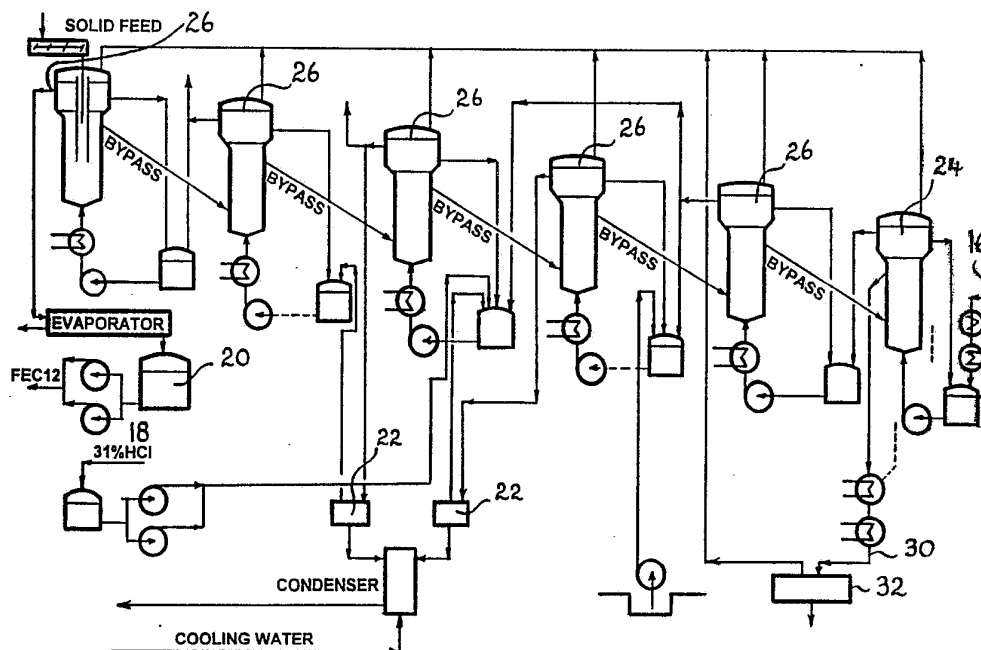




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(54) Title: CONTINUOUS LEACHING OF TREATED TITANIFEROUS ORES WITH ALCOHOL SOLUTIONS



(57) Abstract

The continuous leaching of treated titaniferous ores with alcohol solutions. In particular, the invention forms a part of a process for the beneficiation of titaniferous ores to produce a product high in titanium dioxide, and low in other metal oxides, which is suitable for use as a pigment, or is suitable for the subsequent production by chlorination of titanium dioxide pigments, or for the production of titanium metal.

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"CONTINUOUS LEACHING OF TREATED TITANIFEROUS ORES WITH ALCOHOL SOLUTIONS"

THIS INVENTION relates to the continuous leaching of treated titaniferous ores with alcohol solutions. In particular, the invention forms a part of a process for the beneficiation of titaniferous ores to produce a product high in titanium dioxide, and low in other metal oxides, which is suitable for use as a pigment, or is suitable for the subsequent production by chlorination of titanium dioxide pigments, or for the production of titanium metal.

Several methods exist to produce a product high in titanium dioxide suitable for such uses. However, these existing methods generally rely on a specific feedstock which, in most cases, is itself of a high titanium dioxide level (such as the mineral "rutile"). The present invention relates to the production of the same product but from a relatively low grade feedstock (such as the mineral "ilmenite").

One of the first processes developed during the 1960's and 1970's to upgrade ilmenite to a product containing 95 to 96% titanium dioxide was the Murso process, the subject of United Kingdom Patent 1225826. The purity of the product (which came to be known as "synthetic rutile") together with its particle size and chlorination characteristics was such that it could successfully substitute for natural rutile in its conventional uses. Furthermore, initial tests using the Murso process indicated that it could be applied successfully to all commercial ilmenites whether they be in the form of beach sands or rock deposits.

Commercial grades of ilmenite generally contain about 46 to 65% titanium dioxide combined with 30 to 45% iron oxides. In upgrading ilmenite, iron oxides (and oxides of manganese and magnesium which substitute for iron oxides in the

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ilmenite lattice) have to be removed if the required quality is to be obtained. The Murso process achieves this desired quality in six major steps:

1. Oxidation
2. Reduction
3. Leaching of the reduced product
4. Solid-liquid separation
5. Drying - Calcination
6. Recovery and recycling of hydrochloric acid from ferrous chloride liquors.

The breakthrough of the Murso process was generally in the use of the initial oxidation and reduction steps. Referring firstly to the oxidation step, titaniferous ores such as ilmenite contain a mixture of ferrous and ferric oxide. Thus, the oxidation stage heats the material in a fluid bed or rotary kiln in the presence of excess atmospheric air. This treatment was required to ensure that all the ferrous oxide was converted to the ferric oxide form. There is then a crystal structure change that is beneficial to the following reduction stage.

During the reduction stage the oxidised ore is reduced using either a solid or gaseous reducing agent to convert the ferric iron to the ferrous stage without continuing to the formation of metallic iron. This conversion reaction makes the ore more amenable to the following leaching process which utilises hydrochloric acid.

In the reduced state, the ore is preferably leached using a hydrochloric acid solution. However, various improvements to the Murso process have resulted in (amongst other things) the addition to the leachate of metal chlorides, such as ferrous chloride, to facilitate the leach process.

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At the completion of the leach cycle the solids are filtered from the spent acid liquors and are washed with water and refiltered to remove the excess water. The final step of recovering hydrochloric acid from ferrous chloride liquors is then undertaken to produce fresh hydrochloric acid which is recycled to the leach step, together with solid iron oxide which may be used as a feed material in the iron industry.

The Murso process, together with the various variations thereon, has not been successfully commercialised on a large scale. This is due mainly to the poor economics of the process as a result of significant difficulties with the leaching step and the acid regeneration stage. Accordingly, an aim of the present invention is to overcome, or at least partly alleviate, some of the difficulties with the leaching step. In this respect, a further solution to these problems has been described in our copending application titled "Continuous Leaching of Treated Titaniferous Ores With Inter-Stage Evaporation", while difficulties that are also encountered in the acid regeneration stage, which themselves contribute to the poor economics of the original process, are described in a further copending application titled "Acid Washing of Leached Solids from the Beneficiation of Titaniferous Ores".

The present invention provides a process for the continuous leaching of treated titaniferous ores, said process comprising subjecting a treated titaniferous ore to an acid leach wherein an alcohol species is added to the leachate.

In particular, the present invention provides a process comprising subjecting synthetic ilmenite to an acid leach, the synthetic ilmenite having been produced by oxidising substantially all iron values associated with titanium in a titaniferous ore to the ferric state and by then reducing

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substantially all of the iron values to the ferrous state, wherein an alcohol species is added to the leachate.

The addition of the alcohol species allows for lower temperatures to be used during leaching due to the leach operating at a lower boiling point. For example, if ethanol is substituted for the water component in the leach, the boiling point will be about 94°C compared with a 20% hydrochloric acid/water mixture which boils at 108°C. Furthermore, a wider choice of plastic materials may be used in equipment construction.

While ethanol is here used as an example of a suitable acid, and indeed ethanol is the preferred alcohol, other alcohols such as methanol and ethylene glycol may be used. Ethanol is the preferred alcohol as it has been found to be particularly effective in lowering the reaction temperature.

Further still, the use of an alcohol/acid solution allows for the economic multiple re-crystallisation of the ferrous chloride liquors to produce an iron oxide product after acid regeneration that is of sufficient high purity as to possibly command a market premium.

The addition of an alcohol species is most preferably used in conjunction with the use of small inter-stage evaporators located between the leach stages. The combination of the alcohol species and the inter-stage evaporators assists in providing an optimum balance between acid strength and ion concentration over several stages of leaching with only the water component produced by the reaction being removed. The use of more than one evaporator and only removing a small portion of the water at each stage is also the most energy efficient method of evaporation.

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The purpose of the leaching in the overall process is to dissolve selectively iron and other metal oxides from the ilmenite lattice with a minimum loss of titanium values. However, some titanium does go into solution and a certain amount of it is subsequently precipitated from the solution as a fine material. Thus, the main factors which affect the rate of leaching, production of fines, titanium dissolution and its hydrolysis are acid concentration, mixing velocity and leaching temperature. Both high acid concentration and high temperature favour higher rate of leaching. However, other factors such as titanium loss in solution, reduction of fines, materials of construction for leaching vessels, and economic recovery of hydrochloric acid influence the choice of acid strength, temperature of leaching and the method of mixing.

With this in mind, the original Murso process found the optimum conditions for leaching to be 20% hydrochloric acid and a temperature of 108 to 110°C at atmospheric pressure in a fluid bed contactor. Subsequent variations to the Murso process discuss the merits of using a leachate with an increased chloride ion concentration over a hydrochloric acid solution but fail to describe a mechanism for maintaining constant chloride concentrations in a continuous operation.

As it is also preferable to maintain the acid concentration at a maximum during the leach cycle to prevent the formation of fine material and to maintain a high rate of iron dissolution, the substitution of the water component with an alcohol species and the removal of water produced during the reaction, by the preferred use of the inter-stage evaporators, assists in maintaining the high level of chloride ion concentration even towards the completion of the leach cycle when most of the acid has been depleted. In this respect, weak acid solutions extend the leach

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period and promote the formation of fine material, both of which are undesirable.

A further advantage of maintaining a high level of chloride ion concentration in the leach liquor is gained in the improved energy efficiency of the acid regeneration stage where a lower concentration of water requires less energy in the evaporation stages.

The present invention will now be more specifically described in relation to a preferred embodiment. However, it will be understood that the generality of the invention as described above is not to be limited by the following description. To assist in this description, reference should be made to the flow diagrams of Figures 1 and 2.

A low grade titaniferous ore such as ilmenite containing a mixture of ferrous and ferric oxide is subjected to temperatures in the order of 850 to 1000°C in the presence of excess air in a fluid bed or rotary kiln (oxidation reactor 10) for periods of one or more hours. Substantially all of the ferrous oxide is converted to the ferric oxide form and the ilmenite undergoes a crystal structure change that is beneficial to the following reduction stage.

The oxidised ore is then reduced (at reduction reactor 12) using either a solid reducing agent such as carbon or a gaseous reducing agent such as carbon monoxide, hydrocarbon gases, hydrogen or mixtures of these, to convert the ferric iron to the ferrous state without continuing to the formation of metallic iron. Conversion of the oxidised product to the synthetic ilmenite is relatively rapid and efficient when carried out by hydrogen at 850 to 900°C. The reduction step makes the synthetic ilmenite more amenable to the leaching process to be conducted with hydrochloric acid.

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The synthetic ilmenite is then preferably leached in a counter current fluid bed system (indicated at 14 in Figure 1 and in detail in Figure 2) using a 15 to 20% hydrochloric acid solution containing 15 to 25% ferrous chloride at temperatures between 90 and 110°C. This solution is made up by a combination of the fresh acid 16, the alcohol containing acid 18 and the ferrous chloride solution 20, and enters the system primarily through the acid wash 24.

An alcohol species is added to allow for lower temperatures to be used during leaching and to enhance the process economics as less energy is required to achieve the required chloride balance throughout the leach cycle. The alcohol species, preferably ethanol, is added to the fresh 31% hydrochloric acid 18 as a dilutant to form the 20% hydrochloric acid solution required.

Furthermore, the alcohol species added is preferably substantially removed from the leachate by evaporation prior to the leachate being processed in the following acid regeneration stage. In this preferred form, allowance is made for a leachate nearly saturated in ferrous chloride to be regenerated again.

Two small inter-stage evaporators 22 are also preferably located between various leaching stages to assist in maintaining an optimum balance between acid strength and ion concentration and to thus give an improvement in leach kinetics. The removal of water in this way is also advantageous in later stages of the process due to a lower amount of energy being needed to evaporate the remaining water. However, it will be appreciated that the use of the inter-stage evaporators is not essential for this invention.

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Vacuum flash evaporators are preferably used to ensure an acceptable efficiency of separation of water and acid between leaching stages. These evaporators and their associated condensers enable 14% acid to be evaporated to 16% acid with little loss of acid to the condensate. The size of the evaporators will of course be dependent upon plant capacity and solution throughput.

It will also be appreciated that while the number of leach stages 26 illustrated is five, the actual number required is governed by the residence time required for complete dissolution of the iron and other metal oxides. For example, reaction times have been found to vary from one hour to six hours, depending on the feedstock, and as such the number of leach stages needed has varied from three to eight. Furthermore, the number of evaporators used is generally dependent upon the number of leach stages.

An acid washing stage 24 preferably concludes the leach cycle and is preferably a counter current acid washing stage in a vessel similar to the leach vessels 26. As the fresh acid used in the acid wash is only marginally diluted with residual ferrous chloride from the leached solids, the wash acid from this stage advantageously becomes the feed acid to the leach circuit (via stream 28). It will be appreciated that this acid wash, and also the acid leach, may be conducted in any known manner that is appropriate, using any type of process and apparatus. In particular, counter-current or co-current operations may be used, or mechanical agitation or the like may be adapted.

The solids exiting from the acid wash 24 in stream 30 are then separated from the wash acid by filtration 32 and the filtrate is returned to the wash acid stage. Thus, the now semi dried solids are dried 34 at controlled temperatures up to 400°C either in a fluid bed or rotary kiln to remove

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any contained acid, while the acid vapour is passed through recovery scrubbers 36.

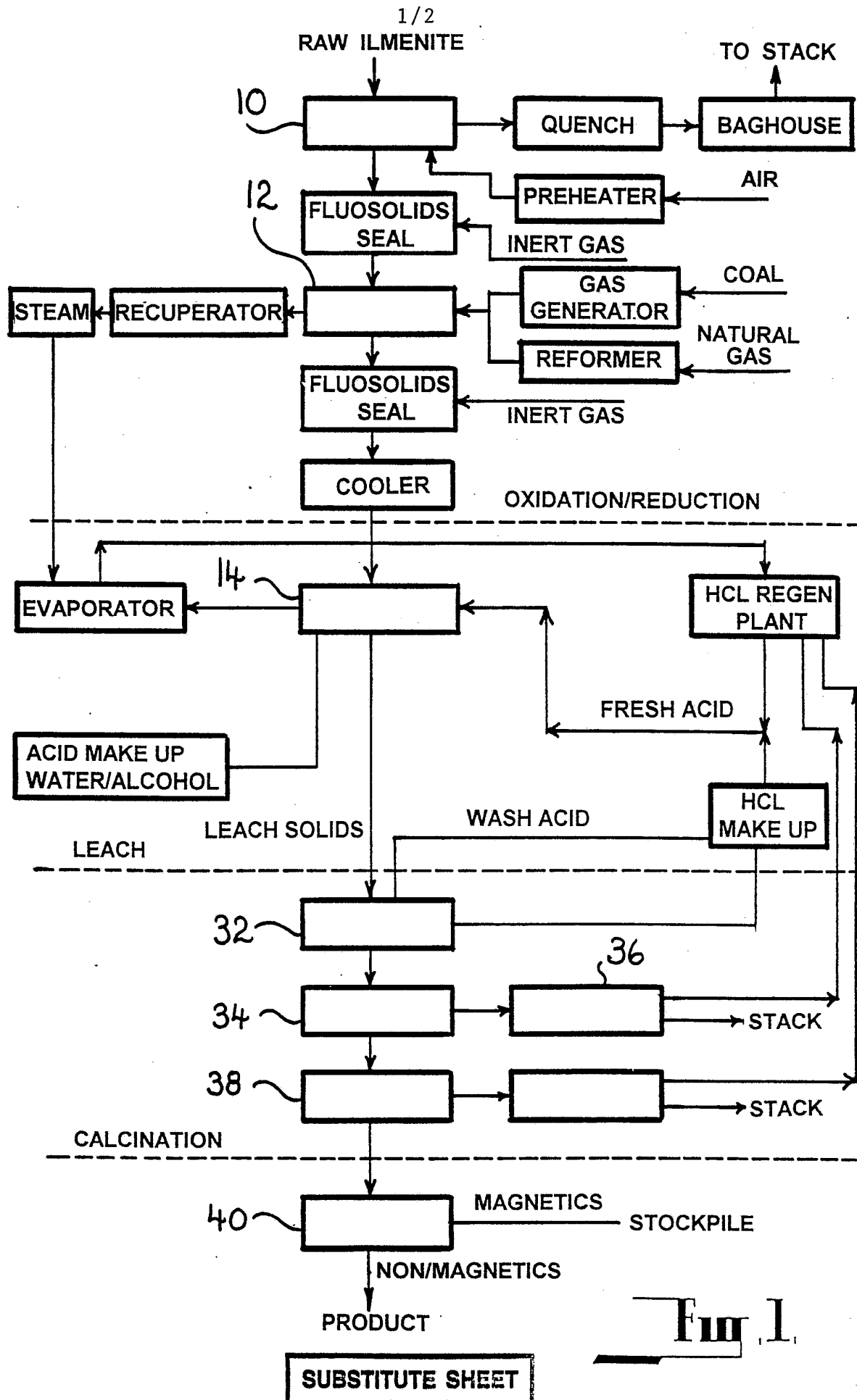
The calcination process 38 for the dried solids is then conducted at 800 to 850°C for a period of 30 to 60 minutes to stabilise the crystal structure and to remove any final traces of moisture, iron chloride and hydrochloric acid. After cooling from the calcination stage the solid material can be passed through a magnetic field 40 to remove any incompletely leached material or any other magnetic material not effected by the acid leach. The non magnetic fraction is recovered as the synthetic ilmenite product.

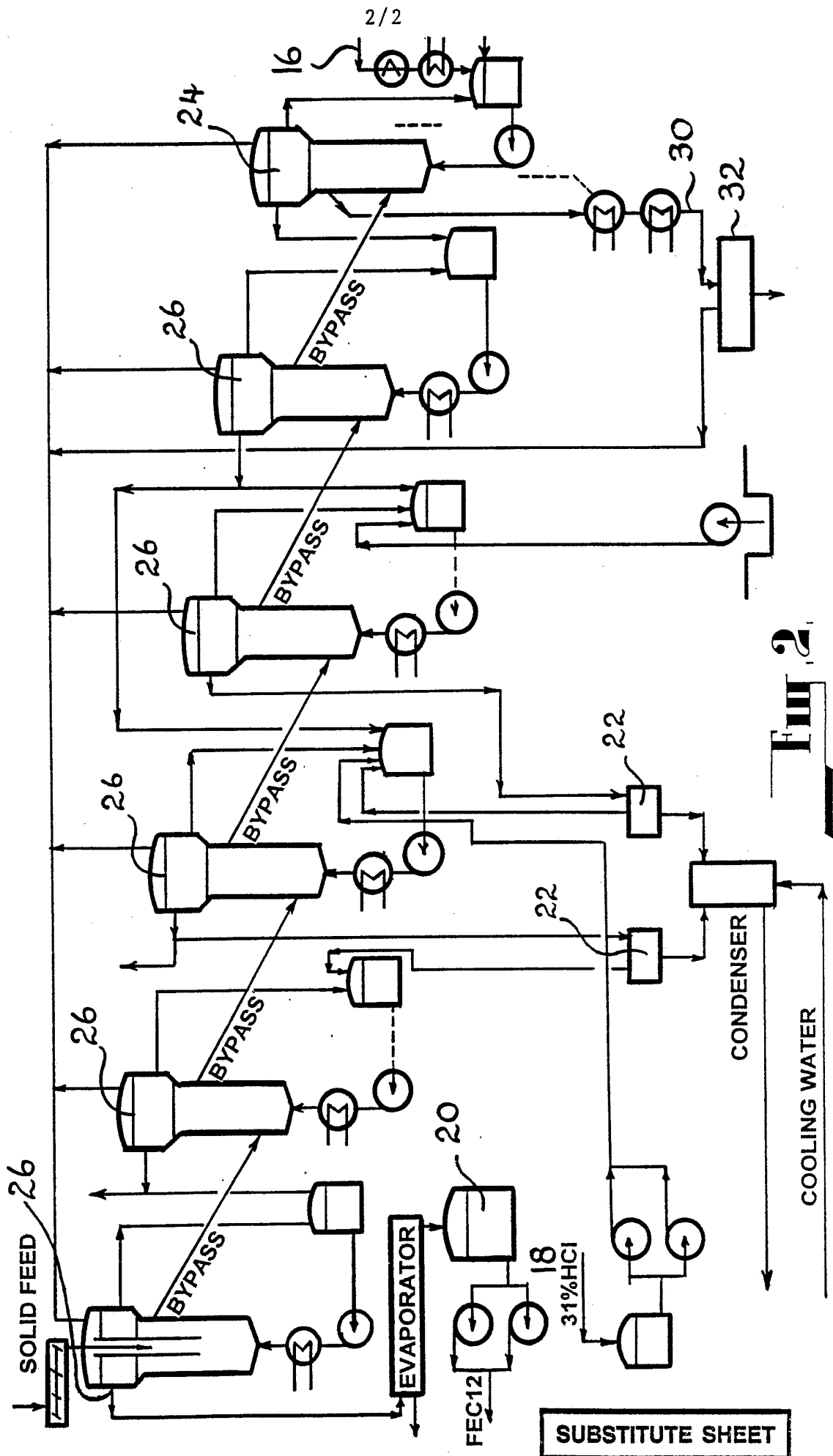
Those skilled in the art will appreciate that there may be many variations and modifications of the processes described herein which are within the scope of the present invention.

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CLAIMS

1. A process for the continuous leaching of treated titaniferous ores, said process comprising subjecting a treated titaniferous ore to an acid leach wherein an alcohol species is added to the leachate.
2. A process according to claim 1 wherein the alcohol species is selected from the group of ethanol, metanol and ethylene glycol.
3. A process according to claim 1 or claim 2 including the use of small inter-stage evaporators between leach stages.
4. A process for the continuous leaching of treated titaniferous ores, said process comprising subjecting synthetic ilmenite to an acid leach, the synthetic ilmenite being produced by oxidising substantially all iron values associated with titanium in a titaniferous ore to the ferric state and by then reducing substantially all of the iron values to the ferrous state, wherein an alcohol species is added to the leachate.
5. A process for the continuous leaching of treated titaniferous ores, said process comprising oxidising substantially all iron values associated with titanium in a titaniferous ore to the ferric state, reducing substantially all of the iron values to the ferrous state to produce synthetic ilmenite, and subjecting the synthetic ilmenite to an acid leach wherein an alcohol species is added to the leachate.
6. A process according to claim 1 substantially as herein described in relation to the accompanying drawings.

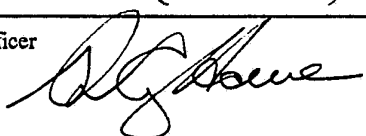


**SUBSTITUTE SHEET**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU93/00096

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁵ C22B 3/06, 3/16 // C22B 34:12					
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols) IPC C22B 3/00, 3/06, 3/16, 3/10, 34/12, 53/00					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU : IPC as above					
Electronic data base consulted during the international search (name of data base, and where practicable, search terms used) Derwent : C22B and (Ti or Titanium) and leach: JAPIO : C22B and (Ti or Titanium) and leach: Chem Abs : (Ti or Titanium) and leach: and (alcohol or methanol or ethanol or glycol)					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.			
X	The Aus IMM Bulletin and Proceedings, Volume 291, No.5, issued July 1986, I. Girgin and L. Türker, "Hydrochloric acid leaching of ilmenite - effect of alcohol species", pages 61-64 Whole document	1,2,4,5			
X	International Journal of Mineral Processing, Vol.24, issued 1988 (Elsevier, Amsterdam), I. Girgin, L. Türker, D. Goodall, "The Dissolution of Ilmenite in HCl-H ₂ O, HCl-CH ₃ OH and HCl-C ₂ H ₅ OH Systems - A Theoretical Approach", pages 173-184 Whole document	1,2,4,5			
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.					
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; vertical-align: top;"> * Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 10%; vertical-align: top; text-align: center;"> "T" "X" "Y" "&" </td> <td style="width: 60%; vertical-align: top;"> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family </td> </tr> </table>			* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
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Date of the actual completion of the international search 9 June 1993 (09.06.93)		Date of mailing of the international search report 17 JUNE 1993 (17.06.93)			
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929		Authorized officer  VIVIENNE THOM Telephone No. (06) 2832157			

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
A	GB,A, 1225826 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 24 March 1971 (24.03.71) Page 4 line 123 - page 5 line 39	1-6
A	WO,A, 90/10721 (BUTLER) 20 September 1990 (20.09.90) Page 4 line 31 - page 5 line 2 and claim 10	1,2,4,5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU93/00096

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
GB	1225826	DE	1758261	DK	131477	FI	49182
		FR	1575768	US	3597189		
WO	90/10721	AP	151	AU	52606/90	BR	9007193
		CA	2045551	CN	1046942	GB	2248631
		GR	90100161	NZ	232793	US	5215575
		ZA	9001703				