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3,450,257

## PROCESSING OF CLAY

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4 Claims

### ABSTRACT OF THE DISCLOSURE

A method of removing titanium mineral impurities from a clay containing at least 40% by weight of particles smaller than 2 microns equivalent spherical diameter which comprises conditioning the clay at a solids content of at least 30% by weight for a time sufficient to dissipate therein at least 25 horsepower hours of energy per ton of solids and thereafter subjecting the clay to a froth flotation process in the presence of an activator consisting of a water-soluble salt of an alkaline earth metal or a heavy metal.

### BACKGROUND OF THE INVENTION

This is a continuation-in-part of application Ser. No. 435,340 filed Feb. 25, 1965 and now abandoned.

This invention relates to the processing of clays, of which kaolin and china clay are examples, containing at least 40% by weight of particles smaller than 2 microns equivalent spherical diameter, and is more particularly concerned with a method of treating such clays to improve the brightness thereof by removing titanium mineral impurities therefrom.

Titanium mineral impurities occur in some clays as mined and, if they are colored, they detract from the appearance of the clay. It has previously been proposed to remove impurities by forming a suspension, or slurry, raising the pH of the slurry of the clay to an alkaline value, for example by the addition of ammonium hydroxide, and subjecting the slurry to a froth flotation process. In general the froth flotation process comprises adding a collector, for example oleic acid, to the alkaline slurry of the clay, conditioning the slurry by agitating the slurry in a tank for a time sufficient to dissipate therein about 5 to 10 horsepower hours of energy per ton of solids, adding a frothing agent, for example pine oil, to the conditioned slurry, and then passing air through the slurry in a known manner in a froth flotation cell to effect separation of the impurities from the clay. However, many clays naturally contain a high proportion, i.e. greater than 40% by weight, of particles of extremely small dimensions, i.e. two microns equivalent spherical diameter or smaller, and these clays are therefore natural slimes; such particles are difficult to separate by a simple froth flotation process of the type described above. The individual, extremely small particles of the clay are grouped together into large masses and are loosely bound by interparticulate forces i.e. they are flocculated. Such masses may have impurities included and held therein and these impurities, which are bound in the larger masses, are not therefore capable of being separated by a simple froth flotation process. In fact, in many industrial froth flotation processes, all the material consisting of particles smaller than 50 microns is separated from the crude ore and discarded. In order to try to overcome this problem it has been proposed to deflocculate the clay before treating the same by a froth flotation process. To effect the deflocculation, it has been proposed to add, for example, sodium silicate to the clay slurry before the addition of the ammonium hydroxide.

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It has also been proposed to add an activator to the slurry before carrying out the froth flotation process, see for example United States Patent No. 2,894,628 in which it is proposed that the froth flotation process described above should be carried out in the presence of an activator selected from ammonium, potassium and magnesium sulphates. However, all of these known processes only work efficiently with coarse clays, i.e. clays containing not more than 30% by weight of particles smaller than 2 microns, and do not work efficiently with clays containing a high proportion, i.e. greater than 40% by weight, of particles smaller than 2 microns equivalent spherical diameter.

### SUMMARY OF THE INVENTION

I have now discovered that the difficulties which arise when attempting to refine by a froth flotation process clays containing more than 40% by weight of particles smaller than 2 microns equivalent spherical diameter are, to a large extent, due to surface contamination of the particles which reduces the effective difference between two different mineral particles. To overcome these difficulties I propose, in accordance with the present invention, to subject the particles to a thorough scrubbing prior to carrying out the froth flotation process and to carry out the froth flotation process in the presence of an activator which is a water-soluble salt of an alkaline earth metal or a heavy metal. More particularly, according to the present invention there is provided a method of treating a clay containing at least 40% by weight of particles smaller than 2 microns equivalent spherical diameter in order to separate therefrom titanium mineral impurities, which method comprises the steps of:

(a) Mixing the clay in the form of an aqueous slurry having a solids content of at least 30% by weight with an alkali to raise the pH of said aqueous slurry to an alkaline value, a deflocculant, a collector for the titanium mineral impurities, and an activator consisting of a water-soluble salt of a metal chosen from the alkaline earth metals and the heavy metals;

(b) Conditioning the clay slurry at said solids content of at least 30% by weight for a time sufficient to dissipate therein at least 25 horsepower hours of energy per ton of solids;

(c) Adding to the conditioned clay slurry a frothing agent; and

(d) Introducing the conditioned clay slurry containing the frothing agent into a froth flotation cell and subjecting the conditioned clay slurry to a froth flotation process.

Herein the term "alkaline earth metals" is to be understood to include magnesium, and the term "heavy metals" refers to metals having a specific gravity which is greater than 4.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

To accomplish the thorough scrubbing of the particles before carrying out the froth flotation process, it is essential that the conditioning of the clay slurry be carried out before the frothing agent is added thereto and at a solids content of at least 30% by weight. However, it is preferred that the solids content of the aqueous clay slurry be in the range of from 40% to 60% by weight.

The activator, which is a water-soluble salt of an alkaline earth metal or a heavy metal, is advantageously a water-soluble salt of barium, calcium, cupric copper, ferrous iron, plumbous lead, magnesium, manganous manganese, strontium or zinc. Examples of suitable salts are lead acetate, lead nitrate, barium chloride and calcium chloride. The amount of activator employed is generally in the range of from 0.2 to 2.0 lbs. per ton of solids in the clay slurry.

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The alkali used for raising the pH of the slurry to an alkaline value can be ammonium hydroxide although it will be appreciated that other similar materials may alternatively be used.

The deflocculant can be, for example, sodium silicate. The collector for the titanium mineral impurities can be, for example, oleic acid, and the frothing agent can be, for example, pine oil.

After the clay slurry has been conditioned and before it is treated in the froth flotation cell it is advantageously diluted with water to a solids content of from 15 to 20% by weight.

The whole of the necessary quantities of the activator and of the collector are not necessarily added to the aqueous slurry of the clay before the beginning of the froth flotation process. Indeed, it has been found advantageous to add about one half the required quantity of each of these reagents prior to initiating the froth flotation process; and, thereafter, during the froth flotation process, to add further, smaller quantities of collector and activator, there preferably being a period of conditioning of the aqueous slurry of the clay after each further addition of reagent.

In order that the invention may be more clearly understood and readily carried into effect, reference will now be made to the following example.

#### Example

In this example, a sample of kaolin from Georgia, United States of America, was employed. The chosen sample contained 45% by weight of particles smaller than 2 microns equivalent spherical diameter and showed a relatively high coloration. The clay was formed into an aqueous slurry having a solids content of 40% by weight. Sodium silicate was then added to the suspension in the amount of approximately 4 lbs. of silicate per ton of clay in order to deflocculate the clay. The slurry was then partially conditioned by agitation for 6 minutes with a high-speed stirrer. After the agitation, lead acetate, as activator, was added in the amount of 1.25 pounds per ton of clay, followed by 10% ammonium hydroxide solution in the amount of 2 pounds per ton and oleic acid in the amount of 3 pounds per ton of clay. The resulting clay slurry was further conditioned for a period of 6 minutes with the high-speed stirrer. The use of the high-speed stirrer and the total conditioning time of 12 minutes at the high solids content means that there was dissipated in the clay slurry about 30 horsepower hours of energy per ton of solids. After being conditioned, the clay slurry was diluted to form a slurry having a solids content of 16%. The resulting diluted slurry was treated in a froth flotation cell after the addition of pine oil as a frothing agent. At intervals of 20 to 25 minutes, further quantities of lead acetate and oleic acid were added at from 1/4 to 1/2 of the original amount, each addition being followed by a conditioning period before restarting the froth flotation process. The total time of the froth flotation process was about 100 minutes.

The total consumption of reagents per ton of clay was as follows:

	Lbs.
Oleic acid .....	6.75
Ammonium hydroxide .....	2
Lead acetate .....	2.5
Sodium silicate .....	4

To determine the degree of purification of the clay, brightness values were measured both for the original clay and for the product of the process just described. The brightness of the clay was determined by measuring the percentage reflectance of violet light having a wave length of 458 millimicrons. The results of the tests are given in the table below. The clay treated by the process just described will for brevity be referred to as "Clay A."

For comparison purposes, two separate samples of clay

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were processed by known methods. The first sample was formed into a slurry, conditioned for a time sufficient to dissipate therein about 10 horsepower hours of energy per ton of solids and treated with ammonium hydroxide to raise the pH level to pH 9; a froth flotation process was then carried out in known manner, using oleic acid as a collector and pine oil as a frothing agent. The clay treated by this method is referred to as "Clay B" in the table below. The second sample of comparison clay, "Clay C," was treated in the same way as was Clay B except that sodium silicate was added before alkalination to ensure substantially complete deflocculation of the clay in the suspension.

TABLE

	Clay A	Clay B	Clay C
Percent reflectance to violet light:			
Initial.....	82.1	82.9	81.9
Final.....	85.9	84.1	84.6
Difference.....	3.8	1.2	2.7
Percent recovery.....	85	97	90
Flotation time (min.).....	100	100	100

I claim:

1. A method of treating a clay to remove therefrom titanium mineral impurities, said method comprising the steps of:

- (a) mixing a clay containing at least 40% by weight of particles smaller than 2 microns equivalent spherical diameter in the form of an aqueous slurry having a solids content of clay of at least 30% by weight with an alkali to raise the pH of said aqueous clay slurry to an alkaline value, a deflocculant, a collector for the titanium mineral impurities, and an activator consisting of a water-soluble salt of a metal chosen from the alkaline earth metals and the heavy metals;
- (b) conditioning the aqueous clay slurry at said solids content of at least 30% by weight for a time sufficient to dissipate therein at least 25 horsepower hours of energy per ton of solids;
- (c) adding to the conditioned aqueous clay slurry a frothing agent; and
- (d) introducing the conditioned aqueous clay slurry containing the frothing agent into a froth flotation cell and subjecting the conditioned aqueous clay slurry to a froth flotation process.

2. A method according to claim 1, wherein the aqueous clay slurry is conditioned at a solids content of clay of from 40% to 60% by weight.

3. A method according to claim 2, wherein the conditioned aqueous clay slurry is diluted to a solids content of clay of from 15% to 20% by weight before it is subjected to a froth flotation process.

4. A method according to claim 1 wherein the heavy metal has a specific gravity greater than 4.

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