United States Patent [19]

Smith, III

[11] **3,744,630**

[45] **July 10, 1973**

[54] **KAOLIN FLOTATION PROCESS**

[75] Inventor: **Samuel Joseph Smith, III,** Sandersville, Ga.

[73] Assignee: **Thiele Kaolin Company,** Sandersville, Ga.

[22] Filed: **Nov. 2, 1970**

[21] Appl. No.: **86,341**

[52] **U.S. Cl.** **209/166**

[51] **Int. Cl.** **B03d 1/02**

[58] **Field of Search** 209/166, 167

[56] **References Cited**

UNITED STATES PATENTS

2,249,570	7/1941	Lane	209/166
3,432,030	3/1969	Oliver	209/5
3,450,287	6/1969	Condy	209/5

Primary Examiner—Frank W. Lutter
Assistant Examiner—Robert Halper
Attorney—Merriam, Marshall, Shapiro & Klose

[57] **ABSTRACT**

Titanium mineral impurities are removed from Kaolin by forming an acidic dispersion of Kaolin, water and dispersing agent (acidic relative to the flotation pH), adding a collector to the dispersion, conditioning the acidic dispersion, raising the pH by the addition of reagent to the dispersion, subjecting the dispersion to a froth flotation step and recovering the Kaolin having a reduced titanium mineral impurity content.

15 Claims, No Drawings

KAOLIN FLOTATION PROCESS

The present invention relates to a process for removing discoloring mineral components from aluminosilicious components such as kaolin clay. More particularly, the present invention relates to a process of removing titanium mineral impurities from kaolin clay by a novel and improved method of froth flotation.

Titanium mineral impurities naturally occur in many kaolin clays, and such mineral impurities cause a color in the clay which detracts from the appearance of the clay. The prior art has proposed many systems for removing the impurities, including froth flotation systems. Such prior art processes generally involve forming a suspension or slurry containing clay, water and dispersing agents, raising pH of the slurry of the clay to an alkaline value, such as by the addition of ammonium hydroxide and other reagents and subjecting the slurry to a froth flotation process. In general, the froth flotation processes of the prior art comprise adding a collector such as for example oleic acid to the alkaline slurry of the clay, conditioning the slurry by agitating the slurry in a tank for a time to dissipate energy in the clay, adding a frothing agent such as pine oil to the conditioned slurry, and then passing air through the slurry in a known manner.

The prior art froth flotation processes have had difficulty in economically floating clays which contain a high proportion of fine particles. For instance, clays which contain greater than about 40 percent by weight of particles finer than about −2 microns equivalent spherical diameter, or smaller, have been difficult to clean up using prior art flotation processes. Various solutions to this problem have been proposed including U.S. Pat. No. 2,894,628, which describes the use of various activators, and U.S. Pat. No. 3,450,257, which describes the dissipation of large quantities of energy into the clay slurry prior to the froth flotation step.

The present invention is directed to an improved method of froth flotation which not only removes an equal or greater amount of the titanium mineral impurities than the prior art process, but which results in the recovery of a higher percentage of clay product than is possible through the use of the prior art processes.

The present invention is accomplished by forming an acidic aqueous slurry of the clay containing the titanium mineral impurities, using conventional dispersing agents in the conventional amounts. The pH of the slurry must be acidic relative to the pH at which the flotation takes place. A conventional amount of tall oil or similar collector is then added to the acidic slurry and the slurry is conditioned by agitation. The amount of conditioning used will vary with the exact type of clay being processed, but for most clays it is preferred to condition in a high intensity mixer for about 10 minutes, in addition to the time required to mix in the reagents. However, for some fractions of some clays, lesser amounts of energy input give satisfactory results. After the conditioning step, the pH of the slurry is raised to an alkaline value, preferably between about 8 and 10, and the slurry is subjected to a conventional froth flotation step. Simply stated, the present invention departs from the prior art in that after the collector is added, the conditioning step is carried out at an acidic pH, the pH is then raised to an alkaline value whereupon the slurry is floated. The prior art procedure, wherein the slurry containing the collectors was

treated with alkaline material prior to the conditioning step, seemed logical since the alkaline material would tend to saponify the collectors which were generally fatty acids. This in turn would seem to promote wetting of the mineral impurities by the saponified collector. However, it has been found that the procedure of the present invention yields a significantly greater recovery than if the conditioning is carried out at an alkaline pH as is conventional in the art.

Although applicant does not wish to be bound by any theory, it is postulated that the titanium mineral impurities are agglomerated or aggregated during the conditioning at the acidic pH, and the agglomeration facilitates the subsequent removal of the impurities during the froth flotation step. It is postulated that the improvement results from agglomeration to form larger particles which are easier to remove in the froth flotation step. The apparent agglomeration makes it possible to use a somewhat lower proportion of reagents than is generally recommended by the prior art.

Briefly, the preferred mode of the present invention requires the production of a clay-water slurry at about 40 percent by weight solids. Sufficient sodium silicate is added to deflocculate the clay and the sodium silicate is mixed into the slurry. Next lead acetate, an activator, is added to the slurry with further mixing. Tall oil, which acts as a collector for the titanium dioxide, is then added and mixed into the slurry. The slurry must be acidic with respect to the flotation pH at this point in the process. The slurry is subjected to high energy conditioning from about 5 to about 60 minutes. Following the conditioning, sufficient ammonium hydroxide is mixed into the conditioned slurry to raise the pH in excess of 9.0. The slurry is diluted to about 20 percent solids and fed into a flotation cell wherein the impurities are floated off and the purified clay is recovered.

Although the examples set forth below are largely directed to flotation processes carried out on crude clay, the present invention contemplates the use of the process in connection with refined clay, partially refined clay, and blends of refined clay and crude clay. For instance, very dramatic results have been obtained by applying the process of the present invention to a coarse clay, which is the reject from a process which removes coating grade clay from a crude clay. Further, a coarse clay fraction resulting from the removal of coating grade clay and filler grade clay from a crude clay may be used. Good results have been obtained using blends of crude clay and the coarse clays described above.

The present invention is particularly useful for brightening the coarser fractions of kaolin clay, although whole crude clay, prior to fractionation into various particle size fractions, can be substantially brightened by the use of the present invention. However, the flotation operation of the present invention is not as effective when the clay feed is of too fine particle size. My invention is particularly suitable for the treatment of such coarser clay kaolin fractions as exemplified by those clays of commerce not containing more than about 30 percent by weight of −2 micron (equivalent spherical diameter) particles and not more than about 15 percent by weight of −1 micron particles, and for the treatment of crude kaolin before any fractions are removed. Further, the present invention has proved to be useful in treating whole crude clay, which is subsequently fractionated to produce a high brightness coating grade clay.

It has been found that most kaolins, when made up in aqueous dispersion are acid in that they are below 7.0 pH. Most kaolin, when made into a dispersion using sodium silicate will have a pH of about 6.5. Although some kaolins are alkaline in the absolute sense and will yield dispersons of as high as 8.0 pH, slurries made from such kaolins are acidic with respect to the pH at which the flotation step is carried out. As is more fully explained below, the flotation step is preferably carried out at about 9.0 to 10.0 pH.

In carrying out the present invention, the initial dispersion must be acidic with respect to the pH at which the flotation takes place. For most clays, using conventional dispersing agents, upon forming an aqueous dispersion, the initial pH will be below 7.0 and for most clays it is unnecessary to adjust the naturally achieved acid pH. However, the present invention contemplates adjusting the pH, either by adding acidic or alkaline reagents to the initial dispersion. Since the best results have been achieved with clay dispersions of less than 7.0 pH, it is usually not advantageous to raise the pH and little advantage has been observed in lowering the pH.

The clay which is to be treated is made up in an aqueous slurry before the flotation reagents are added. Generally speaking the slurry used to admix the reagents and to condition the slurry should be about 40 percent by weight clay solids. Although higher or lower solids content slurries can be used, it is generally considered necessary to use a slurry containing about between 30 and 70 percent by weight solids in order to get efficient conditioning after the addition of the reagents. Some of the best results have been achieved by conditioning at between 60 and 70 percent solids. Slurries containing less than about 30 percent by weight of solids seem to require the use of more energy to give the clay particles the same degree of conditioning. Higher solid slurries, are more difficult to handle and become unpumpable as solids content rise much above 70 percent by weight.

The kaolin clay which is purified and brightened by the present invention is dispersed using conventional dispersing or deflocculating agents such as sodium hexameta-phosphate, sodium carbonate, sodium silicate, or combinations thereof. These reagents are used in conventional amounts and from about 0.2 to about 20 pounds per ton have been found satisfactory. As is described in the examples, sodium silicate is the preferred dispersing agent, and from about 4 to 10 lbs. per ton are generally preferred.

In carrying out my flotation treatment, any of the well-known negative ion collectors, such as a fatty acid or a fatty acid salt, may be used. I prefer to use tall oil (an oleic acid product of vegetable extraction) as the collector because of its relatively low cost. However, any equivalent negative ion collector, such as red oil (oleic acid of animal source) may be employed. The present invention also comtemplates the use of a number of different anionic oleophilic collector reagents including coconut oil fatty acids, linoleic acid, stearic acid, lauric acid, resin acids, sulpho-oleic acid, the petroleum sulfonates such as American Cyanamid's reagent 825, and alkali or ammonium salts of such materials. The present invention contemplates the use of only a small portion of such collector reagents. It has been found that from about 0.02 to about 1 percent by weight of the collector reagent, based on the weight of the dry clay, should be used. This range is equivalent from about 0.4 to about 20 lbs. per ton. The preferred range for the collector is from about 1 to 6 lbs. of tall oil per ton of clay, with the optimum shifting within that range, depending upon the clay feed used. Higher amounts of the collector oil may be used and the removal of titanium mineral impurities is facilitated thereby, but there is a tendency to leave some of the oily collector as a residue in the clay. The presence of the oil in the clay is, of course, undesirable since it reduces the brightness. The higher amounts of collector reagent also tend to make the floated clay foamy.

In the flotation of some clays, it has been found highly desirable to add an activator. Generally speaking, the present invention contemplates the use of an activator which is provided by adding to the clay dispersion a small amount of a water soluble salt of a metal of Group II or higher in the Periodic Table. Although the activator ions used by the prior art including magnesium, calcium, strontium, barium, or mixtures of these may be used, the best results have been achieved using lead ion. It has been found convenient to use lead acetate as a source of a lead ion. A small amount of activator is adequate. For instance, from about 0.5 to 1.0 pound of lead acetate per ton of clay gives good results.

The feed kaoline slip will normally contain some of the required activator ions, chiefly calcium ions, by derivation from the kaoline as mined, or the water used in processing. The deficiency in the amount of activator ions may be corrected by the addition of the required amount of an oxide, salt, or hydroxide of magnesium, lead, calcium, strontium, or barium. The added quantity of the compound must be sufficiently soluble to dissolve in water present in the slurry mixture, but care must be taken to avoid raising the pH of the slurry to an alkaline value. For some clays, no additional activator is required.

In practicing the present invention, it is essential to condition the aqueous dispersion after the collector and the activator have been added to the slurry, but before the addition of major portions of the alkaline reacting reagents. It is essential that a major portion of the conditioning step, and preferably at least 75 percent ore more of the conditioning, be carried out at an acid pH or at a relatively acid pH. It has been found that the preferred range is from about 5.5 to 7.0 pH for carrying out the conditioning treatment. The conditioning treatment is carried out by agitating th mixture of clay, water, collector reagents and activator ions from about 5 to about 60 minutes, although between about 10 and 20 minutes is usually suitable. While it is essential that the major portion of the conditioning take place at an acidic pH, and it is preferred that at least 75 percent of the conditioning take place at an acidic pH, a short conditioning immediately prior to the flotation step (as illustrated in Example I, for instance) is contemplated by the present invention. It is essential that at lease some portion of the conditioning take place at an acid pH after the collector reagent has been added to the slurry, but prior to the addition of the alkaline reagents.

In the conditioning step, any intensity of agitation that will produce good mixing will suffice, but for optimum results a high intensity mixer is preferred. Such high intensity mixing may be obtained by using high speed Cowles mixer, a colloid mill, a "Kady Mill" or the like. While an Inframo mixer (a low intensity mixer) may be used for mixing the dispersing agent, the collector, and

the activator with the clay, such low intensity mixers are not generally adequate to perform the conditioning step. The Inframo mixer has been demonstrated to be adequate for conditioning some coarse clay fractions, but high intensity conditioning is essential for all fine clays and most coarse clays too.

After the slip has been conditioned, the slurry is prepared for the flotation step. It is essential that the flotation take place at an alkaline pH. Therefore, it is necessary to raise the pH from the acidic value at which the conditioning was conducted to an alkaline value by the addition of an alkaline reagent. Although various alkaline reagents may be used, ammonium hydroxide has produced excellent results and is generally preferred. Preferably the flotation is carried out at a pH between 9 and 10, although higher or lower values can be used on some clays. Preferably the flotation process is carried out after diluting the slip to approximately 20 percent by weight solids. Again, higher or lower percentages of solids can be used in the flotation step, although generally between 15 and 25 percent by weight solids are preferred.

In carrying out the present invention it is desired that no frothing agent be employed. It has been found that the addition of the frothing agent to the slurry following the conditioning step, such as is usually done in the prior art, is not necessary, and merely adds to the materials which must be removed from the clay slurry prior to the time it is sold. done

The following examples serve to illustrate the flotation of kaolin using several specific activators and tall oils, but it is understood that these examples are set forth merely for illustrative purposes and many other reagents are within the scope of the present invention.

EXAMPLE I

A clay slurry was prepared from 2,000 grams of dry clay obtained from a mine in Washington County, Ga. The clay was dispersed in water using 8.5 pounds per ton of N-band sodium silicate and sufficient water to produce a slurry containing 40 percent by weight solids. This was mixed for 5 minutes in a Cowles Dissolver, a high energy mixer, whereupon 0.5 pounds per ton of lead acetate was added. The slurry was again mixed for 5 minutes in a Cowles Dissolver, whereupon 3 pounds per ton of tall oil were added. Following the tall oil addition, the slurry was conditioned in a Cowles Dissolver for about 5 minutes. Following the conditioning step, 3 pounds per ton of ammonium hydroxide was added in order to give a pH of 9.4. The slurry was conditioned 5 additional minutes with the Cowles Dissolver and diluted to 20 percent by weight solids, transferred to a flotation cell and floated for 30 minutes.

After floating, 86 percent of the clay containing 1.14 percent by weight TiO_2 was recovered. This product was settled to a coating grade clay, flocced with sulfuric acid, bleached with 4 pounds per ton of sodium hydrosulfite, filtered and dried to produce a clay having a GE brightness of 86.8.

A control sample, which was not floated, contained 1.81 percent titanium dioxide and had a GE brightness after settling and bleaching of 86.0.

A similar experiment wherein the ammonium hydroxide was added prior to the conditioning step produced a similar product, but only 45 percent of the clay containing 1.43 percent by weight TiO_2 was recovered.

EXAMPLE IIA

Using the same clay described in Example I, containing 1.81 percent titanium dioxide, the process of the present invention was carried out. All mixing was done in a Cowles Dissolver. A slurry was made up at 40 percent solids using 8.5 pounds per ton of N-brand sodium silicate to give a slurry having a pH of 6.0. After mixing for 5 minutes 0.5 pounds per ton of lead acetate was added and mixed for 5 minutes to give a pH of 5.9. Three pounds per ton of tall oil was then added to the slurry to give a pH of 5.7. The slurry was subjected to a 5 minute conditioning step as shown in Example I, using the Cowles Dissolver. Then 3 pounds per ton of ammonium hydroxide was added to give a pH of 9.4. The slurry was given an additional 5 minutes conditioning and was then diluted. After dilution to 20 percent solids the pH was still 9.4, whereupon the slurry was fed to the flotation cell. The resulting product contained 1.24 percent titanium dioxide and represented a recovery of 86 percent of the clay. The clay was settled, flocced and bleached to give a GE brightness of 87.3.

EXAMPLE IIB

A similar test was run to that described in Example IIA above, but prior to the addition of the lead acetate, 0.75 pounds per ton of ammonium hydroxide was added to the slurry. After the addition of the lead acetate and the tall oil the pH of the slurry was 6.5. The material was subject to conditioning at 6.5 pH. After the conditioning step, additional ammonium hydroxide was added to raise the pH to 9.1. The slurry was diluted to 20 percent solids, whereupon the pH was 9.0. Flotation of the material gave a recovery of 69 percent of a product containing 1.20 percent titanium dioxide. The brightness was approximately the same as that achieved by Example IIA.

EXAMPLE III

Example III was run using a process similar to Examples I and II except no lead acetate was used as an activator, and 8 pounds per ton N-brand sodium silicate instead of 8.5 pounds was used. Also, a similar but different sample of clay from the first two examples was used. Several runs were conducted in which the conditioning was carried out at different pH levels by adding varying amounts of ammonia to the slurry prior to the addition of the tall oil.

Table III

	A	B	C	D	Control
pH after Silicate Addition	5.8	5.8	5.8	5.8	
Pounds of Ammonia	0	0.75	1.50	2.25	
pH after Ammonia		5.9	6.4	7.4	
Ph after Tall Oil		5.7	6.2	6.7	
pH after All Ammonia	8.2	7.9	8.0	7.9	
pH after Dilution to 20% solids	8.5	8.2	8.3	8.3	
TiO_2 in Product	0.93	1.11	0.86	0.91	1.55
Recovery %	86	84	84	84	
G.E. Brightness*	88.6	86.1	88.2	87.8	87.0

* % Brightness measured on settled clay.

EXAMPLE IV

The clay used for this example was a typical kaolin from Washington County, Ga. containing 1.69 percent TiO_2 by weight. 13,320 grams crude clay (10,000 grams dry clay) were blunged to around 63 percent solids using a Cowles type mixer and 4 pounds per ton N brand sodium silicate with 8 minutes blunging time. This was settled 2 minutes per inch to remove sand. 2,000 grams of this degritted crude was diluted to 40 percent solids and 1 pound per ton N-brand silicate was added and the slip stirred for 5 minutes with an Inframo mixer (low energy). One pound per ton lead acetate was added and the slip was stirred an additional 5 minutes. Three pounds per ton tall oil were added to give a pH around 6.5 and the slip was conditioned 20 minutes using a high intensity Cowles type mixer. After this conditioning 4 pounds per ton aqueous ammonia were added and the slip was stirred 5 minutes using the Inframo mixer yielding a 9.8 pH. This slip was diluted to 20 percent solids in the flotation cell giving 9.6 pH, and floated for 30 minutes removing a discolored froth. After 30 minutes the cell was drained giving 87 percent recovery and 0.5 percent TiO_2. The product was settled to approximately 80 percent -2μ particle size, flocced, bleached with 3 pounds per ton sodium hydrosulfite, filtered, and dried. This settled clay had a brightness of 89.8 compared to 85.8 on the not floated control sample.

Example V shows another flotation test using the same crude clay feed used in Example IV. The pH was checked moreoften in Example V, and a control sample was run.

EXAMPLE V

The sample conditioned at acid pH with the tall oil present was run as follows. 2,660 grams crude clay (2,000 grams dry) were blunged 8 minutes at approximately 60 percent solids with 5 pounds per ton N-brand sodium silicate. This was settled 2 minutes per inch to remove the sand. This clay had a 6.5 pH. One pound per ton additional silicate was added and stirred 5 minutes with the Inframo mixer giving 7.0 pH. One pound per ton lead acetate was added and water to cut the solids to 40 percent. This was stirred 5 minutes with the Inframo giving 6.8 pH. Three pounds per ton tall oil were added and the slip was conditioned 23 minutes on a Cowles mixer at 2,100 rpm with a 4 inch Cowles blade. This gave 6.8 pH. Four pounds per ton ammonia were added and the conditioned slip was cut to 20 percent solids and floated 30 minutes removing a discolored froth. The clay was drained from the cell yielding 80 percent recovery and 0.62 percent TiO_2. This product was settled to 81 percent -2μ particle size, flocced, filtered, reslurried to around 20 percent solids, bleached with 3 pounds per ton sodium hydrosulfite, filtered, and dried. This gave a brightness of 90.1.

CONTROL FOR EXAMPLE V

The control sample with the ammonia added before conditioning was run as follows. 2,660 grams crude clay (2,000 gm dry) were glunged 8 minutes at approximately 60 percent solids with 5 pounds per ton N-brand sodium silicate. This slip had a 6.6 pH after settling 2 minutes per inch to remove sand. One and one tenth pound per ton additional silicate was added and the slip was stirred 5 minutes with the Inframo mixer giving 7.3 pH. One-and-one-tenth pound per ton lead acetate was added and water to cut the solids to 40 percent. This was stirred 5 minutes with the Inframo giving 6.9 pH. Four pounds per ton ammonia were added and stirred 5 minutes with the Inframo giving 9.9 pH. Three pounds per ton tall oil were added and the slip was conditioned 20 minutes on a Cowles mixer at 2,000 rpm with a 4-inch Cowles blade. This gave 9.4 pH. The conditioned slip was cut to 20 percent solids and floated for 30 minutes removing a discolored froth. The clay was drained from the cell yielding 81 percent recovery and 0.80 percent TiO_2. This product was settled to 81 percent -2μ particle size, flocced, filtered, reslurried to 20 percent solids, bleached with 3 pounds per ton sodium hydrosulfite, filtered, and dried. This gave a brightness of 89.0. The brightness on the clay without flotation was 86.0.

The following examples illustrate the flotation of coarse clay. All of the conditioning for Examples VI through IX was done with a low energy inframo mixer.

EXAMPLE VI

A crude kaolin from Washington County, Ga. was mined and refined using a conventional commercial process. After removal of a No. 2 coating clay, the coarse reject remaining was used for this test. This feed clay contained 1.42% TiO_2. One-half pound of calgon per ton and one-half pound soda ash per ton were added to 2,000 grams of clay and mixed for 5 minutes with an inframo mixer at 40 percent solids. Three pounds of tall oil per ton were added and the slip was conditioned for 5 minutes. Three pounds of ammonia per ton were added and the slip was mixed 5 minutes with the inframo giving 9.8 pH. Five thousand milliliters of water were added cutting the solids to 20 percent and the pH to 9.5. The conditioned clay was subjected to froth flotation for 30 minutes removing a discolored froth. After floating, the clay contained 0.45 percent TiO_2 and represented a 90 percent recovery.

EXAMPLE VII

Another sample of a coarse clay fraction remaining after separating a No. 2 coating clay from production was used for this example. The feed clay contained 1.29 percent TiO_2. Two thousand grams of dry clay were mixed at 40 percent solids with 4 lb./T N brand silicate and an inframo mixer. One-half pound of lead acetate per ton was added, the slip was mixed 5 minutes, and 3 pounds per ton of tall oil were added. After conditioning for 5 more minutes, 4 pounds per ton of ammonia were added and the sample mixed 5 additional minutes with the inframo mixer giving 10.1 pH. Five thousand milliliters of water were added giving 20 percent solids and 9.8 pH. The sample was floated 30 minutes yielding a product with 90 percent recovery and 0.41 percent TiO_2.

EXAMPLE VIII

A sample of clay from Washington County was blunged with three-fourths pound of calgon per ton and three-fourths pound of soda ash per ton and settled 1 minute per inch to remove sand. The degritted clay was then settled 24 minutes per inch at 37 percent solids and a No. 2 coating clay was removed. The coarse, remaining after the coating clay was removed, was used for this Example. This coarse clay contained 1.50% TiO_2.

Seventeen-hundred-twenty grams of this coarse clay were blunged 5 minutes at 40% solids with 0.25 pounds per ton of calgon and 0.25 pounds per ton of soda ash using an inframo mixer. Three pounds of tall oil per ton were added and mixed with the inframo mixer for 5 minutes. Three pounds of ammonia per ton were added and mixed 5 minutes giving 9.8 pH. Forty-three-hundred milliliters of water were added cutting the percent solids to 20 percent and the pH to 9.5. The conditioned clay was floated for 30 minutes removing a discolored froth, after which the cell was drained yielding a product with 91 percent recovery and 0.42% TiO_2.

EXAMPLE IX

A sample of coarse reject remaining after a No. 2 coating grade clay was removed was used for this example. The feed material contained 1.33% TiO_2. Two thousand grams of clay were blunged at 40 percent solids and flocced to a 3.6 pH with sulfuric acid. After 8 minutes mixing with the inframo mixer 3 pounds per ton of tall oil were added and the slip was conditioned 5 more minutes. Two pounds of N brand silicate per ton were added giving 4.9 pH, and after conditioning 5 minutes 3 pounds per ton of ammonia were added. After 5 minutes further mixing in the inframo mixer, the pH was 9.3. Five-thousand milliliters of water were added cutting the solids to 20 percent and the pH to 9.0. The sample was floated for 30 minutes removing a discolored froth. The cell was drained yielding a product with 94 percent recovery and 0.60 percent TiO_2.

A second test was run where the conditioning was done between 7 and 8 pH that gave 71 percent recovery and 0.80% TiO_2.

EXAMPLE X

Another sample of coarse material remaining after a No. 2 coating grade clay was removed was used for this example. Two thousand grams of clay containing 1.35% TiO_2 were blunged to 40 percent solids with a Cowles type mixer and sulfuric acid was added to lower the pH to 3.5. This was mixed 13 minutes with the Cowles type mixer and 3 pounds per ton of tall oil were added. This was conditioned 5 minutes and 2 pounds per ton of N brand silicate were added increasing the pH to 4.8. After conditioning 5 minutes we added 3 pounds per ton of ammonia and mixed an additional 5 minutes at 8.9 pH. Five-thousand milliliters of water were added cutting the solids to 20 percent and the pH to 8.8. The conditioned sample was floated 30 minutes removing a discolored froth. The cell was drained yielding 93 percent recovery and 0.61% TiO_2.

The type of flotation machinery employed in carrying out the present invention is not critical, and many of the flotation machines described in the prior art can be used. In particular, the Steffensen flotation machine or the Denver-Sub A flotation machine, also known as Fahrenwald machine, may be used.

The flotation treatment of the present invention can be used in the place of conventional bleaching steps, or can be employed in conjunction with one or more bleaching steps in which case a marked improvement in the brightness of the final product results.

The forms of invention herein shown and described are to be considered only as illustrative. It will be apparent to those skilled in the art that numerous modifications may be made therein without departure from the spirit of the invention or the scope of the appended claims.

I claim:

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

A. Forming an acidic slurry having a pH from about 3.5 to less than about 7.0 by mixing clay, water and dispersing agents, said slurry containing at least 30 percent by weight of clay solids,

B. Adding to said slurry an anionic oleophilic collector for the titanium mineral impurities,

C. Conditioning said acidic aqueous clay slurry with intense agitation, while maintaining an acidic pH,

D. After at least a major portion of the conditioning, raising the pH of said slurry to at least about 8.0 by adding an alkaline reagent, and

E. Introducing the conditioned aqueous clay slurry into a froth flotation cell, subjecting the conditioned aqueous clay slurry to a froth flotation process, removing titanium mineral impurities with the froth, and recovering clay having a reduced titanium mineral impurities content.

2. A method as described in claim **1,** wherein an activator is added to the slurry prior to the conditioning step.

3. A method as described in claim **2,** wherein said activator is lead acetate.

4. A method as described in claim **3,** wherein from about 0.5 to about 1 pound of lead acetate per ton of clay is used.

5. A method as described in claim **1,** wherein said conditioned clay slurry is diluted to a solids content of from about 15 to 25 percent by weight prior to the froth flotation process.

6. A method as described in claim **1,** wherein the aqueous slurry contains at least 40 percent solids prior to the conditioning step.

7. A method as described in claim **1,** wherein from about 0.4 to 20 pounds per ton of said anionic oleophilic collector is used.

8. A method as described in claim **7,** wherein the collector is a fatty acid.

9. A method as described in claim **8,** wherein said collector is tall oil.

10. A method as described in claim **9,** wherein from about 1 to 6 pounds of tall oil per ton of clay is used.

11. A method as described in claim **1,** wherein the pH of the slurry is raised to at least 9 prior to said flotation step.

12. A method as described in claim **11,** wherein ammonium hydroxide is used to raise the pH.

13. In an improved method of flotation to remove titanium mineral impurities from kaolin comprising mixing clay in the form of an aqueous slurry with sufficient alkali to raise the pH to at least about 8.0, a deflocculant, and a collector, conditioning the slurry by intense agitation, introducing the conditioned slurry into a froth flotation cell, and subjecting the conditioned aqueous slurry to a froth flotation process, the improvement comprising performing at least a major portion of said conditioning of said slurry at a pH of from about 3.5 to less than about 7.0, prior to the addition of said alkali.

14. A method as described in claim **13,** wherein said conditioning step follows the addition of said collector, but prior to the addition of said alkali.

15. A method as described in claim **13,** wherein said slurry contains at least 40 percent solids during said conditioning step.

* * * * *