gas stream and therefore do not cause plugging or defluidization.

The above-described low temperature capability of the present process enables the use of particularly impure titaniferous materials containing high levels of calcium, magnesium, and iron impurities that previously had to be avoided in conventional fluid-bed chlorination processes. For example, ilmenite can be chlorinated at low temperatures in the present process without the extreme plugging problems encountered at conventional temperatures in fluid-bed chlorination processes. Similarly, the non-fluid bed embodiments can effectively chlorinate impure titaniferous materials.

A further advantage realized from the use of low temperatures in the present process is the ability to increase the $TiCl_4$ production rate or alternatively decrease the carry-over losses of ore and carbon. The gases in the fluid bed expand when heated to reaction temperature. This expension is considerably less at low temperatures. Therefore, when using a conventional amount of chlorine-providing material, the velocity of the gases in the fluid bed would be lower and entrain less ore and carbon in the off gas. Alternatively, more chlorine could be used during low temperature operation of the present process compared to conventional temperature operation and increase the production of $TiCl_4$ without any increase in the gas velocity.

When the present process is operated in a fluid-bed reactor at conventional chlorination temperatures of greater than about 800°C. to about 2000°C., other benefits can be realized. Vanadium values present as impurities in the titaniferous raw materials chlorinate along with the titanium values; however, instead of being very difficult to separate from the titanium values, the chlorinated vanadium values produced are in a different physical form from the chlorinated titanium values and therefore easily separable. For example, between about 450°C. and 136°C., the chlorinated titanium values (primarily $TiCl_4$) are gaseous whereas the chlorinated vanadium values produced (believed to be VCl_3) are solid, and below about 136°C. to about -25°C. the chlorinated titanium values are liquid, while the chlorinated vanadium values remain solid. Furthermore, the chlorinated vanadium values are insoluble in both the gaseous and the liquid chlorinated titanium values. Therefore, below about 450°C., a conventional solid-gas separation or solid-liquid separation is effective to remove the vanadium values contained in the chlorinated titaniferous material.

A preferred solid-gas separation is the use of a cyclone separator at a temperature of about 140°C. to about 300°C. and preferably about 175°-200°C.; such separation is used in conventional chlorination processes to collect particulates in the $TiCl_4$ gas stream, but does not remove vanadium values during conventional processing.

Preferred solid-liquid separations are decanting and filtration.

A further benefit derived from operation of the present process at temperatures above about 800°C. is an enhancement of the CO content of the tail gas produced. Tail gases are those gases that accompany the product as it leaves the chlorinator and must be disposed of as an effluent of the process. Specifically, the CO_2:CO ratio in the tail gases of a conventional fluid-bed chlorination process is about 1 or 2:1. Such tail gas must be treated before being expelled into the environment because of the high CO level (about 33-50%). This gas cannot support combustion; therefore, treatment by mere burning is precluded and other effective treatments are costly. However, when the present porous carbon is reacted with titaniferous material during chlorination according to the present invention, the CO_2:CO ratio is reduced to about 0.01 or 0.02:1 (about 98 or 99 percent CO). Even though this tail gas contains substantially more CO than does the tail gas from conventional processes, this tail gas can be burned directly before expelling into the atmosphere as a means of treatment and thus is substantially easier and less expensive to treat than the tail gas of conventional processes. Alternatively, the CO-rich tail gas can be used for its fuel value by burning it in a boiler, kiln, or other.

The tail gases produced by the non-fluid-bed embodiments of the present invention are believed to be similarly enhanced in CO values, however, not to the extent of the fluid-bed tail gases. A still further benefit of the case of porous carbon in the present chlorination process is a surprising increase in reaction rates and degree of completion. In the case of low-temperature chlorination and down-flow chlorination it is this feature which makes these processes feasible.

The porous carbon reductant useful in the present invention can be produced from non-porous carbon by reacting in a fluidized bed at an elevated temperature with air, CO_2, and/or steam until micropores are produced. Typically about 5% or more of the carbon will be burned off during such treatment. Generally the more micropores produced and the higher internal surface area created, the higher the carbon burn-off will be. Therefore, it is preferred to treat to a minimum effective internal surface area in order to obtain maximum yield from the carbon raw materials. This treatment should be carried out above about 400°C. When steam or CO_2 is used, the reaction is endothermic. When air is used, the reaction is exothermic and will maintain itself without the introduction of any outside heat source. Preferably, such process is carried out on a continuous basis with a continuous feeding of carbon and removal of treated product.

An economic and advantageous carbon source is coal. Preferably, the coal used in high rank (anthracite) rather than low rank (bituminous) because the high rank coals attain a higher internal surface area during the above treatment. The coal introduced into the treatment process can be either wet or dry. Dry coal is actually preferred; however, wet granular coal is a much more readily available commercial product. Water is present in such wet coals to hold down dusting during transportation, as a remnant from washing, flotation or other processing or from unprotected storage.

Other processes for making high internal surface area carbons are readily available. Any available process for increasing the internal surface area of carbon can be used for making a porous carbon reductant useful in the present invention, so long as a sufficient amount of the internal micropores are produced. Such processes are typically used for producing activated carbon. Commercially available activated carbons have surface areas of about 3000m^2/g. and are effective in the instant process. However, such materials are substantially more expensive at this time than the above-described treated coals. Also, it has been found that the commercially available activated carbons are not as effective and efficient in the present process as the above-described treated coal.

The following examples show ways in which the present invention has been practiced. The examples are not intended to be limiting of the invention. In the examples, all temperatures are in degrees Centigrade and all percentages in parts by weight, unless otherwise specified.

EXAMPLE 1

Australian rutile ore containing about 96% TiO_2 and having a particle size such that substantially all of it would pass through a 40-mesh screen and be retained on a 140-mesh screen was chlorinated by blending with a porous carbon reductant and reacting with chlorine in a fluid-bed reactor. The reactor consisted of a 3-inch diameter quartz tube with a porous quartz gas distributor plate near one end.

The porous carbon reductant was prepared by treating granular anthracite coal having a particle size such that it would substantially pass an 18-mesh screen and be retained on a 100-mesh screen. The treatment consisted of heating the coal in a fluid bed in air at about 450°C. until about 15% of the coal burned off and about 163m^2/g. of internal surface had formed. Surface area as expressed here and throughout this specification is "effective surface area" as determined from the N_2 adsorption isotherm at -195°C. and application of the standard Brunauer, Emmett, and Teller (BET) procedure. A Digisorb 2500-Automatic Multi-Gas Surface Area and Pore Volume Analyzer manufactured by Micromeritics Instrument Corporation, Norcross, Georgia, was used to make these measurements. Granular anthracite coal is substantially amorphous with very little carbon crystallinity.

The rutile ore and porous carbon were then blended together in a ratio of about 3:1 and charged into the reactor to form a bed of about 12 inches deep.

The bed was fluidized by passing N_2 gas through it, and the reactor was heated to about 575°C. After heat up, the fluidizing gas was switched to Cl_2 with a small measured amount of N_2 added to provide a standard for off-gas analysis. The Cl_2 feed rate was predetermined to provide a Cl_2 flow of about .35 feet per second and thus a contact time of 3 to 3.5 seconds with the materials in the fluid bed.

The reactor temperature was raised in 20-25° intervals, allowed to stabilize, and CO, CO_2, N_2, Cl_2, and $COCl_2$ levels in the off-gas were determined. Percentage of Cl_2 consumed was then calculated and plotted against temperature. This graph is shown in Figure 1.

The CO_2/CO ratio was used to determined carbon consumption and thus additions required to maintain the fluid-bed depth.

EXAMPLE 2

In the procedure of Example 1 a steam-treated porous carbon reductant was used in place of the air-treated carbon.

The present carbon was prepared by heating similarly sized granular coal in a fluidized bed in the presence of super-heated steam at a temperature of about 890°C. until about 40% of the coal burned off. The steam-treated coal had a surface area of about $680m^2/g$.

A plot of temperature vs. percent Cl_2 consumed is shown in Figure 1.

EXAMPLE 3

In the procedure of Example 1 similarly sized untreated granular anthracite coal was used in place of the porous carbon reductant. This granular coal had a surface area of about $0.1m^2/g$.

A plot of temperature vs. percent Cl_2 consumed is shown in Figure 1.

EXAMPLE 4

In the procedure of Example 1 similarly sized granular bituminous char was used in place of the porous carbon reductant. The bituminous char is not porous and thus has only external surface; however, it is substantially amorphous with very little carbon crystallinity. The surface area of the bituminous char was about $0.3m^2/g$.

A plot of temperature vs. percent Cl_2 consumed is shown in Figure 1.

EXAMPLE 5

In the procedure of Example 1 calcined petroleum coke having a particle size such that it would substantially pass through a 10-mesh screen and be retained on a 40-mesh screen was used in place of porous carbon reductant. The petroleum coke was nonporous and had a surface area of about $0.3m^2/g$.

The petroleum coke was substantially crystalline having about 58% crystalline carbon and about 42% amorphous carbon.

A plot of temperature vs. percent Cl_2 consumed is shown in Figure 1.

EXAMPLE 6

Wet, granular (-18 mesh), anthracite coal was placed in a fluid-bed reactor and fluidized by introduction of hot steam at a superficial velocity of 0.8 feet per second at a temperature of 890°C. A plot of surface area versus carbon burn-off is shown in Figure 2. Coal treated according to this example is effective in the present process.

EXAMPLE 7

In the procedure of Example 6, CO_2 at 950°C. was used in place of steam. A plot of surface area versus percent of carbon burn-off is shown in Figure 2. Coal treated according to this example is effective in the present process.

EXAMPLE 8

In the procedure of Example 6, air at 450°C. was used in place of steam. A plot of surface area versus percent of carbon burn-off is also shown in Figure 2. Coal treated according to this example is effective in the present process.

Figure 2, a graph, is attached.

EXAMPLE 9

Rutile ore containing about 96.1% TiO_2, 1.2% Fe_2O_3, and 0.4% V_2O_5 was chlorinated in a fluid-bed chlorinator at 1000°C. Chlorine gas and a coal treated in accordance with Example 6 having a 5% carbon burn-off were used. A fluid-bed depth of 14-15 inches was maintained by continuously feeding fresh ore and treated coal. The chlorination was run for a period of 3 hours, and the CO_2:CO ratio in the chlorinator tail gas was measured about every 10 minutes via gas chromatography. The gaseous product stream was allowed to cool partially and was passed through a solid-gas cyclone-type separator. The temperature of the gas stream passing through the separator was controlled at about 175°C., however, the actual temperature varied between 150° and 200°C. The solids collected in this separator include fluid-bed blow-over, $FeCl_2$ and most of the vanadium values (believed to be VCl_3). $TiCl_4$ was then condensed from the product gas stream and solid were allowed to settle. These solids are present mainly due to the inefficiency of the cyclone separator, and contain essentially the same components as the cyclone solids. The clear sample of supernatant $TiCl_4$ was poured off and analyzed for vanadium. The surface area of the carbon source, the average CO_2:CO ratio, and the vanadium impurity level in the $TiCl_4$ product are shown in Table I.

EXAMPLE 10

In the procedure of Example 9, coal treated in accordance with Example 6 having a 40% carbon burn-off was used. Data from this chlorination are also shown in Table I.

EXAMPLE 11

In the procedure of Example 9, coal treated in accordance with Example 3 having a carbon burn-off of 5% was used. Data from this chlorination are shown in Table I.

EXAMPLE 12

In the procedure of Example 9, carbon prepared according to Example 3 having a 15% carbon burn-off was used. Data from this chlorination are also shown in Table I.

EXAMPLE 13

In the procedure of Example 9, granular (-8 mesh) anthracite coal was used without pretreatment. Data from this chlorination are also shown in Table I.

EXAMPLE 14

In the procedure of Example 9, granular petroleum coke (-8 mesh) was used. Data from this chlorination are also shown in Table I.

TABLE I

Example Number	Treatment	% Carbon Burn-off	Carbon Surface Area ($m^2/g.$)	CO_2:CO (average)	Vanadium Impurity Level (ppm)
4	Steam @ 890°C.	5	104	0.08	101
5	Steam @ 890°C.	40	540	0.006	<5
6	Air @ 450°C.	5	55-63	0.1	225
7	Air @ 450°C.	15	163	0.06	<5
8	None (Coal)	0	0.1	0.4	225
9	None (Petroleum Coke)	0	<0.1	2.2	780

EXAMPLE 15

In order to further characterized the carbons useful in the present invention, three high surface area carbons were selected. Using the BET technique, surface area in <20 Å diameter pores were measured and then surface area in >20 Å diameter pores were measured. The total surface area is the sum of these two measurements.

These carbons were then heated to 1000°C. in a N_2 atmosphere (to simulate heating to chlorination temperatures) and the respective surface areas were again measured. Data are shown in Table 2.

The data show that heating air-treated coals to chlorination temperature results in a loss of surface area in both <20 Å and >20 Å diameter pores. Steam-treated coals lose surface area due to a decrease in <20 Å diameter pores only. Charcoal, in contrast to the treated coals, gains surface area after heating to a chlorination temperature, due mainly to the formation of small pores.

(TABLE II ON PAGE 18)

TABLE II

Carbon Source Pretreatment	Anthracite Air @ 450° to 15% Burn-off		Anthracite Steam @ 890° to 10% Burn-off		Hickory Charcoal Not Specified	
Heated to 1000°C. in N_2	No	Yes	No	Yes	No	Yes
Surface Area in <20Å Diameter Pores	110	41	215	137	0	62
Surface Area in >20Å Diameter Pores	66	9	10	12	19	25
Total Surface Area	176	50	225	149	19	87

In summary, the examples show the improved chlorination achieved when porous carbon reductants are used in place of conventional nonporous carbons. The examples further indicate that the nearly complete removal of vanadium impurities that can be easily accomplished at conventional chlorination temperatures when porous carbon reductant is utilized.

CLAIMS

1. A process for chlorinating a titaniferous material which comprises reacting discrete particles of titaniferous material and porous carbon reductant in the presence of a chlorine-providing material selected from the group consisting of chlorine gas, HCl, an organo-chloride and mixtures thereof in a chlorination reaction zone at a temperature of at least about 600°C. until the titanium content of said titaniferous material is substantially chlorinated, said porous carbon reductant being characterized in that it has micropores having a pore diameter of less than about 20 Å and internal surface area within said micropores of at least about $10m^2/g$. and not substantially above about $1500m^2/g$.

2. The process of claim 1, wherein said titaniferous material and said carbon reductant are each granular materials which substantially pass through an 8-mesh sieve and are substantially retained on a 140-mesh sieve and said chlorination reaction zone is a fluidized bed.

3. The process of claim 1, wherein said titaniferous material and said porous carbon reductant are each powdered materials which substantially pass through a 140 -mesh sieve, said chlorination reaction zone is a down-flow reaction zone and said temperature is between about 800°C. and 1200°C.

4. The process of claim 1, wherein said titaniferous material and said porous carbon reductant are each powdered materials and are maintained in substantially laminar flow as they pass through the chlorination reaction zone, said temperature being between about 1350°C. and 1950°C., the atomic ratio of carbon in said chlorination reaction zone to the oxygen in said zone being greater than 1:1 for formation of CO, the ratio of the moles of chlorine in said chlorine-providing material to the titanium in said titaniferous material being not substantially above about 2 and the ratio of iron to titanium in said titaniferous material being not substantially above 2.

5. The process of claim 1, wherein said porous carbon

reductant is a treated coal.

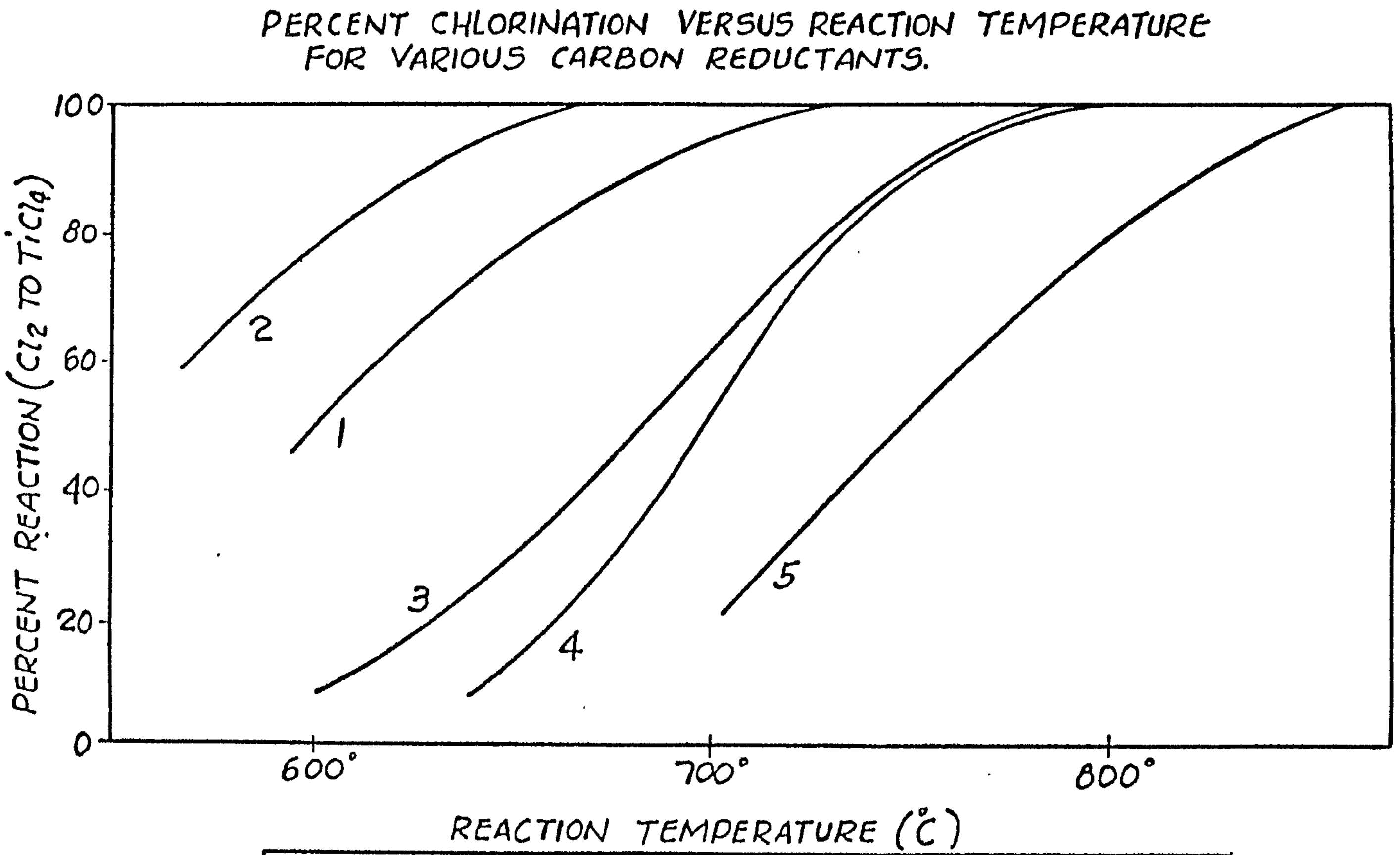
6. The process of claim 5, wherein said coal is anthracite coal.

7. The process of claim 5, wherein said coal was treated by reacting with air, CO_2, or steam at a temperature in excess of about 400°C. until said micropores are produced.

8. The process of claim 1, wherein said porous carbon reductant has an internal surface area in said micropores of at least about $100m^2/g$. and not substantially above $1000m^2/g$.

9. The process of claim 1, wherein said temperature is greater than about 800°C., said chlorination reaction zone is a fluid-bed and substantially all vanadium impurities present in said titaniferous material are reacted thereby such that at temperatures between about 450°C. and -25°C. said reacted vanadium impurities are in a different physical form from said chlorinated titanium content of said titaniferous material.

10. The process of claim 1, wherein said titaniferous material is ilmenite ore.



PERCENT CHLORINATION VERSUS REACTION TEMPERATURE FOR VARIOUS CARBON REDUCTANTS.

EXAMPLE NUMBER	CARBON TYPE	CARBON SURFACE AREA (m^2/g)
1	TREATED ANTHRACITE (POROUS)	163
2	TREATED ANTHRACITE (POROUS)	680
3	ANTHRACITE (NON POROUS)	0.1
4	BITUMINOUS CHAR (NON POROUS)	0.3
5	PETROLEUM COKE (NON POROUS)	0.3

FIG. I

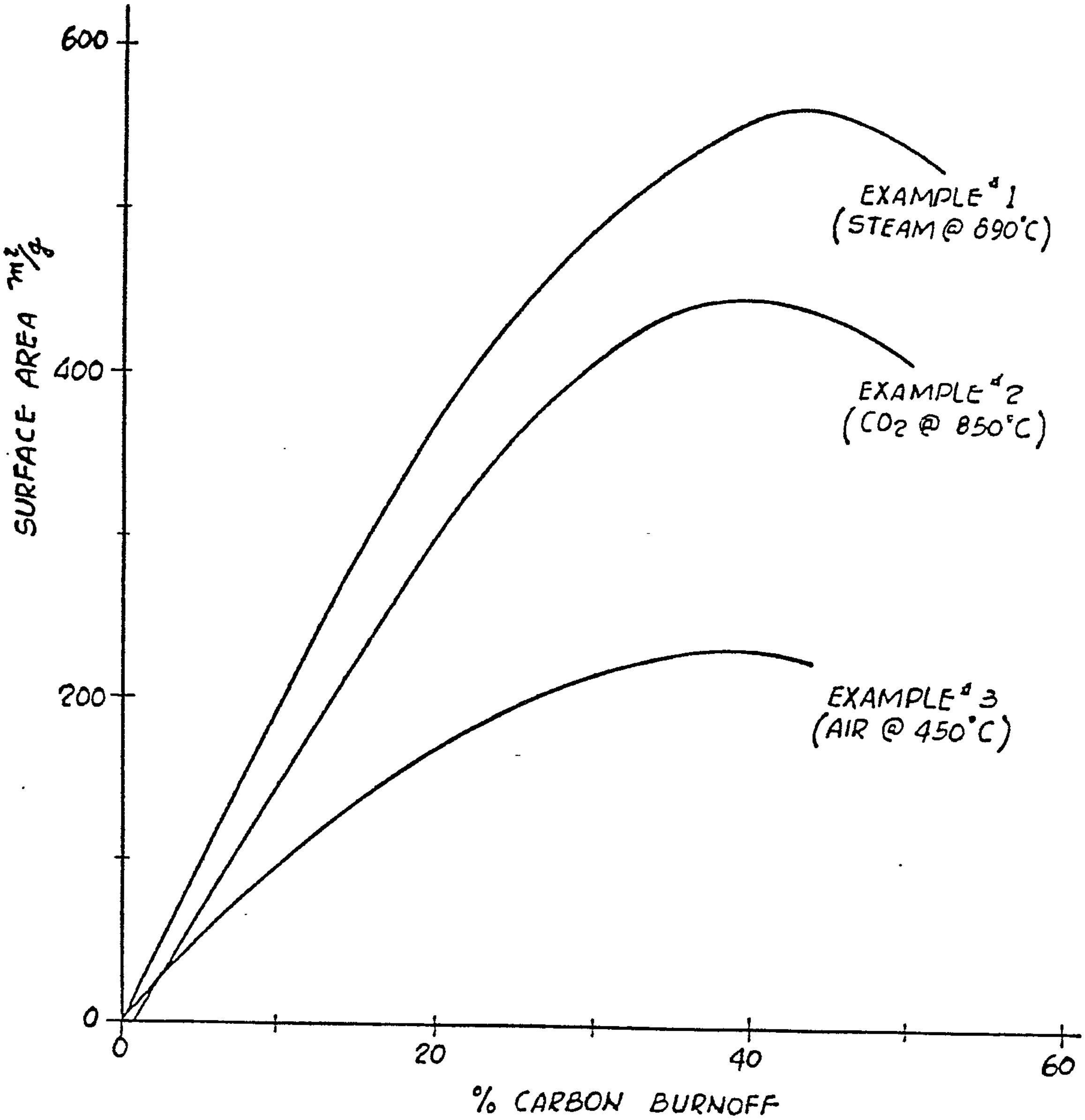

600
400
200
0
SURFACE AREA m²/g
0
20
40
60
% CARBON BURNOFF
EXAMPLE # 1
(STEAM @ 690°C)
EXAMPLE # 2
(CO2 @ 850°C)
EXAMPLE # 3
(AIR @ 450°C)

FIG. 2

0029699

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 80 30 4130.0

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
X	GB - A - 1 431 480 (DU PONT) * claim 1; page 9, lines 20 to 39; example 1 * --	1-6	C 01 G 23/02 C 22 B 1/08 C 22 B 34/12
A	METALLURGICAL TRANSACTIONS B, Vol. 10B No. 2, June 1979 W. E. DUNN, JR. "High Temperature Chlorination of Titanium Bearing Minerals: Part IV" pages 271 to 277 * pages 275 to 276, paragraph 4: "The Effect of Carbon Surface" --		
			TECHNICAL FIELDS SEARCHED (Int. Cl.³)
A	DE - A1 - 2 602 172 (CENTRO SPERIMENTALE) --		C 01 B 31/00 C 01 G 23/00 C 22 B 1/00 C 22 B 34/12
A	ABC-CHEMIE, Band 1 A-K VERLAG HARRI DEUTSCH, Frankfurt/Main, Zürich * pages 30 to 31: Aktivkohle * --		
A	EP - A1 - 0 000 498 (SCM CORP.)		

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☒ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	20-02-1981	KESTEN

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