United States Patent [19]

Oster

[11] **3,787,139**

[45] **Jan. 22, 1974**

[54] **PROCESS FOR THE PREPARATION OF TITANIUN CONCENTRATES FROM IRON-CONTAINING TITANIUM ORES**

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[22] Filed: **Oct. 15, 1971**

[21] Appl. No.: **189,602**

Related U.S. Application Data

[63] Continuation of Ser. No. 808,197, March 18, 1969, abandoned.

[30] **Foreign Application Priority Data**

Mar. 26, 1968 France 68.1860

[52] **U.S. Cl.** .... **423/610,** 423/82, 423/86, 423/493, 75/101 R

[51] **Int. Cl.** **C01g 23/04**

[58] **Field of Search** .... 423/610, 493, 85, 86, 82; 106/300; 23/202 R; 75/101 R

[56] **References Cited**

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[57] **ABSTRACT**

A titanium concentrate is made from an ilmenite or other iron-containing titanium ore by treatment with aqueous hydrochloric acid of the azeotropic concentration while maintaining this concentration by continuously removing excess water by distillation. Preferably, when as much iron as practicable or desired has dissolved, the distillate is returned, or water from some other source added, to the mixture, which is then boiled further for a short time under total reflux to precipitate titanium which may have dissolved.

9 Claims, 2 Drawing Figures

FIG.1.

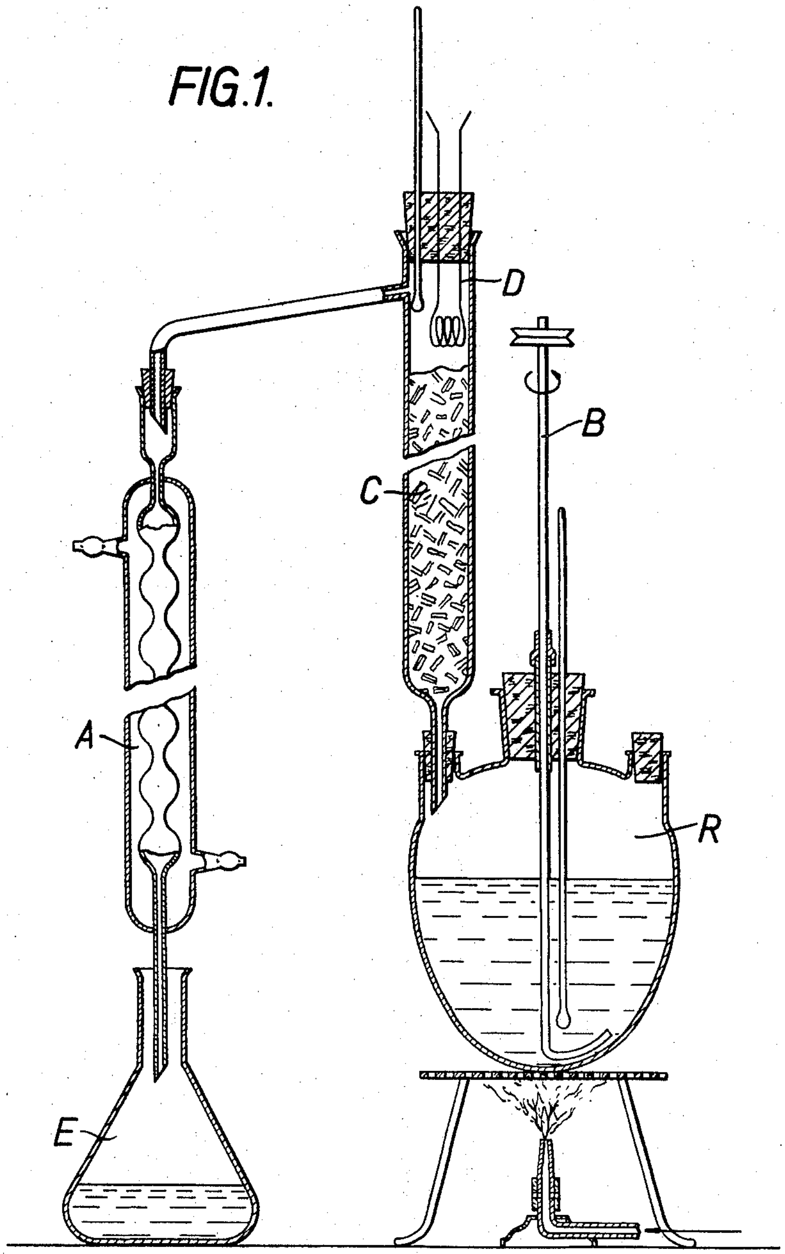

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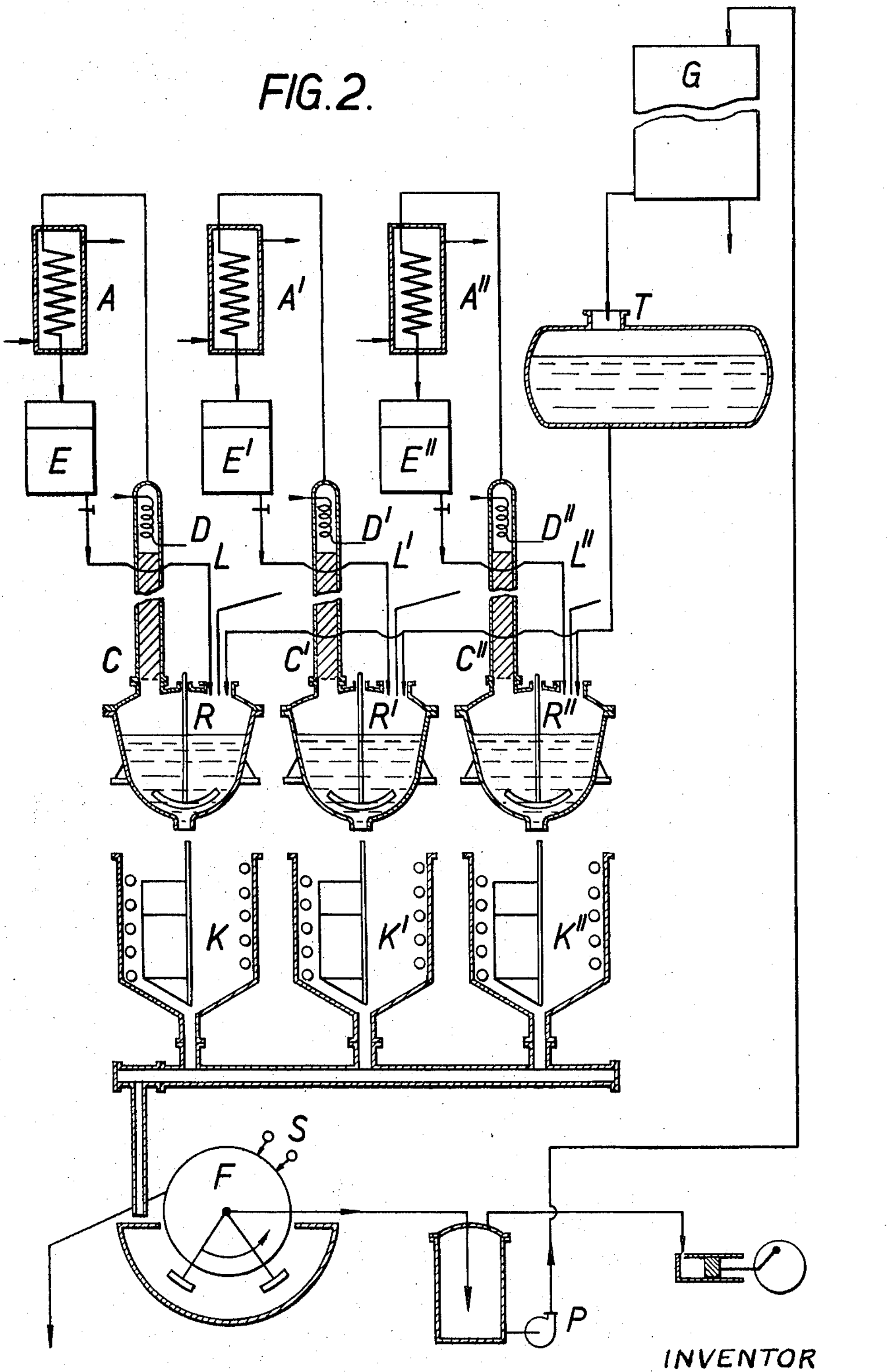
FIG. 2.



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PROCESS FOR THE PREPARATION OF TITANIUN CONCENTRATES FROM IRON-CONTAINING TITANIUM ORES

This is a continuation of application Ser. No. 808,197, filed Mar. 18, 1969 and now abandoned.

The present invention relates to a process for concentrating titanium ores having a basis of titanium dioxide and iron oxide.

It has long been known to prepare concentrates of titanium dioxide from these ores. Such concentrates are useful as starting materials in industry, particularly for the preparation of titanium tetrachloride and titanium metal.

For this reason a series of processes has been developed for the concentration of titanium dioxide in the ores, either in a single stage or in several stages. These processes are either thermal or chemical. In the chemical processes, the iron oxides are selectively dissolved, usually with sulphuric or preferably hydrochloric acid under conditions such that the titanium dioxide is not attacked.

Hydrochloric acid has been used in different ways for this deferrization of titanium ores, particularly of different types of ilmenites. By way of example, by treating a sand containing from 40 percent to 60 percent of titanium dioxide, it has been possible to obtain concentrates containing more than 90 percent thereof. A wide variety of methods, proportions and concentrations of hydrochloric acid have been used.

The quantity of hydrochloric acid and its concentration are determining factors for the selective solution of the iron in the ilmenites. Thus concentrated (35 percent) hydrochloric acid is less suitable for the selective solubilization of the iron of the ilmenites than it is for complete solubilization of both iron and titanium.

In order therefore to avoid as far as possible the dissolution and consequent loss of titanium, it is necessary to use a less concentrated hydrochloric acid. In recent times particular attention has been paid to the azeotropic hydrochloric acid containing 20.24 percent of HC1 because this acid does not have the disadvantageous property of liberating the troublesome hydrogen chloride gas, as does the more concentrated acid.

U. S. Pat. No. 1,325,561 describes incomplete deferrization of the titanium ores by treating them, after previous crushing, at 70°–80° C. and for 12 hours with three times their weight of 20 percent hydrochloric acid. Likewise British Pat. No. 409,847 describes treating the finely crushed ilmenite with hydrochloric acid at 50°–60° C. for the excessively long period of 2 to 3 days, and then raising the temperature to 85°–95° C. to precipitate the titanium dioxide which has also been dissolved.

To facilitate these treatments and improve the results obtained, the ore may be given a preliminary thermal reduction. Thus according to U. S. Pat. No. 2,127,247, ilmenite is mixed with carbon and heated between 500° and 800° C. to ensure that the ferric iron is reduced to ferrous iron after which the ferrous compounds are extracted with a dilute acid which does not attack the titanium dioxide. Such processes are not very economic, and moreover it is preferred to attack the titanium ore directly with the hydrochloric acid, without any previous treatment other than the crushing.

More recently S. Wilska (Chemische Technik 14, 1962, No. 2, pages 103 to 106) has shown that it is not absolutely necessary to effect a preliminary crushing of the ore. However he used 36 percent hydrochloric acid and not the 20.2 percent azeotropic hydrochloric acid, and attempted but without much success, to promote the hydrolytic precipitation of the titanium dissolved by this concentrated acid by adding titanium hydroxide nuclei to the reaction mixture. When he used azeotropic hydrochloric acid in the most favourable case only 91.3 percent of iron was eliminated, and 4.2 percent of titanium dioxide was lost, after 14 hours of reaction. (As will be shown, corresponding figures obtainable by using the process of the present invention are 96.29 percent of iron extracted and 0.84 percent of titanium dioxide lost, after only 12 hours of reaction). For an industrial deferrization, Wilska proposes to carry out the operation in three steps with countercurrent extraction of the ore with the acid, but this increases the loss of acid and triples the cost of the installation.

An object of the present invention is to provide a process for the deferrization of titanium ores which is both rapid and capable of giving concentrates with a high titanium dioxide content with small losses of titanium, without the necessity of a preliminary treatment of the ore apart from crushing as necessary.

The invention comprises a process for the production of titanium dioxide concentrates from iron-containing titanium ores, particularly from various types of ilmenites, by the action of azeotropic hydrochloric acid on the ore, in which the titanium ore is treated with hydrochloric acid of concentration which initially is not substantially above the azeotropic concentration, in amount at least twice the quantity theorectically needed to transform all the iron in the ore into iron chloride and maintaining the concentration of the free hydrochloric acid substantially at the azeotropic level for at least the major part of the duration of the reaction by continuously distilling off excess water and water formed in the process.

The initial concentration of the acid is preferably either at or a little below the azeotropic level, so that the latter is rapidly reached in the early stages of the treatment. A preferred method of carrying out the above process, comprises first boiling the reaction mixture under total reflux for 1½ hours from the commencement of the heating and then continuing the boiling under running conditions for the fractional distillation of the said excess water, usually for about 11½ hours from the commencement of the heating. At the end of this time water is added to precipitate by hydrolysis such titanium dioxide as has dissolved, the amount of water added being nearly equivalent to that which has been eliminated by distillation, and boiling is continued for another half an hour or so under complete reflux, as at the start.

According to one preferred embodiment of the invention, the water which has distilled off in the main reaction is returned to the mixture for the final boiling under reflux; this has the double advantage of recovering such small quantities of hydrochloric acid as may have been entrained in this distillation, and also of saving heat, to which end the distillate is preferably condensed at as high a temperature as possible.

The reaction mixture is then cooled to separate it into a solid and a liquid phase, the solid titanium dioxide concentrate is washed first with azeotropic hydrochloric acid and then with water and then according to circumstances, dried and calcined, and the liquid phase is treated to recover the hydrochloric acid for re-use.

The invention comprises also equipment for carrying the above process into effect which comprises a plurality of reaction vessels each provided with an agitator, and with discharge means at the bottom, a fractionating column communicating with the upper part of each reaction vessel, means for adjusting the reflux rates in each column from 100 percent downwards and capable of causing the column to separate material of boiling point 100° C. from material of boiling point 110° C., a condenser communicating with the upper end of each column, a reservoir adapted to receive and store liquid from each of said condensers, and a valved conduit from each such reservoir to the upper part of the corresponding reaction vessel.

Equipment according to the invention is illustrated in the accompanying drawings, in which

FIG. 1 shows diagrammatically a laboratory apparatus, and

FIG. 2 shows diagrammatically a plant-scale installation.

Like indicia refer to corresponding integers in the two Figures.

Referring now to the drawings the device illustrated in FIG. 1 comprises a reactor R equipped with an agitator B and connected by a distillation column C provided with a dephlogmator D to a condenser A for condensing the aqueous distillate; the condensate is collected in a receptacle E.

The industrial installation illustrated in FIG. 2 comprises three reactors R, R', R'' with their agitators and three distillation columns C, C', C'' with the corresponding dephlegmators D, D', D'' connected to condensers A, A', A'', which are themselves connected to storage reservoirs E, E', E'' receiving the aqueous distillates; the reservoirs in turn communicate with the corresponding reactors by return conduits L, L', L''. The reaction products can be transferred from the reactors R, R', R'' into coolers K, K', K'' which all feed to a single separating plant F, in which the product is separated into a liquid and a solid phase. The liquid phase can be forwarded by a pump P to an acid regenerating plant G, which is connected to a reservoir T for the storage of azeotropic hydrochloric acid.

The invention makes it possible to dispense with a preliminary reduction treatment of the ore, and at the same time to use an azeotropic hydrochloric acid which does not liberate any harmful and corrosive hydrogen chloride gas. In addition, the used acid can easily be regenerated by methods such as the Ruthner process, which permits the simultaneous recovery of the free acid and acid combined with iron in the deferrization liquor.

Furthermore, the process of the invention can be carried out in a single stage lasting only about **12** hours, the speed of reaction always being kept high. While ferric iron is generally extracted less well than ferrous iron, its preliminary reduction, as already stated, is not necessary. Operation in a single stage means that the installation can be very much simplified and cheapened. As regards effectiveness, concentrates can be obtained which have titanium dioxide contents substantially exceeding 90 percent, the losses of titanium being very small.

While the deferrization has been found to proceed better when the amount of hydrochloric acid present exceeds the stoichiometric ratio, it is evident that the excess acid must be limited in amount so as not to cause an inordinate increase in the number of tanks which are used and in the surface of the acid recovery installation. The solution of the iron oxides causes a progressive lowering of the concentration of free hydrochloric acid in the reaction medium below the azeotropic value. This fall slows down the rate of the deferrization, which however, at the boiling point, remains industrially acceptable for about 3 hours. At the end of this time, more than 80 percent of the ferrous iron oxide has dissolved. Thereafter, the reaction speed decreases to the point that, to eliminate another 15 percent of iron, it has in the past been necessary to extend the treatment to 20 hours. The Applicants aim at maintaining as long as possible a high initial deferrization speed beyond the aforesaid 3 hours.

As it is logical to attribute the slowing down of the deferrization to the progressive reduction in the quantity of free acid which is present and consequently to its concentration, it may be thought that at least this concentation should be kept at its initial value. Various attempts have been made in this sense, especially by maintaining a constant hydrochloric acid content in the reaction medium by introducing gaseous hydrochloric acid, so simultaneously re-establishing the quantity and the concentration of free hydrochloric acid, but this involves costly difficulties.

The Applicants have found that this difficulty can be overcome by maintaining the initial concentation of hydrochloric acid, and this is effected by the continuous removal of water by distillation, while retaining in the mixture the azeotropic hydrochloric acid of boiling point 110° C. By this means an industrially acceptable speed of solution of the iron can be maintained beyond the first 3 hours of reaction. Thus by the process of the invention, from an ilmenite with 50/55 percent of titanium dioxide, a concentrate exceeding 90 percent of titanium dioxide and capable of reaching up to 93 to 97 percent of titanium dioxide can be obtained in 12 hours. Such a result could not be obtained by known processes, in which the concentration of an acid is not maintained by distilling off water, unless several times as much acid is used, which would make the final regeneration of the acid more troublesome.

In itself the maintenance of the acid concentration could reduce the selectivity of its dissolving action as between iron and titanium, if only by reducing the hydrolyzing effect of the water present which tends to prevent solution of the titanium. This effect is overcome by the final step in the preferred process, in which about as much water as has been removed is returned, and boiling continued for a short time, usually one-half to 1 hour, under total reflux. This may thus be termed a hydrolytic boil. The total reflux is readily effected simply by increasing the supply of cooling water through the dephlegmator of the column above the reactor.

Obviously, in the case of sands with an abnormally high content of ferric iron, it is possible to promote the deferrization by a reducing action for example, by adding metallic iron, by electrolytic reduction by passage of current into the reaction medium with an electrode provided with a diaphragm, or by some other know reducing means. However such a step is not necessary and will usually be dispensed with.

The invention is illustrated by the following Example.

EXAMPLE

The crushed ilmenite to be treated has the following composition:

TiO_2	52.35%
Total iron (in the form of FeO and Fe_2O_3)	38.34%

Into a 2-litre three-necked flask R (see FIG. 1) are introduced 1,300 cc. of hydrochloric acid of concentration 19.06 percent, slightly lower than that of the azeotropic acid (20.24 percent), which will be quickly reached during the reaction by evaporation of water.

After the introduction of the acid, which is effected with the agitator operating, 300 g. of crushed ilmenite are added all at once. This proportion corresponds, relative to the total iron of the ore, expressed as ferrous oxide, to an acid excess of 124 percent. The flask is then heated and the contents boiled under total reflux for 1½ hours. The heating is then intensified and the operation of the dephlegmator of the column C (which is packed with Raschig rings) is regulated so as to allow water to distil over keeping the concentration of the acid at 20.24 percent. After boiling for 7 hours 25 minutes, the quantity of water collected shows that 73.7 percent of the iron of the ilmenite has been dissolved. After boiling for 11½ hours (total time), all the water distilled from the start is returned to the reaction mixture in the flask R and boiling is continued for another half hour. Heating is then stopped and the flask is cooled by immersing it in a tank through which cold water is flowing. After cooling and decanting off from the solid material, it is possible to draw off by siphoning 868 cc. of limpid deferrization liquid. The residue is poured on to a Buchner funnel equipped with an acid-resistant cloth, and filtered under vacuum, giving another 256 cc. of limpid deferrization liquid, so that altogether a total of 1,124 cc. of this liquid is obtained. Thereafter, the cake is washed, first of all with azeotropic hydrochloric acid and then with water, and then dried and calcined. The final products are:

a. 168.9 g. of titanium dioxide concentrate containing
    92.2 percent of TiO_2 and
    3.37 percent of total iron (ferrous iron plus ferric iron)
b. 1,124 cc. of concentrated deferrization liquid of density **1.205**, containing:
    1 g/l of TiO_2
    67.41 g/l of total Fe (ferrous plus ferric)
    206.0 g/l of Cl^- anion
c. concentrated and dilute washing waters.

The concentrate can serve for the preparation of a pure titanium dioxide.

The loss of titanium, which is eliminated as titanium dioxide with the ferric oxide in the industrial regeneration of the hydrochloric acid, amounts to 0.84 percent of the titanium dioxide of the ore. The ferric oxide is slightly charged with titanium dioxide and also represents a product which can be exploited. The effeciency of the deferrization was 96.29 percent, leaving only 3.71 percent of the initial iron in the concentrate. It can be established by analysis that, during the operation, the proportion of ferric iron originally present has been slightly increased by oxidation of a corresponding part of the ferrous iron.

Starting with an ilmenite such as that treated in the foregoing Example, there are obtained titanium dioxide concentrates which exceed 90 percent of titanium dioxide and which, in the best cases (presence of little ferric iron in the ore) can reach up to 94 percent of titanium dioxide. The corresponding deferrization yield is between 90 and 97 percent. The loss of titanium dioxide by solubilization as recorded is a maximum of only 1 percent.

The process according to the invention has numerous technical advantages. Thus:

a. Azeotropic hydrochloric acid is used in the form which has been recovered from deferrization liquors,
b. Deferrization is effected in a single operation of relatively short duration,
c. Consumption of acid and consequently the amount to be regenerated, are reduced,
d. Loss of titaniumdioxide is reduced to below 1 percent of the titanium dioxide contained in the ore.

The industrial installation illustrated in FIG. 2 can be operated as follows. The three equivalent reactors R, R', R'' are charged with 20.2 percent azeotropic hydrochloric acid (or an acid of slightly lower concentration) coming from the storage reservoir T, and the agitators are rotated. The crushed ilmenite is added to the hydrochloric acid. When the reactors have been filled, heating is started. When the boiling point is reached, the delivery of cold water through the dephlegmators in the top of the Raschig ring columns C, C', C'' is regulated so that all the vapour which is produced is condensed and returns to the reactors. AFter about 1½ hours, the flow of cooling water is reduced to that necessary to ensure the separation of water vapour from the azeotropic acid of boiling point 110° C. the latter being condensed and returned to the reactors. The water vapour, containing only a little hydrogen chloride, is condensed in the condensers A, A', A'', and the water formed is collected in the distillate reservoirs E, E', E''. 30 minutes before the end of the deferrization, the aqueous distillates are returned to the reactors which have supplied them, and full reflux restored by increasing the cold water flow through the dephlegmators. Boiling is then continued for another thirty minutes, after which the contents of all the reactors are transferred to the coolers K, K' and K'', where their temperature is reduced to about 30° C.

The cooled material is passed to the rotary filter F, which separates it into solid titanium dioxide concentrate and deferrization liquid. The concentrate is washed with water on the filter by means of two rows of sprinklers S. The deferrization liquid is sent by the pump P to the regenerator G, which in turn supplies azeotropic hydrochloric acid to the reservoir T ready for re-use.

We claim:

1. A process for the production of a titanium dioxide concentrate from iron-cntaining titanium ore, whereby the speed of deferrization of the ore is kept high, which comprises forming a reaction mixture consisting essentially of a quantity of said ore and an aqueous solution of hydrochloric acid having a concentration approximating the azeotropic HC1 concentration of 20.24 percent by weight, the amount of said acid solution being at least twice that theoretically required to transform the iron oxide content of said ore quantity into iron chloride, boiling said mixture for reaction of the acid with the ore therein and to selectively dissolve the iron content of the ore until 90 to 97 percent of said iron oxide content has been extracted into the liquid phase of the reaction mixture, and during at least the major part of the period of said boiling maintaining the hydrochloric acid in the reaction mixture at substantially said azeotropic concentration by continuously removing from the reaction mixture the amount of water being formed and present therein in excess of the amount of water required therein to maintain the hydrochloric acid therein at substantially said azeotropic concentration, and before the end of the period of said boiling discontinuing said removing of water and adding water into said mixture in an amount sufficient to precipitate by hydrolysis titanium that has disssolved in said liquid phase, and upon the end of said boiling period cooling the reaction material, separating the liquid thereof from the solids therein and washing the separated solids, thus recovering them as a solid titanium concentrate that contains from 90 percent to 97 percent of TiO_2 by weight when dried and calcined.

2. A process according to claim **1**, wherein during an initial reaction period of not longer than about three hours said boiling is effected with total condensation and return as condensate into said mixture of the vapors being boiled therefrom, so as to retain in said mixture during said initial period both the water originally present and the water being formed therein.

3. A process according to claim **1**, said removing of water being effected by conducting the vapors boiled from said mixture into a condensation zone and fractionally condensing in said zone and returning as condensate into said mixture the azeotropic HC1 content of said vapors while passing the remaining water vapor content of said vapors through said zone and away from said mixture.

4. A process according to claim **1**, said washing being effected first with hydrochloric acid of said azeotropic concentration and then with water.

5. A process according to claim **1**, and regenerating from said separated liquid hydrochloric acid for reuse in the process.

6. A process for the production of a titanium dioxide concentrate form iron-containing titanium ore, whereby the speed of deferrization of the ore is kept high, which comprises forming a reaction mixture consisting essentially of a quantity of said ore and an aqueous solution of hydrochloric acid having a concentration approximating the azeotropic HC1 concentration of 20.24 percent by weight, the amount of said acid solution being at least twice that theoretically required to transform the iron oxide content of said ore quantity into iron chloride, during an initial reaction period of not longer than 3 hours boiling said mixture and condensing and returning thereinto as condensate substantially all the vapors being boiled therefrom, then during a substantially longer reaction period boiling the reaction mixture and maintaining the hydrochloric acid therein at substantially said azeotropic concentration by fractionally condensing and returning as condensate into said mixture only the azeotropic HC1 content of the vapors being boiled therefrom while passing the remaining water vapor content of said vapors away from said mixture, to selectively dissolve the iron content of the ore until 90 to 97 percent of said iron oxide content has been extracted into the liquid phase of said mixture, and then adding water into said mixture in an amount sufficient to precipitate by hydrolysis titanium that has dissolved in said liquid phase and continuing the boiling of the mixture during a relatively short final reaction period while again condensing and returning as condensate into said mixture substantially all the vapors being boiled therefrom, and upon the end of said boiling period cooling the reaction material, separating the liquid thereof from the solids therein and washing the separated solids, thus recovering them as a solid titanium dioxide concentrate that contains from 90 to 97 percent of TiO_2 by weight when dried and calcined.

7. A process according to claim **6**, and condensing and collecting as an acidic distillate said water vapor content passed away from said mixture and effecting said adding of water into the reaction mixture by introducing said distillate thereinto.

8. A process according to claim **6**, said initial reaction period being of approximately 1½ hours, said longer reaction period being of approximately 10 hours, and said final reaction period being of approximately one-half to 1 hour.

9. A process according to claim **6**, and at the end of said final reaction period cooling the reaction material, regenerating from the separated liquid hydrochloric acid for reuse in the process.

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