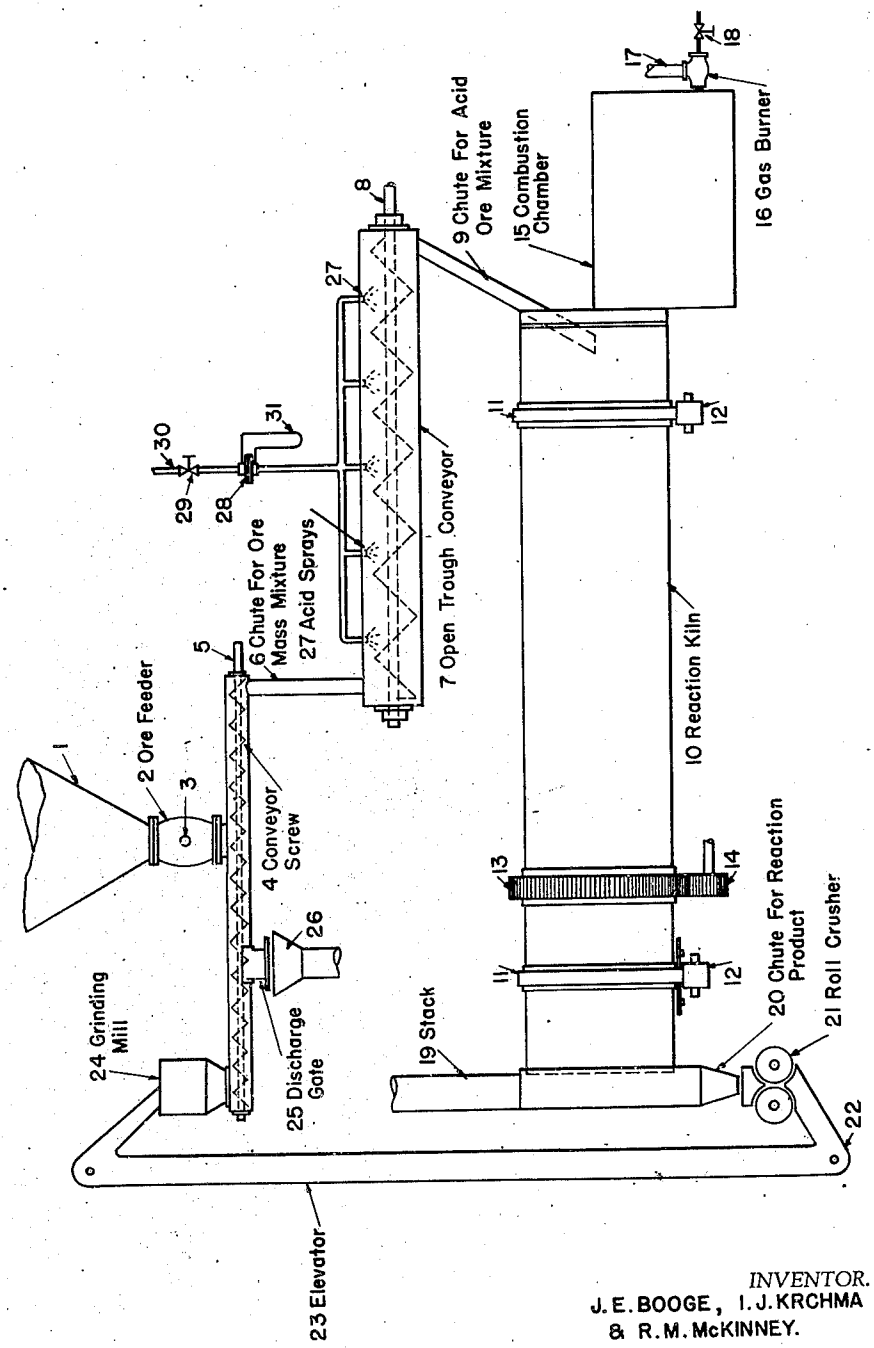
Nov. 2, 1937. J. E. BOOGE ET AL 2,098,026

METHOD OF ATTACKING WATER INSOLUBLE TITANIFEROUS MATERIAL

Filed Nov. 23, 1935



INVENTOR.
J. E. BOOGE, I. J. KRCHMA
& R. M. McKINNEY.

BY

ATTORNEY.

Patented Nov. 2, 1937 2,098,026

UNITED STATES PATENT OFFICE

2,098,026

METHOD OF ATTACKING WATER INSOLUBLE TITANIFEROUS MATERIAL

James E. Booge, Wilmington, Ignace J. Krchma, Elmhurst, and Robert M. McKinney, Roselle, Del., assignors, by mesne assignments, to E. I. du Pont de Nemours and Company, a corporation of Delaware

Application November 23, 1935, Serial No. 51,255

8 Claims. (Cl. 75—115)

This invention relates to a process for sulfating titaniferous ores and titanium rich residues and more particularly to a process for the decomposition of such titaniferous materials with sulfuric acid, preferably in a continuous manner and with good yields.

Our novel method consists particularly in preparing a solid, granular, or disintegrated mass of an insoluble titaniferous material amenable to the attack of an acid, an acid suitable for said attack, and an amount of the solid reaction product as is obtained by the attack of said acid upon said titaniferous material, said reaction product acting physically to solidify and granulate the liquid suspension or pasty mass, which said acid and titaniferous ore produces in the absence of said reaction product. This solid mass is then heated to such a temperature, at which the reaction between said acid and titaniferous ore is initiated. The mass is then maintained at the elevated temperature, preferably under agitation until said reaction is substantially completed.

In a preferred form of our invention this operation is carried out in a continuous cyclic manner. To start such an operation, we mix acid and the titaniferous material and circulate it through a reaction zone where the attack proceeds, part of the reacted material is removed and mixed with fresh amounts of acid and titaniferous material and then returned to the reaction zone.

This novel method is particularly applicable to the decomposition of ilmenite with strong sulfuric acid, in which case the solid reaction products consist essentially of iron and titanium sulfate mixed with unreacted ore constituents and impurities.

We are aware that the prior art discloses various methods and processes for the decomposition of titaniferous ores, such as ilmenite, with sulfuric acid. There are several general types of processes that we shall briefly enumerate hereinafter in order to differentiate between them and our novel process.

One of the first methods proposed for the decomposition or attack, as it shall be hereafter called, was the mixing of ilmenite and sulfuric acid in open pans of various sizes and in varying amounts, concentrations and temperatures. The reaction proceeded as a single isolated process and with very little operating control. The reacted mixture or mass was allowed to cure in the same pan until it was pronounced ready for subsequent treatment. The conversion of the titaniferous material to soluble titanium compounds varied a great deal and there was very little control over the composition of the final product.

Another general type of process was the attack of ilmenite with sulfuric acid in a large cylindrical tank preferably with a cone-shaped bottom. The charge could be agitated by mechanical means or by injection of steam or gases, or by a mixture of all three. The tank could be closed in order to operate under pressure or open to operate under atmospheric conditions. These two general types of processes for sulfating titaniferous material include all those that show any promise of an economical nature.

Both of these general types of treatment have numerous disadvantages which result from the batch nature of the attack. A few of these are briefly given below:

(1) The change in the nature of the mass from a slurry to a solid resulting in mechanical difficulties in handling, etc.

(2) The haphazard nature of the control of the reaction.

(3) The large variation in the composition and physical properties of the product.

(4) The intermittent supply of a product suitable for further processing.

(5) The high cost of maintenance and operation.

This invention has as an object the continuous decomposition of titaniferous materials with sulfuric acid producing a mass containing high conversions of the insoluble titanium to a soluble form. A further object is to provide an attack procedure which will allow the recovery of the insoluble titanium content in various titanium rich residues or muds produced in the later stages of the process for producing titanium dioxide from ilmenite.

A further object is to conduct the reaction in such a manner that the reaction mixture is always in the dry or lumpy state thereby insuring the elimination of all operating difficulties arising from a change in state during the reaction. A still further object is the use of a simple gas-fired rotating kiln for the purpose of carrying out the decomposition of the titaniferous material. Other objects will appear hereinafter.

We have found that these objects may be accomplished by mixing with the ilmenite and acid a suitable amount of the mass produced in the subsequent reaction. The well ground mass is mixed with the incoming ground ore in a screw conveyer, and the mixture subsequently sprayed with the required amount of acid. After thorough mixing the composition should be sufficiently solid to slide easily and without flow into a revolving gas-fired kiln in which the reaction takes place. The reacted mass discharged from the reaction kiln is crushed and ground, and a portion (such as 20%) is returned to the conveyer to be mixed with ilmenite and so on.

The appended drawing shows the arrangement of the necessary equipment.

(1) is a storage bin or hopper for supplying powdered ilmenite or other titanium rich ma-

terial which is fed by means of the ore feeder (2), driven by shaft (3), into the conveyer screw (4), driven by shaft (5). This conveyer screw (4) discharges the ilmenite through chute (6) into the open trough conveyer (7). Driven by shaft (8), this conveyer (7) is provided with sprays or drip pipes (27) for introducing acid at a rate controlled by the orifice (28) and the valve (29), said rate being indicated by orifice (28) and by differential manometer (31). Pipe (30) is the acid supply line. Conveyer (7) discharges through chute (9) into the reaction kiln (10). This kiln revolves on circular tracks (11), carried on rolls (12), and is driven by ring gear (13) and pinion (14). The kiln is heated by gases from combustion chamber (15), supplied by burner (16) having oil supply (18) and air supply (17). Combustion gases and reaction fumes are discharged through stack (19) while reaction products drop through chute (20) and from there through roll crusher (21) to the boot (22) of the elevator (23).

This elevator (23) discharges into fine grinding mill (24) which in turn discharges into screw conveyer (4). In the screw conveyer housing (4) there is provided the discharge gate (25) through which the finished product is discharged continuously in finished product hopper (26). A portion of the finished product is permitted to mix in conveyer (4) with the powdered ilmenite and the sulfuric acid.

The conveyer used for mixing the recirculated mass, ore and acid may be any suitable type of mixing device in which a dry mealy substance will be submitted to thorough mixing. Any other mixing device, particularly of the continuous type, could be used.

In starting the operation the kiln (10) is brought up to a reaction temperature of approximately 180° C. by means of burner (16) and combustion chamber (15). With the finished product discharge gate (25) closed, crushed ore is fed from bin (1) at a rate controlled by feeder (2) through screw conveyer (4) into mixing conveyer (7). During the passage of the ilmenite through conveyer (7) it is sprayed with acid of the desired strength and in sufficient quantity to give a mealy mixture that will drop satisfactorily through chute (9). This mixture of ore and acid, which contains less acid than that required to return a satisfactory mass and conversion, is brought to reaction temperature in kiln (10) with any accompanying evaporation of water if necessary. The reacted mass is discharged as a dry mixture of ore and mass which falls through crushing rolls (21) and is carried by elevator (23) through fine grinding mill (24). The operation is continued in this manner until examination of the product from the mill (24) indicates suitable composition for lixiviation. At this time the gate (25) is opened to discharge a part of the product from the conveyer (4) into the finished product hopper (26). The remaining portion is mixed with fresh ilmenite in conveying screw (4) and the mixture treated as outlined above.

It will be understood that we have used the term ilmenite throughout to indicate not only the ore usually referred to as such, but also a residue obtained by attack of this ore, such residue being relatively less rich in titanium than the original ore. We moreover include, by our use of the term ilmenite, the muds which are produced in the usual and well-known process for producing titanium dioxide from ilmenite, such muds being coagulated colloidal slimes, rich in unreacted titanium, produced in the purification or clarification of the titanium sulfate solution. Our process is moreover applicable to other titanium rich ores.

The titaniferous materials which we have used for decomposition were ilmenite and the various residues obtained from the subsequent process. Material A contained 44.2% insoluble TiO_2 and 23.8% Fe as the oxides. Material B was somewhat poorer in titanium containing 32.4% TiO_2 and 15.6% Fe. Material C was a wet residue obtained from filter pressing, the leachings of a titanium sulfate solution obtained by attacking ilmenite with sulfuric acid; it contained 49.5% solids and 23.1% TiO_2 on a wet basis. Both fresh acid and dilute waste acid were used. The following is the analysis of the dilute acid: 1.274 specific gravity; 37.0 grams per liter of Fe; 7.5 grams per liter of soluble titanium expressed as TiO_2; 356.0 grams per liter of total H_2SO_4; 22.1% of the total weight is free H_2SO_4.

Example #1

The titaniferous material used was a combination of 114 parts by weight of material C plus 119 parts by weight of material A. This was slurred up with 135.4 parts by weight of free H_2SO_4 as fresh acid. This resulting mixture was divided into three equal portions. First portion was baked at 180° C., then crushed and mixed with second portion. This mixture was rebaked after which the operation was repeated with the third portion. The resulting dry mass gave the following results upon lixiviation: 90.5 grams per liter soluble TiO_2; 36.4 grams per liter Fe; 263.0 grams per liter of total H_2SO_4; 45.2 parts by weight of soluble TiO_2 produced; and an overall recovery of soluble TiO_2 of 56.6%. This recovery, although poor compared to the 80–90% which can be obtained by the proper attack of ilmenite, is very high for the recovery of valuable soluble titanium from residues, which have previously been of no value and have constituted a disposal problem.

Example #2

The titanferous material used was a mixture of 100 parts by weight of material C plus 100 parts by weight of material B. This was slurried with 600 parts by volume of a dilute acid containing 132.8 parts by weight of free H_2SO_4: The resulting mixture was treated at 180° C. as given in Example #1. The final dry mass gave the following results upon lixiviation: 46.2 grams per liter soluble TiO_2; 172.0 grams per liter of total H_2SO_4; 42.7 grams of soluble TiO_2 produced; and an overall recovery of soluble TiO_2 of 78.0%.

While the conditions employed in the above two examples gave us very good results, we do not mean to infer that we are limited to these specific ones. The process can be used for fresh ilmenite as well as for the three grades of residues hereinbefore mentioned. In fact, any titaniferous material containing varying amounts of TiO_2, ferrous and ferric oxides with other impurities can be used.

One of the advantages of our invention is that we can employ almost any concentration of acid to carry out the necessary decomposition. If a comparatively weak acid is used as in Example #2, it is necessary to lower the rate of solid feed to the kiln and increase the amount of decomposed mass recirculated in order to have sufficient H_2SO_4 for decomposition after the neces-

sary evaporation has taken place in the first portion of kiln. The temperature of the kiln may also be raised above 180° C. in order to insure faster evaporation. While we used 180° C., this is rather the minimum temperature that can be employed rather than the optimum.

Consequently it can be seen that, depending on the titaniferous materials and the properties of the acid used, a wide variety of conditions for the operation of our invention can be employed.

The advantages and improvements of our novel method for the treatment of ilmenite with sulfuric acid are given hereinafter in order to differentiate our process from all those heretofore disclosed. The return of sufficient of the final solid mass, so that the reaction mixture is always solid or nearly so, insures the elimination of all operating difficulties arising from a change in state during the reaction. The use of a simple gas-fired kiln causes the mixture to be attacked continuously. Uniform and high conversions are obtained by this kiln. A fine product suitable for further treatment is continually discharged from the system. The operation is automatic and requires very little supervision after it has been started. The operation is continuous and minor changes can be made in operating conditions in order to obtain the optimum results. The simple equipment used makes for low operating and maintenance costs. The continuous nature of the process lessens manual labor and supervision costs. The use of the gas-fired kiln also allows the use of nearly any acid concentration.

We claim:

1. The process of recovering soluble sulfates of iron and titanium from ilmenite ore, which comprises the steps of mixing ilmenite with solid iron and titanium sulfates obtained in a previous operation of attacking ilmenite ore with sulfuric acid, adding to said mixture an amount of sulfuric acid adapted to react with said ilmenite ore, adjusting the amounts of the ingredients of said mixture so as to obtain a solid, granular product before said ilmenite has reacted with said acid, feeding said granular material into a reaction zone in which it is heated to about 180° C., maintaining said mass under agitation at elevated temperature until said ilmenite has reacted with said acid, separating from the solid reacted mass a substantial part thereof and mixing it with a fresh portion of ilmenite and sulfuric acid and submitting this mixture to a subsequent heating step.

2. The process of claim 1 with the additional steps of leaching the remaining part of the reacted mass with water to recover an aqueous solution of iron and titanium sulfates, and returning the water insoluble residue to an operation where a water insoluble titaniferous material, sulfuric acid and solid iron and titanium sulfates are mixed to form a solid granular material which is heated to an elevated temperature at which the reaction between sulfuric acid and the insoluble titaniferous material is initiated.

3. A continuous process for producing soluble titanium compounds from titaniferous ores, comprising introducing a mixture of such titaniferous ore and sulfuric acid into a reaction zone, on completion of the reaction therebetween discharging the resultant product from said reaction zone and separating a portion thereof, returning said separated portion together with a fresh charge of ore-acid mixture to said reaction zone, and regulating the proportion of said returned product with respect to said fresh charge as to maintain the combination charge during its treatment in said zone in substantially solid, granulated state.

4. A continuous process for producing soluble titanium compounds from titaniferous ores, comprising introducing a mixture of a titaniferous ore and sulfuric acid into a reaction zone maintained under an elevated temperature, discharging the reacted product from said zone, separating a portion thereof in which both sulfated and undissolved residues are contained, and returning to said reaction zone in finely-divided form the portion so separated in admixture with a fresh charge of ore-acid mixture, whereby passage of the resultant mixture through said zone in substantially solid, granulated state is effected.

5. In a process for producing water-soluble titanium compounds wherein a comminuted titaniferous ore is subjected to treatment within a reaction zone in the presence of sulfuric acid, the step of incorporating in the ore-acid mass prior to its introduction into said reaction zone, a portion of an end product of reaction from said process adapted to maintain said mass in substantially solid, granulated state during its treatment in said reaction zone.

6. In a process for the production of water-soluble titanium compounds wherein a titaniferous material is subjected to treatment with sulfuric acid within a heated reaction zone, the step of diluting the reaction mass prior to its introduction into said reaction zone with a controlled quantity of the solid end components obtained from a previous operation of the process whereby the treatment of said reaction mass within said reaction zone is effected in a substantially dry, solid and granulated state.

7. A continuous process for treating insoluble titaniferous ore to obtain soluble titaniferous compounds therefrom, comprising admixing said ore with sulfuric acid and controlled quantities of a solid end product of reaction from the process, introducing the combined mixture into a reaction zone wherein it is subjected to elevated temperature and agitation conditions, discharging the reacted product from said zone, separating a portion thereof, and returning to said reaction zone together with a fresh ore-acid mixture charge the portion so separated whereby said charge is maintained in substantially solid, dry, granulated state during its treatment in said reaction zone.

8. A continuous cyclic process for sulfating a titaniferous ore, comprising introducing into a reaction zone a mixture of said ore, sulfuric acid and a regulated proportion of a solid, finely-divided end product of reaction from a previous operation of the process, maintaining said reaction zone under temperature and agitation conditions adapted to effect a complete interaction therebetween, discharging the reacted products from said zone and separating a portion thereof containing sulfated products and undissolved residues, and returning to said reaction zone together with a fresh charge of ore-acid mixture the portion so separated whereby the combined mass passes through said zone in substantially solid, granulated state.

JAMES E. BOOGE.
IGNACE J. KRCHMA.
ROBERT M. McKINNEY.