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(54) A PROCESS FOR THE BENEFICATION OF TITANIFEROUS ORES

(71) We, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION, A body corporate established under the Science and Industry Research Act, 1949, of 314 Albert Street, East Melbourne, in the State of Victoria and MURPHYORES INCORPORATED PTY. LTD. a company incorporated under the laws of the State of Queensland, of 127 Eagle Street, Brisbane, in the State of Queensland, both of the Commonwealth of Australia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the beneficiation of titaniferous ores and is particularly concerned with the production of an "up-grade" rich in titanium dioxide (TiO_2) and suitable for use as a feed material in the production of high purity titanium oxide and titanium metal.

At the present time, rutile is in great demand for the production of TiO_2 , as it is substantially free from iron and can therefore be readily processed. However, the immense and ever expanding developments in use of high purity titanium oxide by the pigment and paper industry, combined with the increasing demand for titanium metal, appears to be outstripping the available sources of rutile. Due to this and because of

the large and readily extractable deposits of other titaniferous ores throughout the world, 35 the development of economic processes for beneficiating such ores to a point where the TiO_2 content becomes comparable with that of rutile is of considerable importance. However, the other titaniferous ores—such as 40 ilmenite—vary considerably in composition so that, as stated by one authority in the field, "the proliferation (of beneficiation methods) has probably come about since 45 work in most places has been directed at a particular source and type of ilmenite that is easily obtained in that place".

The currently favoured method of producing TiO_2 from rutile is one in which the rutile is first chlorinated to give titanium 50 chloride (TiCl_4) which is converted to TiO_2 by burning, the chlorine thus generated being recycled. It is therefore a pre-requisite of the chlorination process that as pure 55 grade of TiO_2 , as possible is used in order to reduce chlorine consumption to a minimum. On the other hand, the traditional process for producing TiO_2 is based on reacting a high grade ilmenite, or slags rich 60 in TiO_2 , with sulphuric acid. Here again, there are economic and technological advantages (for example, decreased acid consumption, increased tank capacity and output, decreased need of scrap iron, contraction of waste disposal problems etc.) in 65 using an acid soluble form of TiO_2 rather

[Price 25p]

than ilmenite.

It is important therefore that upgrades of titaniferous ores should not only contain very high proportions of TiO_2 but should provide no difficulty when used as feed material for either of these processes. For example, upgrades intended for the sulphuric acid process for the manufacturing of pigment grade TiO_2 must be soluble in sulphuric acid. On the other hand, the chlorination process developed for rutile invariably involves the use of fluid bed reactors and, for this reason, one of the main pre-requisites of an acceptable upgrade substitute for rutile is that the particle size range of the upgrade product should be substantially the same as rutile. Consequently, beneficiation methods based upon slagging, fusion, etc. are of limited interest. Current beneficiation methods are therefore based either upon the direct leaching of iron from ilmenite, or the leaching of metallic or carbide iron by a variety of aqueous systems after a substantially complete reduction of the iron values in the ore to metallic or carbide iron.

The many known direct acid leaching processes suffer from the poor reactivity of natural titaniferous ores such as ilmenites and therefore involve the use of high acid concentrations and temperatures such that leaching operations have to be carried out under pressure. The reactivity of these ores is so poor that even under such conditions the times required for adequate leaching are protracted. For example, in one of the more recent acid leaching processes (U.S. patent No. 3,193,376) a two stage leaching cycle has been adopted using pressures of between 30 and 35 psig at each stage and even so, leaching times of 4 to 6 hours per stage are needed. Furthermore, in each stage relatively concentrated hydrochloric acid (HCl ; 20°Be, 32%) has to be injected. Temperature and acidity parameters are stated to be critical if the production of "fines" is to be kept to a minimum. Although the process is claimed to be capable of producing material containing about 93% w/w TiO_2 these figures appear to be very specific to the particular type of ore employed. Moreover, with some ores significant amounts of titanium values are precipitated in a finely divided form whilst leaching. Finally, the efficient recovery of 20°Be HCl from chloride containing effluents by existing commercial processes is considerably more difficult and expensive than the recovery of HCl of significantly lower concentrations.

In another direct acid leaching process (U.S. patent No. 2,127,247) an attempt has been made to overcome the similarity in reactivity to acid leachants of ferric oxide (Fe_2O_3) and TiO_2 in natural partly altered ilmenite by preliminary chemical reduction

of ferric values to the ferrous state. Reduction temperatures are limited to a maximum of 800°C since high temperatures, it is stated, cause a substantial decrease in the solubility of the residues in 80% sulphuric acid. Additionally, it is stated that the leaching stage subsequent to the reduction stage must be carried out at temperatures above the boiling point of the leachant and above atmospheric pressure in order to obtain a high degree of enrichment of TiO_2 by avoiding substantial solution of titanium values.

In the second group of prior art processes involving the leaching of metallic or carbide iron, the aim is to achieve as high a degree of reduction in the iron values as possible, since this is usually the factor determining the quality of the final material. When hydrogen is the reductant, complete chemical reduction of the iron values to metallic iron is a fairly slow process even when preceded by an oxidation stage; and, perhaps of more importance, thermodynamic considerations—even for equilibrium conditions at 900°C—limit the utilization of hydrogen to about 5%. For this reason, the hydrogen injected must be free from significant amounts of contaminants and dehydration and re-pressurizing stages must be incorporated before the unused hydrogen is recirculated to the reactor. Reduction by carbon is also a slow process even operating in the temperature range 1100 to 1200°C and calls for close control of the atmosphere above the reacting mass if the particle size and the physical nature of the product is not to be radically altered by sintering processes. The unreacted carbon is later recovered, in a separate operational stage by suitable physical methods, for re-use albeit in a less chemically active form than formerly.

Leaching of such reduced material usually involves contacting the reduced material with aqueous solutions containing various additives, sometimes in the presence of oxygen when a form of accelerated rusting occurs. See for example U.S. Patent No. 3,252,787, Australian Patent No. 247,110, and German Patent No. 1,218,734. Such processes are claimed to produce a beneficiated product containing up to 90% w/w TiO_2 . Here again, it is likely that the practicability of this type of process is very dependent upon the detailed composition of the particular titaniferous ore body employed.

The general object of the present invention is therefore to provide an improved process for the beneficiation of titaniferous ores which will, preferably, avoid the disadvantages associated with each of the above mentioned classes of prior art process and, yet, will not add significant disadvantages of its own. Thus, it would be advantageous if the treatment processes

were less severe and the treatment times shorter. Similarly, it would be desirable for the improved process to be less selective in respect of ore types and yet be capable of producing upgrades having TiO_2 contents above the levels currently obtained by the prior art processes.

The present invention is able to achieve these objects and advantages as it is based upon the surprising discovery that, if the natural ore is oxidized to convert the iron values associated with titanium to the ferric state and then deoxidizing said iron values, the material obtained in this way is so chemically active that it is readily and directly leachable.

Although it is preferred that substantially all of said iron values are deoxidized to the ferrous state, we have found that a substantial advantage over prior art processes can still be obtained if the deoxidization results in up to 20% w/w of said iron values, based on the weight of the ore, being present in the metallic state.

Accordingly, in its broadest aspect, the present invention provides a process for the treatment of titaniferous ore, comprising the steps of oxidizing substantially all of the iron values associated with titanium in the ore to the ferric state; and deoxidizing substantially all (as herein defined) of said iron values to the ferrous state or ferrous and metallic states, the amount of said iron values in the metallic state following the deoxidization not exceeding 20% w/w of the ore. In the most preferred aspect of this invention substantially all of the said iron values are deoxidized to the ferrous state.

The invention also provides a titaniferous ore product:

- (i) displaying the X-ray powder diffraction pattern of ilmenite;
- (ii) in which substantially all (as herein defined) of the iron values originally associated with the titanium in the ore therein are in the ferrous state or ferrous and metallic states;
- (iii) containing not more than 20% w/w of metallic iron; and
- (iv) which is in a reactive state such that said iron values which are in the ferrous state or ferrous and metallic states can be leached out by treatment with 20% w/w hydrochloric acid at 108°C to 110°C and atmospheric pressure.

The statement that "substantially all" of the iron values are in, or are deoxidised to, the ferrous state or ferrous and metallic states means that at most 3% by weight of the ore after deoxidation is in the ferric oxide (Fe_2O_3) state.

Before discussing the implications of this

discovery and its application in the present invention, it should be understood that, in the present specification, the preferred titaniferous ore is natural ilmenite but ores having TiO_2 : Fe ratios outside the normally accepted range for ilmenite are also included within the ambit of this term. Usually titaniferous ores of the ilmenite variety have an average TiO_2 content of between 50 and 55% but there are massive deposits in which the proportion of TiO_2 is as low as 20% as mined and, possibly, 45% after ore dressing. Furthermore, since for the purposes of the present invention the chemical properties or activity of the materials produced by the above mentioned successive process of oxidation and deoxidation are so significantly different from those of the natural ore, this material will be referred to as "synthetic ore" or "synthetic ilmenite" to distinguish it from the natural ore.

The conversion of the iron values associated with titanium in the natural titaniferous ore to the ferric state may be achieved by a simple process of oxidation which, preferably, is conducted at a temperature below that at which sintering of particles occurs. Because the naturally occurring ores differ considerably in the ratio of their ferric and ferrous values, the time required for oxidation is dependent upon that ratio but this process parameter can be readily adjusted to suit the particular ore. The preferred method of oxidation is by the action of gaseous oxygen suitably diluted with at least one other gas which is inert under the reaction conditions; atmospheric air therefore being especially preferred for this purpose. The use of pure oxygen is possible but less desirable due to the difficulty of controlling temperature uniformly and the consequent danger of sintering. Similarly, it is possible but not preferred to employ oxygen containing compounds such as carbon dioxide, water or mixtures thereof, which are capable of oxidizing iron to the ferric state under the process conditions.

The deoxidation step may be carried out using any material suitable for the conversion of ferric iron to ferrous. Solid reagents such as carbon may be used but gaseous reagents are preferred; these include carbon monoxide, hydrocarbon gases, hydrogen, and mixtures of these in or with other gases such as water gas, producer gas and hydrogen-rich gas mixtures from catalytic reforming processes. Conversion of the oxidized product to the synthetic ore is extremely rapid and efficient when carried out by hydrogen at 850 to 900°C. Hydrogen utilization usually exceeds 75% under these conditions thereby obviating the need to recycle unused hydrogen. For this reason, dehydration and re-pressurizing facilities are

not required; neither is it necessary to use pure hydrogen—we have obtained satisfactory results when using impure hydrogen, such as that obtained by reforming organic materials such as naphtha.

The use of excessive amounts of hydrogen may lead to the formation of metallic iron in the titaniferous material. This imposes no considerable disadvantage beyond the economic penalty, arising from the fact that the hydrogen utilization falls to about 5% after formation of the synthetic ilmenite has occurred, and the possible hazards if hydrogen is evolved during subsequent leaching operations. We have detected the beneficial effect of the synthetic ilmenite when excess hydrogen has been used to the point where the reduced titaniferous material contains not more than 20% w/w of metallic iron, i.e. to the point where the x-ray powder diffraction pattern of ilmenite becomes difficult to detect.

Having formed the synthetic ore, the preferred but not necessarily exclusive method of beneficiation is by acid leaching. The preferred acid is hydrochloric acid since this can be readily generated from hydrolysable or reducible chlorides by well known commercial and readily available techniques which present the possibility of producing iron oxide powder or metallic iron powder as saleable by-products along side the recovered hydrochloric acid. Furthermore, since sensibly all the iron values associated with titanium in the synthetic ore are in the ferrous state, the amount of leachant required is a minimum and significantly less than in those processes which leach natural ores in which a substantial part of the iron values are in the ferric state.

Because of the enhanced activity of the synthetic ore compared with that of the natural ore, we have found it practicable to use a 20% solution of hydrochloric acid as leachant instead of the more concentrated acid used in existing processes dealing with natural ores. The ability to use such a dilute HCl solution (slightly less concentrated than the constant boiling mixture at one atmosphere pressure) considerably simplifies the leaching operation which, preferably takes place at from 105 to 110°C. Thus, we have found that a single treatment of synthetic ore, or sufficiently low siliceous and aluminous gangue content with 20% hydrochloric acid, in quantity corresponding to about 20% excess over the stoichiometric amount required for dissolution of the undesired acid soluble non-titaniferous values in the ore, carried out for about four hours at 108 to 110°C at atmospheric pressure under reflux conditions, produces a pale-yellow residue which contains 95 to 97% w/w TiO_2 and is of substantially the same particle size range as the natural ore. (A quantity of

soluble titanium species corresponding to about 1% w/w of the initial TiO_2 passes out in the ferrous chloride effluent).

Such a product is soluble in the sulphuric acid solutions commonly used in the art and this, together with the non-degradation of particle size, makes the product a suitable feed material for both sulphuric acid and chlorination processes, providing that the nature and extent of the residual and concomitant impurities are acceptable. Moreover, the only adaption of the process to suit a particular ore required is in the aforementioned requirement for complete oxidation of the iron values associated with titanium in the natural ore to the ferric state since, provided that is done, the leachability of the synthetic ore produced seems to be essentially constant regardless of the natural ore employed. Although it is not claimed that the process of the invention will remove all contaminants from any natural ore, it has been found that the process described above effects a considerable decrease in the extent of manganese and magnesium contamination and, to a lesser degree, in the chromium and aluminium contamination. Finally, it will be noted that the upgrade made by the process of this invention is not only of a superior grade to those prepared by other known processes but it also has a TiO_2 content at least comparable with, that of best grades of rutile in current commercial production.

Having broadly indicated the nature of the present invention and shown that the objects and advantages desired have been substantially achieved, more specific examples and embodiments of the invention will now be described by way of example and illustration.

Before describing the particular examples and embodiments, however, some attempt will be made to explain the remarkable difference between the natural titaniferous ore employed as a starting material and the synthetic titaniferous ore produced prior to leaching. To illustrate in an objective manner the benefits effectively associated with the synthetic ore, the following tests were conducted on a sample of ilmenite from the east coast of Australia and containing about 11.9% w/w Fe_2O_3 , 30.8% w/w FeO , and 52.9% w/w TiO_2 .

1. The natural untreated ilmenite was leached counter-current wise in two stages by a 20% excess of a 32% solution of hydrochloric acid under a pressure of 35 psig at 110°C in accordance with published instructions. The total treatment was conducted over a period of eight hours and the final dry product was found to contain 79% w/w TiO_2 , the TiO_2 losses in the

effluent being about 0.5% of the TiO_2 originally present.

2. The natural untreated ilmenite was treated in a single stage with a 20% excess of a 20% hydrochloric acid solution at 110°C for four hours under reflux conditions. The dry product contained 72.9% w/w TiO_2 with an effluent loss corresponding to 0.5% of the TiO_2 originally present.

3. The natural untreated ilmenite was treated with hydrogen at 875°C until the ferric values present originally had been reduced to the ferrous state. This material was then leached at 110°C for four hours with a 20% excess of 20% hydrochloric acid under reflux conditions. The dry product contained 76% w/w TiO_2 with an effluent loss corresponding to 0.6% of the TiO_2 originally present.

4. The natural ilmenite was oxidized by air for two hours at 875°C before being leached with 20% hydrochloric acid as described in 2) above. The product contained 55.2% w/w TiO_2 with an effluent loss corresponding to 5.6% of TiO_2 originally present.

5. After oxidizing in air as described in (4) above, the material was treated with hydrogen at 875°C for five minutes in order to produce synthetic ilmenite. After acid leaching for 3 hours but otherwise as in (2) above, a pale-yellow product was obtained which contained 97.1% w/w TiO_2 with an effluent loss corresponding to about 1.2% of the TiO_2 originally present.

It will be noted that the TiO_2 content of the material made by the process of this invention (para. 5 above) not only is of a far superior grade than those prepared by the methods described in paras 1 to 4 above, but also has a significantly higher TiO_2 content than that of most grades of rutile in current commercial production. Clearly, therefore, the synthetic ilmenite must differ significantly from the natural ilmenite.

Whilst it is difficult to specify the precise nature of the changes occurring during the formation of the synthetic ilmenite, it is thought that, during the deoxidation stage when the ilmenite structure is being formed, the development of this structure is extremely rapid in comparison with that which probably occurred during the formation of the natural ilmenite. As a result, a material is produced which possesses many structural defects and lattice strains which, it is considered, are largely responsible for the enhanced chemical reactivity.

We therefore prefer to carry out the oxid-

ation stage at relatively low temperatures (e.g. about 900°C) both for economy reasons and in order to facilitate the formation of hematite (Fe_2O_3) and rutile (TiO_2) as separate phases with a minimum amount of pseudo-brookite ($\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$).

A modification of the process of this invention renders it particularly useful for the treatment of titaniferous ores containing appreciable quantities of associated chromium minerals and other minerals having magnetic properties.

In both the conventional sulphuric acid leaching process and the more recent chlorination process, the presence of appreciable quantities of chromium mineral in association with the titaniferous ores is undesirable. In the sulphuric acid process the unselective nature of the acid digestion stage takes chromium values into solution along with titanium and iron values. Chromium values in solution are of great concern since not only are they difficult to separate from the subsequently precipitated titanium species, but they also have a pronounced colouring effect on the final titanium dioxide product. In the chlorination process, substantially all of the chromium values, together with iron and impurity metals present in the ore may be separated readily from the titanium values after chlorination. Chromium minerals therefore do not result in significant contamination of the final titanium dioxide product in this case but the presence of significant amounts of iron and chromium species in the charge increases the consumption of chlorine per unit weight of titanium dioxide produced and this imposes an economic penalty on the chlorination process.

To achieve a reduction in chromium concentration, consistent with the use of one or other of these processes, it has been necessary in the past to subject the ore to an initial magnetic separation step to thereby produce a titanium-rich and chromium-rich fraction. However this has provided only a partial solution since the similarity in the magnetic susceptibilities of ilmenite and chromite (which is the main chromium-containing impurity usually associated with titaniferous ores) prevents a clean separation of those minerals. Thus, if titaniferous ores containing chromite are to be exploited effectively for their titanium values, significant losses of ilmenite will be incurred when lowering the chromium content to an acceptable level by magnetic methods.

We have found that if an ilmenite ore containing chromite is subjected to the oxidation and reduction stages of the process described above, the chemical activity of the iron oxide component of the ilmenite that is, the iron values associated with titanium, is enhanced, as has been described,

but that if the iron oxide component of the chromite, is not materially changed.

This result thus offers a material advantage for the up-grading of ilmenite ores containing chromite and which, as a consequence, have been of little economic value. For, after the above treatment, the ore may be subjected to a suitable leaching operation, as described above, to remove the activated iron values originally associated with titanium, and thereby leave a product comprising essentially titanium dioxide and substantially unaltered chromite. This product is readily amenable to further up-grading since, although untreated ilmenite is strongly magnetic, the up-grade, or "synthetic rutile", derived from this mineral is not. Thus it is now possible to use a magnetic separation step to separate the unchanged magnetic chromite from the leached product.

Thus when the ore contains magnetic materials it is possible, according to the invention, to subject the ore after leaching to a magnetic separation treatment, to remove substantially all of the magnetic materials from the ore.

The present invention thus provides a process for up-grading titaniferous ores containing chromium-containing minerals, wherein said ore is subjected in turn to oxidizing conditions sufficient to convert substantially all of the iron values associated with titanium to the ferric state, without significant oxidation of the iron component of the chromium-containing mineral; and then to deoxidizing conditions sufficient to convert substantially all (as herein defined) of said iron values from the ferric state to the ferrous state or ferrous and metallic states, the amount of said iron values in the metallic state not exceeding 20% w/w of the ore, and the iron component of the chromium-containing mineral being unchanged; whereafter the ore is leached to remove substantially all of the deoxidised iron values, and then subjected to a magnetic separation treatment to remove substantially all of the chromium-containing mineral, thereby leaving an up-grade, rich in titanium dioxide and substantially free of chromium values.

While natural chromite will be the form in which chromium minerals will normally be encountered in association with titaniferous ores, ratios of chromic oxide to iron outside the normally accepted range for chromite are to be understood as being included within that term in the following description.

It will also be appreciated that while the present invention provides a means for obtaining an up-grade rich in titanium dioxide but low in chromium, it also provides a further advantage over the prior art prac-

tice in yielding a means for obtaining a clean chromite fraction, substantially free of titaniferous values. This clean high-chromite fraction may therefore be further processed by known means for the recovery of chromium compounds or metallic chromium, without the need for an extensive and costly purification step to remove titaniferous values.

Thus, in a further aspect of the present invention, there is provided a process for up-grading titaniferous ores containing associated chromite, whereby the ore is treated as described above to thereby provide both a titanium-rich up-grade, substantially free of chromium values, and a chromium-rich up-grade substantially free of titanium values.

To further portray the nature of the present invention, the chosen embodiment illustrated in the accompanying drawings will now be described. In the drawings:—

Figure 1 is a flow sheet of a typical process according to the invention; and

Figure 2 is a flow sheet of a modified form of the process for chromite-containing ilmenites.

Referring firstly to Figure 1, natural ilmenite enters an oxidation stage A where it is oxidized by air in a suitably heated reactor. Both this stage and the following deoxidation stage may be conveniently carried out in a single reactor although for convenience of description two separate stages are shown. The reactors may be of any suitable known type and may be of the stationary or fluid bed type, or alternatively may be of the counter-current type in which the solid and gaseous reactants each move in opposite directions through the reactor.

After oxidation at A the oxidized material is subjected to a deoxidation stage B in which the material is treated with hydrogen or hydrogen containing gases. This results in the formation of synthetic ilmenite as hereinbefore described.

The synthetic ilmenite passes to a leaching stage C where it is leached, in conventional apparatus with 20% aqueous hydrochloric acid which dissolves out the ferrous iron and other acid-soluble non-titaniferous impurities, leaving an up-grade which is rich in titanium dioxide. The liquid and solid phases are separated in stage D which consists of any suitable known apparatus such as a batch or continuous filter, decanter, centrifuge or any suitable combinations thereof. The solid up-grade product is then washed and dried and calcined.

The aqueous ferrous chloride liquor then passes to a conventional hydrochloric acid recovery process F which is here shown separated from the rest of the process by the dotted line E-E. The recovery process illus-

trated is the "Aman" process in which the ferrous chloride liquor is oxidized and hydrolyzed with steam to form hydrochloric acid vapour and ferric oxide. The acid is returned to the leaching stage C as a 20% solution, make-up acid being added if necessary.

The invention is further illustrated by the following examples:

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EXAMPLE 1

150 gm. of ilmenite from east coast of Australia (Gladstone) having the following typical analysis:

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TiO ₂	52.9%
Fe ₂ O ₃	11.9
FeO	30.8
Cr ₂ O ₃	0.15
MnO	1.77
MgO	0.46
Al ₂ O ₃	0.23
CaO	0.05

20

25 was oxidized in a 4.5 cm. diameter fluid bed reactor using air as the fluidizing gas for two hours at 870°C. The oxidized ore was then deoxidized by passing hydrogen through the fluid bed for five minutes at 30 870°C. The material was cooled to room temperature in a non-oxidizing atmosphere.

70 gm. of the deoxidized material was then leached with 200 gm. of 20% hydrochloric acid solution under refluxing conditions for three hours. The temperature of leaching was maintained at 108-110°C and agitation was provided by shaking the flask. At the end of leaching time, the contents were allowed to cool, filtered, washed with 40 water and the residue dried and then ignited at 800-850°C. The ignited product analysed as follows:

TiO ₂	97.1%
Fe ₂ O ₃	1.08
Cr ₂ O ₃	0.14
MgO	0.08
MnO	0.05
Al ₂ O ₃	0.3
CaO	0.03

50

EXAMPLE 2

Ilmenite from Quilon (India) containing 60.3% TiO₂, 9.7% FeO and 24.8% Fe₂O₃ 55 was oxidized, deoxidized and leached as in example 1. The leached product on drying and ignition analysed as follows:—

TiO ₂	95.8%
Fe ₂ O ₃	0.7

60

EXAMPLE 3

Mined and dressed titaniferous material from Tahawas (U.S.A.) containing 44.4% 65 TiO₂, 36.7% FeO and 4.4% Fe₂O₃ was

ground to -30 mesh (British Standard) and then treated as in example 1 and 2 above except that the leaching time was increased from three to four hours. The upgraded material analysed as follows:

70

TiO ₂	83.8%
Fe ₂ O ₃	3.0
SiO ₂	5.2
CaO	1.0
MgO	0.8
Al ₂ O ₃	3.6
Cr ₂ O ₃	0.02

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The analysis showed that the iron removal in this case was good, but that the TiO₂ content of the product was much lower due to the presence of large percentage of insoluble gangue material.

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EXAMPLE 4

Ilmenite from west coast of Australia having 55.2% TiO₂, 23.4% FeO and 17.8% Fe₂O₃ was treated as in example 1. The upgraded material had the following 90 analysis.

TiO ₂	96.6%
Fe ₂ O ₃	1.0

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The process shown diagrammatically in Figure 2 is essentially the same as that of Figure 1. A natural ilmenite having associated chromite enters the oxidation stage A where the iron values associated with titanium are oxidized by air in a suitably heated reactor.

After oxidation at A the oxidized material is subjected to the deoxidation stage B in which the material is treated 105 with hydrogen or hydrogen containing gases. This results in the formation of a "synthetic" ilmenite, as described above.

The deoxidized material (which is now essentially a mixture of synthetic ilmenite and chromite) passes to the leaching stage C where it is leached with 20% aqueous hydrochloric acid. This dissolves out the ferrous iron of the synthetic ilmenite, as well as other acid-soluble non-titaniferous 115 impurities, but not the ferrous iron of the chromite, thereby leaving a titanium dioxide rich residue containing chromite. The liquid and solid phases are separated as before in liquid separator D, the aqueous ferrous 120 chloride liquor then passing to the hydrochloric acid recovery process F.

The solid product from D is washed and dried and passed to magnetic separator G, which consists of any suitable known apparatus, to effect a clean separation of the product into a non-magnetic titanium dioxide rich fraction and a magnetic chromite fraction. The up-grade may then be treated to recover titanium values by known 130

methods, whilst the chromite may be used for the recovery of chromium values.

This modification of the invention is further illustrated by the following example

5 5.

EXAMPLE 5

Samples of six ilmenite ores having associated chromite were subjected to the process of the present invention. 150 gm
10 samples were oxidized in a 4.5 cm diameter fluid bed reactor using air as the fluidizing gas for two hours at 870°C. The oxidized ore was then deoxidized by passing hydrogen through the fluid bed for five minutes
15 at 870°C. The material was cooled to room temperature in a non-oxidizing atmosphere and then leached in 400 gm of 20% hydrochloric acid under reflux conditions for three hours. The temperature of leaching was

maintained at 108-110°C and agitation was 20 provided by shaking the flask. At the end of the leaching time, the mixture was cooled, filtered, washed with water and the residue dried thoroughly. The residue was then passed through a magnetic separator to produce non-magnetic up-grade rich in titanium
25 dioxide and a magnetic fraction rich in chromite. Analysis of the products at each stage are as presented in Table 1.

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EXAMPLE 6 (Comparative Example)

A single sample of ilmenite (Ore II in Table I) was passed through a high intensity induced roll separator using progressively increased magnetic fields. The mass
35 fractions of the products of the different stages together with their analyses are given in Table II.

TABLE I

Ilmenite	Composition of Raw Material (Wt.%)				Composition after Oxidation, Deoxidation and Leaching (Wt.%)				Composition after Oxidation, Deoxidation, Leaching and Magnetic Separation (Wt.%)				Titaniferous Fraction		Chromite Fraction	
	Composition after Oxidation, Deoxidation and Leaching (Wt.%)				Composition after Oxidation, Deoxidation and Leaching (Wt.%)				Composition after Oxidation, Deoxidation, Leaching and Magnetic Separation (Wt.%)				Titaniferous Fraction		Chromite Fraction	
	TiO ₂	Fe	Cr ₂ O ₃	Cr ₂ O ₃ / TiO ₂	TiO ₂	Fe	Cr ₂ O ₃	Cr ₂ O ₃ / TiO ₂	TiO ₂	Fe	Cr ₂ O ₃	Cr ₂ O ₃ / TiO ₂	TiO ₂	Fe	Cr ₂ O ₃	Cr ₂ O ₃ / TiO ₂
Ore I	49.5	28.03	4.81	0.097	72.5	4.01	7.27	0.1	95.15	0.8	0.17	0.0017	95.15	0.8	0.17	0.0017
Ore II	51.1	32.5	1.27	0.024	91.97	1.18	2.29	0.024	97.02	0.3	0.08	0.0008	97.02	0.3	0.08	0.0008
Ore III	51.84	32.2	1.19	0.022	91.94	1.22	2.1	0.022	96.78	0.41	0.06	0.0006	96.78	0.41	0.06	0.0006
Ore IV	51.7	32.5	1.01	0.019	92.6	1.14	1.86	0.02	96.58	0.44	0.09	0.0009	96.58	0.44	0.09	0.0009
Ore V	50.19	32.8	0.88	0.017	91.82	0.91	1.7	0.018	97.52	0.39	0.17	0.0017	97.52	0.39	0.17	0.0017
Ore VI	47.36	28.5	5.65	0.119	71.69	5.94	8.35	0.116	97.7	0.4	0.05	0.0005	97.7	0.4	0.05	0.0005
	n.d. : not determined															

TABLE II

Current (amps)	Mass Fraction %	Analysis of Product (wt.%)				Cr ₂ O ₃ / TiO ₂	
		TiO ₂	Fe	Cr ₂ O ₃	Cr ₂ O ₃ / TiO ₂	Cr ₂ O ₃ / TiO ₂	
0.2	26.7	50.9	34.9	0.2	0.0039	0.0039	
0.4	61.3	51.8	33.0	1.07	0.02	0.02	
1.0	12.0	50.7	25.2	5.59	0.11	0.11	

These results show that in order to obtain ilmenite containing less than 0.2% Cr_2O_3 by magnetic separation methods, approximately 73% of the ilmenite has to be rejected. On the other hand, by the method of the present invention the production of an upgrade containing more than 95% TiO_2 and about 0.1% Cr_2O_3 is achieved with the loss of as little as about 1% of the TiO_2 values.

- It will be appreciated that further modifications may be made to the procedure just described. For example, it will be apparent, and it has been demonstrated, that the basis for upgrading by magnetic methods may be applicable to ilmenites containing other iron-containing impurities which are not associated with titanium, e.g., silicates, whose stability is such that their iron content is sensibly unchanged during the oxidation, deoxidation and leaching operations of the upgrading process.

EXAMPLE 7

- The upgraded material obtained in Example 3, after passage through a magnetic separator, produced in a non-magnetic fraction significantly richer in titanium dioxide than the original upgraded material. Analysis of the non-magnetic fraction was as follows:—

	TiO_2	92.26%
	Fe_2O_3	1.7 %
	Cr_2O_3	0.01%
35	MgO	0.17%
	Al_2O_3	0.79%

WHAT WE CLAIM IS:—

1. A process for the treatment of titaniferous ore comprising the steps of oxidising substantially all of the iron values associated with titanium in the ore to the ferric state; and deoxidizing substantially all (as herein defined) of said iron values to the ferrous state or ferrous and metallic states, the amount of said iron values in the metallic state following the deoxidation not exceeding 20% w/w of the ore.
2. A process as claimed in claim 1, wherein the deoxidation is carried out so that substantially all of said iron values are deoxidised to the ferrous state.
3. A process as claimed in claim 1 or claim 2, wherein the oxidation is carried out at a temperature below that at which sintering of the ore occurs.
4. A process as claimed in any one of the preceding claims, wherein oxidation of the ore is carried out by contacting the ore with an oxidant comprising gaseous oxygen, a mixture of oxygen with at least one other gas which is inert under the reaction conditions, or a compound containing oxygen and which is capable of oxidising iron to the ferric state under the reaction conditions.

5. A process as claimed in claim 4, wherein the oxidant is atmospheric air.

6. A process as claimed in any one of the preceding claims, wherein the deoxidation is carried out by contacting the oxidised ore with a reductant comprising hydrogen, carbon monoxide, hydrocarbon gases, or a mixture containing any two or more of these gases.

7. A process as claimed in claim 6, wherein the reductant is hydrogen.

8. A process as claimed in claim 5 or claim 6, wherein the deoxidation step is carried out at a temperature of from 850°C., to 900°C.

9. A process for producing an upgrade material rich in titanium dioxide from a titaniferous ore which comprises carrying out the process of any one of claims 1 to 8, and leaching the thus treated ore to remove substantially all of the iron values therefrom.

10. A process as claimed in claim 9, wherein the ore is leached with acid.

11. A process as claimed in claim 10, wherein the acid is hydrochloric acid.

12. A process as claimed in claim 9, wherein the treated ore is leached with hydrochloric acid of 20% w/w concentration at a temperature of from 105°C., to 110°C.

13. A process as claimed in any of claims 9 to 12, wherein the ore contains magnetic materials and wherein after leaching the ore is subjected to a magnetic separation treatment, to remove substantially all of the magnetic materials from the ore.

14. A process as claimed in any one of claims 9 to 12, wherein the ore contains a chromium-containing mineral, and wherein after leaching the ore is subjected to a magnetic separation treatment, to remove substantially all of the chromium-containing mineral from the ore.

15. A process for the production of an upgrade material rich in titanium dioxide substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.

16. A process for the production of an upgrade material rich in titanium dioxide substantially as hereinbefore described with reference to Figure 2 of the accompanying drawings.

17. A process for the treatment of a titaniferous ore involving the steps of oxidation and deoxidation substantially as hereinbefore described with reference to any one of Examples 1 to 4 excluding the leaching step.

18. A process for the treatment of titaniferous ores substantially as hereinbefore described with reference to Examples 5.

19. A process for producing an upgrade material rich in titanium dioxide substantially as hereinbefore described with reference

- These results show that in order to obtain ilmenite containing less than 0.2% Cr_2O_3 by magnetic separation methods, approximately 73% of the ilmenite has to be rejected. On the other hand, by the method of the present invention the production of an upgrade containing more than 95% TiO_2 and about 0.1% Cr_2O_3 is achieved with the loss of as little as about 1% of the TiO_2 values.
- It will be appreciated that further modifications may be made to the procedure just described. For example, it will be apparent, and it has been demonstrated, that the basis for upgrading by magnetic methods may be applicable to ilmenites containing other iron-containing impurities which are not associated with titanium, e.g., silicates, whose stability is such that their iron content is sensibly unchanged during the oxidation, deoxidation and leaching operations of the upgrading process.

EXAMPLE 7

- The upgraded material obtained in Example 3, after passage through a magnetic separator, produced in a non-magnetic fraction significantly richer in titanium dioxide than the original upgraded material. Analysis of the non-magnetic fraction was as follows:—

	TiO_2	92.26%
	Fe_2O_3	1.7 %
	Cr_2O_3	0.01%
35	MgO	0.17%
	Al_2O_3	0.79%

WHAT WE CLAIM IS:—

1. A process for the treatment of titanium ore comprising the steps of oxidising substantially all of the iron values associated with titanium in the ore to the ferric state; and deoxidizing substantially all (as herein defined) of said iron values to the ferrous state or ferrous and metallic states, the amount of said iron values in the metallic state following the deoxidation not exceeding 20% w/w of the ore.
2. A process as claimed in claim 1, wherein the deoxidation is carried out so that substantially all of said iron values are deoxidised to the ferrous state.
3. A process as claimed in claim 1 or claim 2, wherein the oxidation is carried out at a temperature below that at which sintering of the ore occurs.
4. A process as claimed in any one of the preceding claims, wherein oxidation of the ore is carried out by contacting the ore with an oxidant comprising gaseous oxygen, a mixture of oxygen with at least one other gas which is inert under the reaction conditions, or a compound containing oxygen and which is capable of oxidising iron to the ferric state under the reaction conditions.
5. A process as claimed in claim 4, wherein the oxidant is atmospheric air.
6. A process as claimed in any one of the preceding claims, wherein the deoxidation is carried out by contacting the oxidised ore with a reductant comprising hydrogen, carbon monoxide, hydrocarbon gases, or a mixture containing any two or more of these gases.
7. A process as claimed in claim 6, wherein the reductant is hydrogen.
8. A process as claimed in claim 5 or claim 6, wherein the deoxidation step is carried out at a temperature of from 850°C., to 900°C.
9. A process for producing an upgrade material rich in titanium dioxide from a titaniferous ore which comprises carrying out the process of any one of claims 1 to 8, and leaching the thus treated ore to remove substantially all of the iron values therefrom.
10. A process as claimed in claim 9, wherein the ore is leached with acid.
11. A process as claimed in claim 10, wherein the acid is hydrochloric acid.
12. A process as claimed in claim 9, wherein the treated ore is leached with hydrochloric acid of 20% w/w concentration at a temperature of from 105°C., to 110°C.
13. A process as claimed in any of claims 9 to 12, wherein the ore contains magnetic materials and wherein after leaching the ore is subjected to a magnetic separation treatment, to remove substantially all of the magnetic materials from the ore.
14. A process as claimed in any one of claims 9 to 12, wherein the ore contains a chromium-containing mineral, and wherein after leaching the ore is subjected to a magnetic separation treatment, to remove substantially all of the chromium-containing mineral from the ore.
15. A process for the production of an upgrade material rich in titanium dioxide substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.
16. A process for the production of an upgrade material rich in titanium dioxide substantially as hereinbefore described with reference to Figure 2 of the accompanying drawings.
17. A process for the treatment of a titaniferous ore involving the steps of oxidation and deoxidation substantially as hereinbefore described with reference to any one of Examples 1 to 4 excluding the leaching step.
18. A process for the treatment of titaniferous ores substantially as hereinbefore described with reference to Examples 5.
19. A process for producing an upgrade material rich in titanium dioxide substantially as hereinbefore described with reference



to any one of examples 1 to 4 including the leaching step.

- 5 20. A titaniferous ore product:
- 10 (i) displaying the X-ray powder diffraction pattern of ilmenite;
- (ii) in which substantially all (as herein defined) of the iron values originally associated with the titanium in the ore therein are in the ferrous state or ferrous and metallic states;
- 15 (iii) containing not more than 20% w/v of metallic iron; and
- (iv) which is in a reactive state such that said iron values which are in the ferrous state or ferrous and metallic states can be leached out by treatment with 20% w/w hydrochloric

acid at 108°C to 110°C and atmospheric pressure.

21. A titaniferous ore product whenever produced by the process of any of claims 1 to 8 and 17 and, excluding the leaching step, claims 15 and 16.

22. A titaniferous ore product whenever produced by the process of any of claims 9 to 16, 18 and 19.

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