July 10, 1962 R. P. GREEN ETAL 3,043,655

METHOD OF RECOVERING TITANIUM COMPOUNDS

Filed March 29, 1960 2 Sheets-Sheet 1

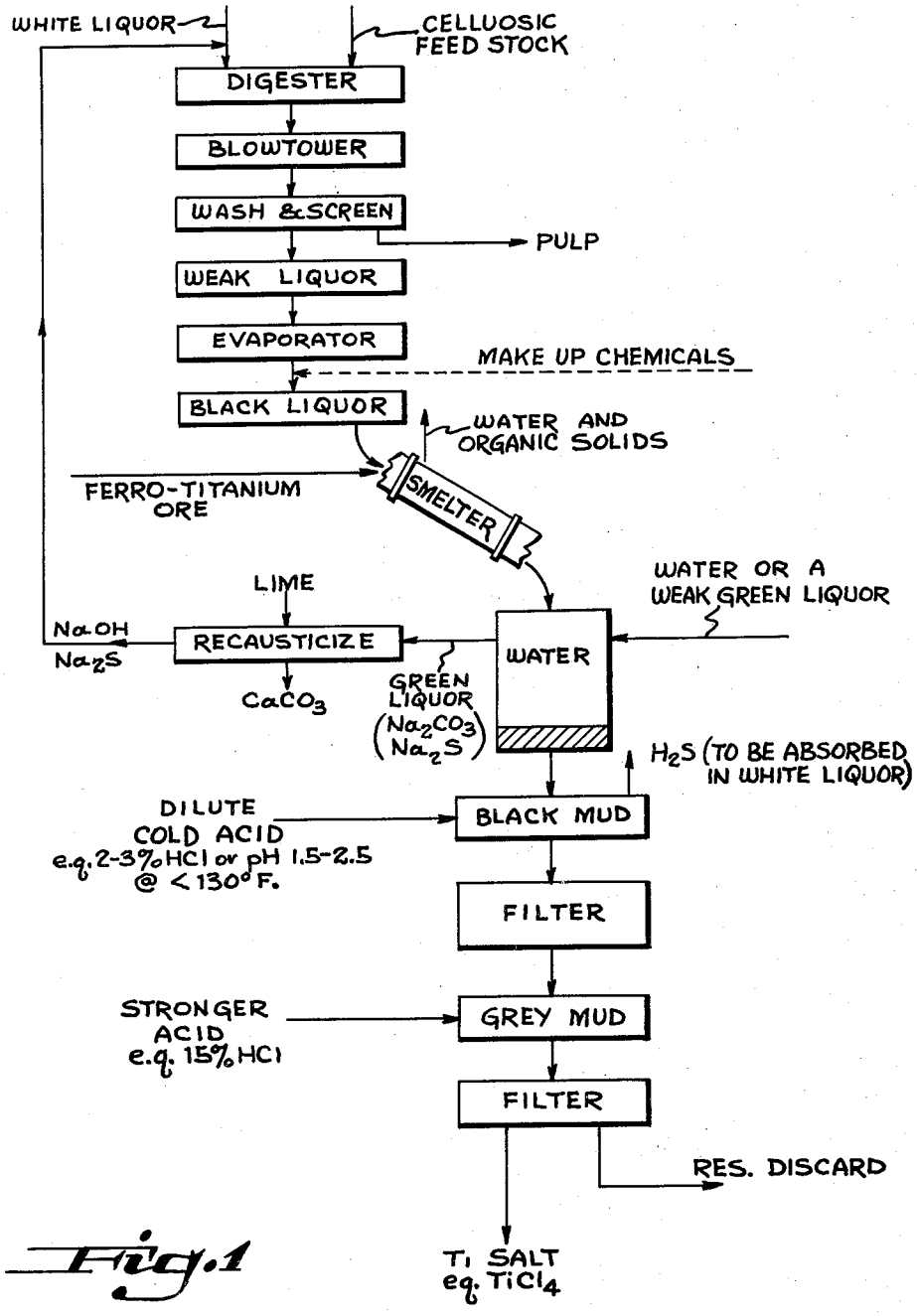


Fig. 1

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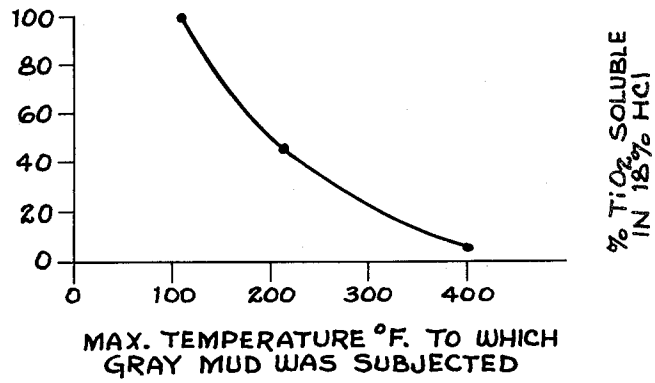


Fig. 2

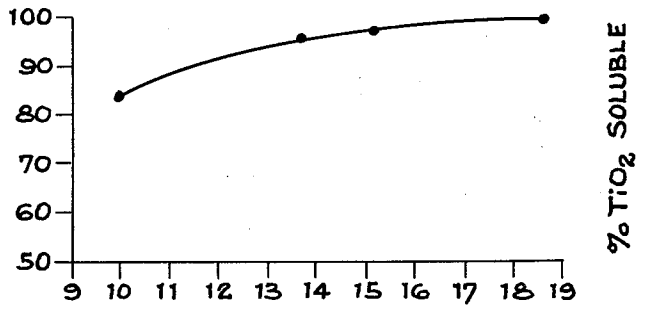


Fig. 3

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METHOD OF RECOVERING TITANIUM COMPOUNDS

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This invention relates to the production of titanium tetrachloride. The invention is directed particularly to the production of titanium tetrachloride from titanium-iron ores as an adjunct to the manufacture of wood pulp by a process employing an alkali-metal sulfur compound, such as the sulfate process.

The mineral ilmenite is an abundantly available titaniferous ore but the titanium dioxide content of the mineral is contaminated with iron. Because of the difficulty of separating iron from the titanium content, titanium and its compounds commonly are produced from the purer but more expensive titaniferous minerals such as rutile. A principal objective of the present invention has been to provide a method for separating iron from the titanium of ilmenite and similar lower grades ores for the production of relatively pure iron-free titanium tetrachloride which in and of itself is useful and from which titanium metal and other titanium compounds readily may be produced by known methods.

A further objective of the present invention has been to provide a process wherein such separation and production may be accomplished as an adjunct to the production of pulp from cellulosic materials such as wood by the sulfate process, the neutral sulfite process, or other pulping processes employing alkali-metal sulfur containing wood digesting compounds which, when smelted, revert to an alkaline pH. More specifically, the objective of this invention has been to provide a process for recovering substantially iron-free titanium tetrachloride from ilmenite ore by the use of spent liquor produced in an alkali-metal sulfur salt process of pulp production but without adversely affecting the regenerability of the spent liquor for reuse in the pulp producing process.

In order to understand the manner in which a relatively pure form of titanium tetrachloride is produced as an incident to the operation of an otherwise wholly unrelated process of producing pulp from wood or the like, a brief description of the sulfate process of producing pulp, which is illustrative of the various processes utilizing alkali metal sulfur salts processes, is first essential.

In the conventional process of making sulfate pulp, wood chips or other material containing cellulosic fiber is digested in a caustic liquor containing a water soluble sulfide such as sodium sulfide and, usually, some alkaline carbonate such as soda ash. The digestion is conducted at elevated temperature and pressure, during which the cellulosic fibers are liberated from the lignins, resins and other organic materials present in the feed stock. At the commencement of the digestion operation the liquor, being clear, is called "white liquor," but as digestion proceeds the organic substances become dissolved, darkening the liquor; the resulting spent liquor is commonly called "black liquor."

Upon completion of the digesting operation the liberated pulp fibers are filtered from the black liquor, and the latter is thickened by evaporation for subsequent recovery and reuse of its inorganic chemical content. Some sodium sulfate is added to the thickened black liquor as chemical make-up. The thickened black liquor is then introduced into a smelter or recovery furnace maintained at a high temperature. In this operation the remaining

water content of the liquor is evaporated, the organic content of the black liquor is burned away, the sodium sulfate is reduced to sodium sulfide, and the inorganic chemical content of the liquor is recovered.

As a result of the smelter treatment the inorganic chemical content of the black liquor emerges from the smelter as a molten stream which is discharged into water or weak green liquor and becomes dissolved therein. The insoluble residue commonly called "dregs," resulting from the combustion, also accompanies the molten discharge from the smelter but settles from the aqueous solution of the inorganic chemical content as "green liquor dregs." These are commonly discarded.

The aqueous solution of inorganic chemicals, now called "green liquor," is suitably recharged by causticizing with lime whereby the sodium carbonate is for the most part converted into NaOH. The resultant "white liquor" is adapted for reuse in the digestion of another batch of cellulosic feed stock.

The present invention is predicated upon the concept of introducing titanium-iron ore, such as ilmenite, along with the stream of black liquor as the latter is charged into the smelter, for coincidental, simultaneous, or conjoint treatment of the two within the smelter such that the high temperature and molten alkaline chemical prevailing within the smelter modify the ore to render it amenable to further chemical treatment at the same time that water is evaporated and the organic matter is being burned from the black liquor for recovery of the pulp reagent chemical content thereof.

The molten smelt produced by this operation is now introduced into water and the alkali-metal chemical content thereof becomes dissolved in the water as has been conventional in the past. However, because of the feed of titanium ore to the smelter along with the black liquor, a larger quantity than heretofore of "dregs" is produced. This contains the titanium and iron compounds of the ore and, for purposes of identification, is called "black-mud." This black-mud is now treated for recovery of the titanium content thereof.

This invention, next, is predicated upon the discovery and determination that treatment of the titaniferous black-mud so produced, with cold or unheated dilute acid effects conversion of the iron content thereof into a ferrous compound which is soluble in the dilute acid while leaving an essentially iron-free titaniferous "gray-mud" which, while insoluble in the cold dilute acid, possesses peculiar but desirable properties of chemical reactivity. From this gray-mud, for example, titanium tetrachloride essentially free from iron and sulfur readily can be formed by reaction of the gray-mud with hydrochloric acid of approximately 15% or more strength by weight.

In particular, it has been discovered that the temperature to which the black-mud resulting from the smelter operation is exposed in the initial or first stage step of removing iron from it, as by means of the dilute acid, determines the reactability of the residual iron-free gray mud in the second stage of the recovery. By conducting the dissolution of iron from the black mud at room temperature or at a temperature not substantially exceeding 130° F., the titanium content of the black mud not only separates sharply from the iron but is left in a state wherein it is much more readily reactive with a stronger acid in the second stage of the process than if the black mud had been subjected initially to hot dilute mineral acid or to temperatures above approximately 130° F. Hence, an important feature of the invention resides in the utilization of cold or unheated dilute acid for stripping iron from a caustic-smelted titanium ore as the means for producing a more readily reactive form of titaniferous material therefrom. Moreover, by utilizing an essentially sulfur-free

acid reagent for the reaction, such as dilute HCl, the gray mud is produced as an essentially sulfur-free product such that its reactivity is not impaired by any subsequent sulfur removing step which would otherwise be required.

Utilization of the black liquor smelter (which forms an essential part of virtually every sulfate type of pulp producing operation) for coincidental digestion of titanium ore to make the same amenable to recovery of the titanium content thereof in accordance with this invention, makes economically feasible the production of large quantities of relatively pure titanium chemicals from relatively low grade or iron containing titanium ores. In the practice of the present process, for example, it is entirely practicable to charge one pound of ilmenite ore into the smelter per each gallon of black liquor charged into the smelter. Although the titanium ore and the black liquor become intimately commingled in their passage through the smelter, neither adversely contaminates the other. The iron content of the smelted titanium ore remains with the black mud so as to permit separation thereof from the green liquor produced through introduction of the molten smelter discharge into water. Therefore, the green liquor remains fit for reconstitution and reuse as white liquor in the pulp digestion process. Also, the companion treatment of the black liquor and the titanium ore in the smelter affords distinct economic advantages since the heat within the smelter performs the double function. For such reasons, the invention is disclosed particularly in relation to its practice as part of or in conjunction with the pulp making process, but it will be understood that the discoveries concerning the effect of temperature in the iron removing step upon the reactivity of the resultant product with other reagents are useful whether the titaniferous black mud has been produced in a pulp-liquor smelting operation or by other or independent pyrometallurgical treatment of the titanium ore.

One manner of recovering titanium tetrachloride in a companion pulp-making operation is illustrated in the accompanying flow diagram, FIGURE 1. As has been conventional in the past, wood chips or other cellulosic material and so-called white liquor are introduced into the digester for liberation of the fiber content of the cellulosic feed stock. The white liquor, typically may be of the following composition:

	G./l. as Na_2O
Caustic soda	57
Sodium sulfide	22
Sodium carbonate	11

The digestion proceeds at elevated temperature, for example, 350° F. for a predetermined period of time, after which the contents of the digester are conventionally blown, and washed to separate the liberated pulp fibers from the black liquor. The black liquor is run through an evaporator to reduce the moisture content and thereby condition the black liquor for addition to the smelter. Sodium sulfate make-up chemical is added at this point as needed to maintain the desired liquor composition. Since, however, part of the sulfur present reacts with the iron during the smelting operation, and is carried out of the system, probably as ferrous sulfide, the make-up chemical must be suitably adjusted in order to produce a white liquor of the proper composition. Instead of adding all of the sulfur as sodium sulfate, suitable chemicals such as NaOH, sulfur or the like or combinations thereof are added to the black liquor, or to the white liquor where feasible and chemically appropriate. In addition reuse is made of the sulfur liberated as H_2S when the iron is dissolved out of the black mud; the H_2S can be reclaimed by absorbing it in NaOH or white liquor and reusing this in the liquor recovery system.

Such black liquor is now charged into the smelter, preferably in the form of a spray. However, in accordance with the present invention, ilmenite or other titaniferous ore is added simultaneously to the smelter, for example, to the extent of approximately 0.5 to 3 pounds thereof per

gallon of the black liquor fed to the smelter or approximately one pound of ilmenite per each five pounds of dry solids in the black liquor. The amount is not precisely critical and more or less may be used depending upon the nature of the smelter and the sulfur content of the black liquor. In general, the ratio should be such that at least sufficient sulfur is present to react with the iron present to produce ferrous sulfide. The ore and black liquor may be added in admixture with each other or as separate feeds. The smelter is operated at a temperature in the range of approximately 1800 to 2200° F., with a controlled supply of air to support combustion of the organic chemical content of the liquor. In tests with commercial equipment, the introduction of the ore into the smelter did not significantly alter the heat balance; in this respect it may be that an exothermic reaction occurs. In any event the smelter operation is not generally different in the practice of the present invention than in conventional recovery of pulping chemicals and therefore need not here be explained in more detail.

Within the smelter, water is evaporated from the black liquor and the inorganic chemicals melt while the sodium sulfate which was added to the black liquor before presmelter evaporation thereof is reduced to sodium sulfide under the reducing conditions provided by the combustion of the organic content of the liquor. The iron content is also believed to be reduced to the ferrou state. Thus, a molten stream is discharged from the smelter consisting essentially of sodium carbonate and sodium sulfide, along with the modified elements of the titaniferous ore which was introduced into the smelter.

This molten stream is now discharged into water. The water soluble inorganic chemicals dissolve while the ash and titaniferous chemicals settle in the form of titaniferous black mud. The water/solids ratio is not critical but prefeably is adjusted to provide a green liquor of desired strength. If desired, the smelt may be cooled prior to the dissolution in water but addition of the smelter discharge while in a molten condition to the water increases the rate of dissolution.

Filtration may be used to facilitate the separation of the black mud from the aqueous solution. If some of the solids are in colloidal form, they may interfere with rapid filtration. However, the addition of white liquor to the water before filtration, approximately in equal volume ratio, avoids this difficulty without loss of the white liquor.

The black mud recovered in this manner consists of a wet paste of 30–50% solids having the following proximate analysis:

TiO_2	30–35% by weight.
Fe	18–21% (=28–33% FeS).
Na_2O	5–10% (=8–17% Na_2CO_3).

The phenomena which actually occur in the conversion of ilmenite ore within the smelter are not fully understood. It is believed that the native ore consists, at least in part, of a loosely bound iron and titanium compound such as ferric titanate, which splits under the elevated temperature and alkaline conditions in the smelter, whereby ferrous sulfide is formed from the iron compound and the sodium sulfide furnished by the black liquor.

The reducing conditions within the smelter, provided through the presence of the carbonaceous content of the black liquor, no doubt also affects the reaction.

In the first stage of recovery of titanium from the titaniferous black mud in accordance with the present invention, dilute hydrochloric acid is added to the black mud at a temperature not exceeding substantially 130° F. In this step the iron content of the black mud reacts with and becomes dissolved in the dilute acid as ferrous chloride. Titanium compounds present in the black mud are not affected by pH's in the range of approximately 1.5–2.0 and, therefore, remain undissolved with no loss thereof. Now the dilute acid containing dis-

solved iron is separated as supernatant liquor from the residual settled mud which, for convenience, is termed "gray mud" throughout this specification.

It is not so much a matter of adding the acid in dilute form as it is controlling the addition quantity to reduce the pH to a value between about 1.5 to 2. With hydrochloric acid, addition of acid at 10% concentration, for example, gives good separation of the iron; the water present in the black mud noticeably reduces this concentration so that at pH 1.8, the concentration is well below 1%. If excessive acid is used so as to lower the pH below 1.5, some or all of the titanium solids will be dissolved, thereby defeating the separation of iron from titanium, or thereby resulting in at least some loss of titanium end-product desired. Also, the use of cold dilute hydrochloric acid has been found to facilitate filtration of the gray mud from the acid; for example, the solids become gelatinous and very difficult to filter if sulfuric acid even of comparable strength is employed. As a general rule the acid strength may be decreased as temperature increases but only at the risk of impairing the degree of separation of the iron from the titanium.

The gray mud is now filtered from the weak acid solution for treatment in the second or final stage of the recovery process wherein the gray mud is reacted with a more concentrated mineral acid, or reagent, for example, hydrochloric acid of 15% strength. In this reaction hydrated titanium compounds present in the gray mud, presumably of oxide form, are converted to soluble titanium chloride although some soluble titanium oxychloride may also be formed.

The following table illustrates the effect that the temperature employed in the first stage (removal of iron from the black mud) has upon the dissolution of titanium from the gray mud in the second stage of the recovery. In this instance, the weak hydrochloric acid used in the first stage was of 7% initial strength, while the stronger hydrochloric acid used to dissolve the titanium from the gray mud was of 18% initial strength.

Table I

Sample	Stage 1 (Conversion of Black Mud to Gray Mud		Stage 2 (Solubilizing the TiO_2 in Gray Mud w./18% HCl at room temperature)
	Acid Used (to pH Approx. 1.8)	Temp. at ° F.	Percent of TiO_2 Solubilized
A	None (black mud)		98
B	H_2SO_4	210	20
C	HCl	210	46-50
D	HCl	165	80
E	HCl	83	96
F	HCl	42	98

The foregoing data is based upon a black mud having a TiO_2 content of 29.4% by weight.

From these data it is apparent that substantially the entire titanium content of the black mud (98%) dissolves readily in 18% hydrochloric acid but, of course, no separation of iron from titanium can be accomplished by such treatment. On the other hand, if temperature near boiling (210° F.) is maintained to facilitate the dissolution of iron from the black mud then only 20 to 50% of the titanium will be dissolved in 18% hydrochloric acid in the second stage of the recovery, depending upon whether dilute sulfuric or dilute hydrochloric acid respectively was employed in the first stage step. It is also to be noted that cold dilute sulfuric acid gives less satisfactory results than cold dilute hydrochloric acid, in that the sulfuric gives rise to the formation of a slime which is very difficult to filter. For this reason dilute hydrochloric acid is preferred as the first step reagent.

The adverse effect of elevated temperature upon the reactivity of gray mud is further illustrated by a solubility test wherein gray mud, wet, just as it came from the filter, was divided into three portions. One of the portions (*a*) was not treated in any way. A second of the portions (*b*) was boiled in water for one hour, then cooled to room temperature. The third of the portions (*c*) was oven dried, ground, heated to approximately 400° F., cooled and rewet with water. Each of the respective portions was then treated with 18% hydrochloric acid at 100° F. for one hour with constant stirring. The solubilities of the gray mud, as determined in this manner, were as follows:

	Percent soluble
Portion (*a*)	99.5
Portion (*b*)	45.1
Portion (*c*)	4.8

FIGURE 2, based on this test, graphically illustrates the manner in which solubility decreases with temperature.

While 18% hydrochloric acid was selected for testing the solubility of the gray mud according to the foregoing examples, it should be noted that reactivity of the gray mud permits the use of considerably weaker acid. The graph, FIGURE 3, illustrates that even when acid of only 12% concentration is employed for reaction with the gray mud, approximately 90% solubility of the titanium dioxide content is achieved.

Thus it will be seen that the gray mud produced by the use of the cold dilute acid is left in a much more reactive state than when high temperatures are employed in the first stage of the recovery. It is believed that this greater reactivity is conferred by a state of greater hydration of the titanium solids in the gray mud. This is confirmed in part by the fact that in filtering samples B and C (Table I) under identical conditions the cake produced from sample B contained 30% solids whereas the cake from sample C contained only 25% solids. On the assumption that most nonhydrated products after filtration hold approximately 50% water only mechanically bound, then it appears that the cake from sample B had approximately 0.5 part of chemically bound water for each part of titanium dioxide while the cake from sample C had 0.8 part as water of hydration per each part of titanium dioxide.

The reactivity of the gray mud is adversely affected not only by high temperatures during the treatment with the dilute acid, but by high temperatures (i.e., above 130° F.) at any time. For example, if the gray mud is subjected to heat after the removal of the iron, it will be less reactive.

It is also very desirable that the black mud and the gray mud be kept relatively moist; the cake formed when the black mud and the gray mud, respectively, are separated from the liquor by filtration or the like, is a suitably wet form for the subsequent treatment. If the mud, the black or the gray, is calcined or heated severely the reactive condition is impaired or destroyed.

Upon recovery of the gray mud from the cold dilute acid, the mud may be reacted readily with stronger acids to form the corresponding Ti salts as end products. Thus, the gray mud produced in accordance with this invention constitutes a new commercial product from which a variety of titanium materials may be produced. For example, to make titanium tetrachloride, the wet cake of reactive gray mud may be slurried with a suitable proportion of hydrochloric acid having a resulting strength (taking into account the water present in the mud) of 12% or more. Reaction occurs at room temperature in approximately 15 to 30 minutes with constant mixing. Stronger concentrations of acid can be employed; as the concentration increases, the percent recovery of titanium values increases but approaches an asymptote. At hydro-

chloric acid concentrations above 20% there is little or no additional gain in recovery. After reaction, antimony oxide and glue may be added to coagulate the remaining solids and the slurry thereby is readily filterable. Reaction may be hastened by using an excess of stronger acid; for example, a 5/1 ratio by weight of HCl/TiO_2 is satisfactory. A ratio of 3/1 by weight of acid will likewise result in essentially complete solubilization of the TiO_2. The excess HCl is readily recoverable by distillation.

An important commercial advantage provided by the present invention is that the removal of iron from the black mud is accomplished entirely by simple wet processing steps and cheap acids without the use of heat. It is also to be noted that although sulfur compounds become commingled with the titanium ore in the smelter, still, sulfur does not appear in the final titanium end product.

While ilmenite is the preferred starting material, other titaniferous-iron materials such as titaniferous-iron slag are also suitable.

Having described our invention, we claim:

1. The method of producing titanium tetrachloride as an adjunct to a pulp-making operation wherein spent pulp digestion liquor containing alkali sulfur compounds is introduced into a smelter for recovery of the caustic chemical content thereof, which method comprises charging an iron-titanium ore into said smelter along with said spent digestion liquor thereby simultaneously to remove water from said spent liquor, burn off the organic contents thereof and expose said ore to the heat and molten caustic chemicals prevailing within said smelter, and thereby producing a mixture of molten caustic chemical and modified titanium ore, the total quantity of elemental and combined sulfur in said liquor being at least equal to that theoretically required to react with the iron present in the ore to produce ferrous sulfide, adding said mixture to water and dissolving water soluble inorganic chemicals of said mixture in said water, separating from the water solution of caustic chemicals a residue of substances insoluble in said water, including the modified titanium ore, acidifying said residue with sufficient hydrochloric acid to produce a mixture having a pH of no less than about 1.5 while maintaining a temperature not exceeding substantially 130° F. thereby to dissolve iron from said residue as ferrous chloride while leaving the titanium content of said residue in a chemically active state, separating the undissolved material from the dilute acid after the iron has been dissolved from the residue, and then treating the undissolved material with hydrochloric acid of at least approximately 12% strength to convert the titanium content thereof into essentially iron-free titanium tetrachloride.

2. The process of claim 1 wherein dissolution of iron from said residue is effected by acidification of the said residue with sufficient hydrochloric that the pH of the mixture is no less than about 1.5 nor greater than about 2.0.

3. A wet process of making an iron and sulfur-free titanium salt from the discharge product of a smelter wherein ilmenite has been subjected to high temperature in the presence of a melt of alkali-metal sulfur compound, the total quantity of elemental and combined sulfur in said melt being at least equal to that theoretically required to react with the iron present in the ilmenite to produce ferrous sulfide, which wet process comprises mixing the smelter discharge product with water to dissolve the water soluble inorganic chemical content thereof, thereby producing a water insoluble residue containing the ilmenite ore in the form to which it had been modified by the smelter treatment, separating the wet residue from the water solution, treating the wet residue at a temperature below approximately 130° with sufficient hydrochloric acid to produce a pH of no less than about 1.5 and thereby dissolve from the residue the iron content thereof as a ferrous compound, separating the dilute-acid-insoluble iron-free material from the iron-containing dilute acid solution and treating the iron-free material with sufficient hydrochloric acid to convert the titanium solids of the iron-free residue into titanium tetrachloride.

4. In the process of making wood pulp wherein wood is digested in an alkaline liquor containing sodium sulfide and wherein the spent digestion liquor, after digestion and removal of the pulp therefrom, is introduced into a smelter for burn-off of the organic solids thereof and for recovery of the inorganic chemical content thereof in the form of a molten product, the wet method of producing a chemically reactive titanium product as an adjunct to said pulp-making operation which wet method comprises, introducing iron-titanium ore into said smelter along with the said spent digestion liquor, the total quantity of elemental and combined sulfur in said liquor being at least equal to that theoretically required to react with the iron present in the ore to produce ferrous sulfide, simultaneously thereby producing in said smelter a mixture of molted caustic material and titanium ore which has been chemically modified by subjection to the heat and caustic material within said smelter, discharging the molten mixture into water and dissolving the water soluble chemical content of said molten mixture, settling insoluble constituents of said mixture from said water solution as a black mud and separating the said solution from the said black mud, treating the said black mud at a temperature not exceeding approximately 130° F. with sufficient acid selected from the group consisting of hydrochloric acid and sulfuric acid to produce a mixture having a pH of no less than about 1.5 to selectively dissolve iron compounds therefrom, and then separating the acid solution containing dissolved iron thereby producing as a remainder, a gray mud containing titanium in a readily reactive state.

5. The process of claim 4 wherein the dilute mineral acid is hydrochloric acid.

6. The process of claim 4 wherein the gray mud is reacted with hydrochloric acid of at least about 12% by weight strength thereby to produce titanium tetrachloride.

7. The process of producing a titanium salt which process comprises treating ilmenite ore with an alkali metal sulfur compound and a carbonaceous reducing agent, said treatment being conducted at elevated temperature sufficient to melt the said alkali metal sulfur compound, for a period of time sufficient to chemically modify the ilmenite ore, and with a total quantity of elemental and combined sulfur at least equal to that theoretically required to react with the iron present in the ore to produce ferrous sulfide, and discharging into water the resulting smelt containing the treated ore thereby to dissolve the water soluble contents of the melt and thereby producing a mud containing modified titanium ore solids, separating the mud from the aqueous solution, treating the mud with a hydrochloric acid to dissolve from the mud any iron which is native to the titanium ore, said dissolution being conducted at a temperature not exceeding substantially 130° F., and at a pH of approximately 1.5 to 2.0, removing the dilute mineral acid containing dissolved iron from the mud, and then treating the mud with sufficient hydrochloric acid of at least 12% by weight strength to produce a mixture of said mud and acid having a pH of less than about 1.5 and thereby converting titanium compounds of said mud into titanium tetrachloride.

8. The method of claim 1 wherein dissolution of iron from said residue is effected by acidification of said residue with sufficient hydrochloric acid that the pH of the mixture is no less than about 1.5 nor greater than about 2.5.

9. The method of claim 4 wherein dissolution of iron from said residue is effected by acidification of said resi-

due with sufficient acid that the pH of the mixture is no less than about 1.5 nor greater than about 2.5.

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CERTIFICATE OF CORRECTION

Patent No. 3,043,655

July 10, 1962

Robert P. Green et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 22, for "molted" read -- molten --.

Signed and sealed this 11th day of December 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents