The present invention relates to a process of sulphating titaniferous ores.

The most common titaniferous ore is ilmenite, which is ordinarily regarded as a ferrous titanate in which the iron and titanium oxides are very strongly chemically combined with each other. This ore is very refractory to the action of acids or other chemical agents. Other common titaniferous ores are rutile and magnetite carrying high percentages of titanium oxide. These ores are used as the raw material for the manufacture of titanium oxide which has a wide use for pigments, etc. In the usual sulphuric acid process of making titanium dioxide from a titaniferous ore such as ilmenite, the first step consists in subjecting the ore to strong sulphuric acid to convert the titanium and iron contents of the ore into soluble titanium sulphates and soluble iron sulphates. The sulphuric acid is usually strong acid containing 80% or more sulphuric acid content. When the sulphuric acid is added to the ground ore, the mixture during the acid reaction tends to form a hard cake. This cake has a tendency to coat the particles of the ore and thus slow up the action of the acid on the ore particles. The usual agitating and stirring devices are not efficient to remove this coating of cake continuously from the particles of the ore, and consequently under such conditions the reaction not only proceeds at a slow rate, but is never carried to a high degree of completion.

In our process the mixture of ore and acid is thoroughly kneaded during the acid reaction attack, so that the particles of the ore are maintained in a loose condition. The kneading causes an attrition of the particles over each other, thus continuously exposing fresh surfaces of the ore particles to the acid attack. This results in speeding up the rate of the acid reaction, and as this reaction is of an exothermic nature the heat evolved from the reaction is very much more effectively used in raising the temperature of the mass than would be the case if the reaction proceeded at a slower rate. Further, owing to the continual removal of the cake from the ore particles, the reaction is completed to a very much greater degree so that very little, if any, of the unattacked ilmenite remains in the reaction vessel after completion of sulphatization.

The drawings—

Figure 1 is a side elevation of a suitable form of kneading machine which may be used in carrying out the process;

Figure 2 is a front elevation, partly in section, along the line II—II of Figure 1;

Figure 3 is a vertical section along the line III—III of Figure 2;

Figure 4 is a top plan view of the kneading tub and blades;

Figure 5 is a section along the line V—V of Figure 4;

Figure 6 is a side view of one of the kneading blades.

In the illustrated embodiment of the kneading machine, reference numeral 2 indicates the mixing or kneading tub in which the ore and acid are thoroughly stirred and kneaded by means of mixing and kneading blades or arms 3 and 4. The shape of the kneading blades 3 and 4 is illustrated in Figures 4, 5 and 6. The tub 2 has a central ridge 5 along its bottom forming two rounded bottom portions in which the kneading blades 3 and 4 rotate. The action of the kneading blades is similar to that of a bread dough kneader. They serve to not only mix the slurry of acid and ore charged into the machine, but also to thoroughly knead the mixture after the acid attack has progressed, breaking up any lumps and causing a thorough attrition of the particles of the stiff mass, so as to expose fresh surfaces of the ore particles to the acid attack.

The tub 2 has an oil jacket 6 arranged to be filled with hot oil supplied through a hot oil circulating system 7 from an external oil heater. The tub is surrounded by a heat insulating jacket 8 which serves to prevent loss of heat.

The tub has a cover 9 having a feed inlet connection 10 through which the acid and ore are supplied to the mixing tub, and an exhaust vent 11 through which the acid fumes may be drawn away.

The mechanism for driving the kneading blades 3 and 4 is as follows: The drive for rotating the kneader blades is from a motor 11 through a sprocket chain drive 12 for driving the shaft 13. The shaft 13 extends lengthwise of the machine and is arranged to transmit power for driving the kneading blades 3 and 4 from both ends of the machine. The gearing connecting the shaft 13 to the kneading blades 3 and 4 is the same at both ends of the machine, so that only the gearing connection at one end of the machine need be described. The shaft 13 carries a pinion 14 which drives a gear 18 on a short shaft 16. A pinion 17 on the shaft 16 drives a large gear 18 on a shaft 19. The shaft 19 carries a gear 20 which meshes with the gears 21 and 22 which are carried on the shafts 23 and 24 of the kneading blades 3 and 4, respectively. The kneading blades 3 and 4 rotate in the same direction as 110.
indicated by the arrows, so as to give the proper mixing and kneading action.

The tub 2 is mounted between end housings 25 which enclose the gearing connections above described. The tub 2 is mounted to turn in housings on the axis of the shaft 19, thus permitting the turning of the end while the gears 21 and 22 of the kneading arms are meshed with the gear 20. The shafts of the gears 20, 21 and 22 are journaled in a pivoted bearing casting 26 which is secured to the ends of a worm wheel 27. This segment is meshed with a worm 28 on a shaft 29. The shaft 29 car4
ribs a worm wheel 30 which is driven by a worm 31 on a shaft 32. The worm 31 is lubricated by a gear 314 dipping in an oil well 31b. The shaft 32 is driven through bevel gearing 33 from a motor 34. Suitable control mechanism for the motor 34 governs and limits the tilting of the tub to discharge the contents after the kneading operation.

The following is a typical example of treatment of an ilmenite ore according to our process. The particular ore in question has had approximately the following analysis:

<table>
<thead>
<tr>
<th>Component</th>
<th>Per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>44.00</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>36.00</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>14.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The ilmenite ore was ground to a fine granular condition. A charge of 500 pounds of the ground ore and 1200 pounds of 80% sulphuric acid was fed together into the kneading machine, the blades 3 and 4 being continuously operated. The sulphuric acid was preheated to about 150°F. The ore was used cold. The oil in the heating jacket 6 was maintained at about 475°F. After the change of ore and acid was fed in, the cover 8 was placed over the kneading machine. About ten to twenty minutes were required for heating the charge and initiating the acid attack. This constituted the first stage of the operation. This was followed by the second stage of the operation which required about seven to twelve minutes. During the second stage of the operation a violent reaction took place between the ore and the sulphuric acid, resulting in the evolution of large volumes of water vapor and a marked increase in temperature due to the exothermic reaction between the acid and the ore. It requires a temperature of about 300°F. to start the rapid attack of the acid upon the ore. As soon as the rapid attack begins, its exothermic reaction raises the temperature of the mass still further. The reaction apparently takes place best at these elevated temperatures and it is therefore of advantage to carry the reaction to completion as soon as possible before the exothermic heat of reaction can be dissipated.

At the beginning of the rapid acid attack the mass is in the nature of a rather thin slurry. This thickens gradually as the reaction proceeds until at the end of the violent reaction it is in the nature of a rather plastic, doughty mass which is still somewhat moist because of the free acid which it contains. At the end of the second stage approximately 75% of the titanium and iron oxides present are converted into the sulphates.

The kneading operation is continued for about fifteen to twenty minutes more, and this constitutes the third stage of the operation. During this third stage of the operation the mass is subjected to a thorough baking due to the residual exothermic heat of the reaction and also to the heat supplied by the hot oil jacket 6. The baking and kneading of the mass is carried to a point where the batch is no longer sticky. The mass will crumble like sand. At the end of the third or baking stage, the kneading machine is tilted and the mass is dumped to a car to be transferred to the usual dissolver or tank in which the sulphated ore is mixed with water to bring the titanium and iron sulphates into water solution. This water solution of the titanium and iron sulphates is then treated in any of the usual ways for the recovery of the titanium dioxide.

The quantity of acid used is determined by analysis of the ore, the amount of acid charged being that which is theoretically required to convert all of the metallic oxides present into sulphates plus about 5 to 10% excess. While the conversion is never quite complete, the yield of sulphates is carried to a high point, varying from about 90 to 95%. This is a greater yield than in the prior processes in which instead of kneading the mass, the ore and sulphuric acid are merely stirred or agitated.

During the first stage of the operation the kneading machine maintains the mass as a fluid readily stirrable slurry. As the second stage of the operation progresses, the titanium and iron sulphates tend to form hard coatings upon the particles of the ore. These sulphates are not soluble in the strong sulphuric acid. They therefore tend to form insoluble envelopes preventing further attack of the acid upon the enclosed ore particles. They also tend to cement the particles together into a hard conglomerate or cake. By the continued kneading action of arms 3 and 4 on the machine, the formation of a hard cake is prevented and the mass is maintained in a loose granular condition as it tends to stiffen and become more solid during the subsequent reaction. Also, as above noted, the kneading causes an attrition of the particles over each other and thus continual grinding off of the insoluble envelopes of the titanium and iron sulphates from the particles and exposes fresh surfaces to the acid attack. This kneading operation is continued during the third or baking stage which insures the utilization of practically all of the acid used to combine with the ore, leaving only from 5 to 10% of the ore unattacked by the acid. Because of the continued kneading of the material, the reaction takes place rapidly and allows maximum utilization of the exothermic heat generated during the second stage; the high temperature of which in turn tends to further speed the reaction and give a maximum recovery.

As stated previously, the kneading action employed in the present process is similar to the action of kneading dough in a bread dough kneader. It is distinguished from the usual mixing, agitating or stirring which have been used previously in the treatment of titaniferous ores with sulphuric acid by the following characteristics: The kneading action maintains all of the mass in a state of constant agitation, not permitting any of it to lie in dead spaces, so that it is unattacked by the acid. The plastic mass is thrown from one blade to the other so that a squeezing and pulling action is exerted on the mass by the motion of the blades against the trough walls, the saddle in the bottom of the trough, and between the blades themselves. The blades have an interweaving action which tends to clear them by shearing away any adhering mass as the blades reach their point of closest proximity. These characteristics of the kneading
action result in increased conversion of the titanium dioxide content of the titanium ore. We have found that when ilmenite ore and sulphuric acid are stirred in apparatus previously employed in this art, not more than 75 to 80% of the titanium dioxide content can be converted to water soluble titanium sulphate, whereas by the kneading action described herein, 90 to 95% soluble sulphate can be obtained.

While we have described one particular example of carrying out our process and have shown a kneading machine which we have found satisfactory to use, it is to be understood that the invention is not limited to the use of the particular kneading machine illustrated or to the specific procedure set forth in the typical example, but that the invention may be otherwise embodied and practiced in the sulphating of titaniferous ores within the scope of the following claims.

We claim:
1. The process of sulphating titaniferous ores, which comprises thoroughly kneading a plastic doughy mass of ground ore and sulphuric acid during the period of acid attack upon the ore, said kneading being substantially identical with that obtainable by kneading said plastic mass in a mixer of the type having walls forming a trough and a saddle in the bottom of the trough and inter-acting blades of a Z or so-called sigma pattern, and characterized by intensive kneading, squeezing and pulling of the mass against the trough walls, the saddle, and between the blades themselves.

2. The process of sulphating titaniferous ores, which comprises kneading a mass of ground ore and strong sulphuric acid while subjecting the mass to external heat until the reaction between the acid and ore is initiated, thoroughly kneading the resultant plastic doughy mass to maintain it in a loose granular condition, said kneading being substantially identical with that obtainable by kneading said plastic mass in a mixer of the type having walls forming a trough and a saddle in the bottom of the trough and inter-acting blades of a Z or so-called sigma pattern, and characterized by intensive kneading, squeezing and pulling of the mixture against the trough walls, the saddle, and between the blades themselves, and continuing the kneading of the mass after the primary reaction has occurred while subjecting it to continued application of external heat to bake the mass and further carry the reaction to substantial completion.

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