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[54] METHOD FOR CONCENTRATING SLIMED MINERALS

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[57] **ABSTRACT**

To concentrate constituents of a mixture of slimed minerals, the mixture is formed into a well-deflocculated aqueous pulp. One (or more) of the constituents is selectively filmed with a hydrophobic coating and flocculated by intensively agitating the deflocculated pulp with a suitable selective polar-nonpolar reagent. The pulp is then allowed to settle under quiescent conditions (i.e., without aeration or intensive agitation). The flocculated hydrophobic particles rise and float on the surface of the deflocculated slip as loosely-bonded agglomerates. The deflocculated slip is separated from the floated matter. Separation may be carried out at higher pulp solids and with less expensive equipment than when froth flotation is employed with a slimed pulp that has been similarly conditioned.

7 Claims, No Drawings

METHOD FOR CONCENTRATING SLIMED MINERALS

BACKGROUND OF THE INVENTION

Great difficulty is experienced in separating slimed mineral species having similar particle sizes unless there is a great difference in particle density between the species or the particles have markedly different chemical properties.

Probably the most successful method for effecting such separation is by froth flotation. Especially good results are realized when the froth flotation procedure described in U. S. Pat. No. 2,990,958 to Green et al. is used. To separate slimed colored titaniferous impurities from fine kaolin clay by the froth flotation process described in the patent, the impure clay is dispersed in water in the presence of sodium silicate which disperses (deflocculates) the clay slip and also wets the clay particles. The dispersed alkaline slip is conditioned (strongly agitated) with an anionic collector selective to the colored impurities. To help collect the colored impurities in the froth, finely divided "carrier" particles such as reagentized calcite particles are incorporated into the pulp. The conditioned pulp is diluted and placed in a flotation cell in which the pulp is agitated while finely divided air bubbles are continuously introduced into the turbulent pulp. The coated impurities and "carrier" particles attach to the air bubbles, which rise in the pulp. These particles are collected at the surface of the pulp in the form of a froth.

The flotation is carried out with dilute pulps (e.g., pulps at about 10 percent solids) in order to minimize mechanical entrainment of dispersed clay in the froth. Reagents which provide a froth with good drainage are also incorporated into the pulp during conditioning. Even with these precautions, however, about half of the clay is usually carried into the froth in the rougher froth flotation step. To recover entrained clay, the froth must be recleaned one or more times by flotation, diluting the pulp before such cleaning to maintain adequate pulp level in the flotation cells and to promote drainage of the clay from the reagentized impurities. The tailings from the rougher and cleaner flotation cells are combined to form a dilute aqueous slip of purified clay. After removal of substantial amounts of water from the clay slip, the thickened slip is bleached and filtered.

From this brief description of the prior art slime flotation method, it is apparent that froth flotation of slimed ore pulps such as a pulp of dispersed discolored clay requires the use of very large amounts of water when carried out under conditions that prevent entrainment of water-wetted particles in the froth. In many locales the water supply is inadequate to permit froth flotation to be carried out on a large commercial scale because the water from the flotation cells contains chemicals which prevent the reuse of the water.

Moreover, froth flotation of slimed ores requires a substantial capital investment because of the initial cost of the flotation cells. Further, the cells have relatively high power requirements and handle relatively small amounts of slimed solids per unit of floor space.

THE INVENTION

An object of the invention is to provide a novel method for separating slimed mineral species which avoids certain drawbacks of froth flotation wherein air bubbles are incorporated into a turbulent pulp and a frothy product is removed from the surface of the pulp.

A more specific object is to provide a method for separating slimed minerals by causing an aqueous mixture of the slimed minerals to separate into a flocculated concentrate of one or more of the minerals and a deflocculated aqueous concentrate of other mineral matter Georgia.

Another object is to provide a rougher concentration step for removing colored titaniferous impurities from kaolin clay, which step may be carried out in a more economical manner than rougher froth flotation of the clay.

I have discovered a novel method for separating dissimilar slimed minerals from each other which includes some of the processing steps utilized in carrying out froth flotation but obviates some of the difficulties inherent therein.

In accordance with the present invention, a dispersed (deflocculated) aqueous slip containing a plurality of slimed mineral species is conditioned with a high energy input in the presence of an emulsified polar-nonpolar reagent that selectively films desired slimed constituents with a hydrophobic coating without forming large (macroscopic) oil globules. The hydrophobic constituents may be composed in part of a finely divided floatable solid added to the slip to promote the collection of a hydrophobic mineral in the original mixture of minerals. The slip is then maintained under quiescent conditions until flocculated hydrophobic particles rise and float on or at the surface of the deflocculated slip in the form of loosely-bonded agglomerates. The deflocculated slip (tailing) is separated from this floated matter. The slip and/or float may be further processed to obtain products of desired composition.

From the brief description of the invention, it is apparent that the process of the invention is similar to froth flotation up to and through the conditioning step. However, in beneficiating a slimed pulp by froth flotation, the separation is carried out under turbulent conditions and air is introduced under the pulp surface. Under these conditions, there is substantial entrainment of unfilmed slimes in the resulting froth unless the conditioned slip is diluted substantially. When using slimed pulps sufficiently dilute to minimize entrainment, the tailing product is therefore obtained at a low solids content.

In carrying out the process of the present invention, in contrast, the separation of flocculated hydrophobic particles from deflocculated water-wetted particles takes place without strong external agitation or injection of secondary air. Under these conditions entrainment of the water-wetted particles is minimized in spite of the fact that the slips may be at higher solids than would be suitable for froth flotation. Thus, the tailing product may be obtained at higher solids without the need for costly flotation equipment and with reduced water requirements.

The following points out some of the advantages of my process as applied to a process in which the valued mineral was recovered in the deflocculated aqueous tailing. In a pilot plant operation of my process with discolored Georgia kaolin clay there was a 70 percent recovery of purified kaolin clay as compared to a 40 percent to 50 percent recovery by froth flotation of a similarly conditioned, diluted pulp of the same type of clay at a similar reduction in colored titania impurity content. With my process, the rougher concentration was carried out in equipment occupying about one-quarter the floor space occupied by the froth flotation cells. Only half as much water was employed when the process of the invention was used and the rougher clay concentrate was obtained at about twice the concentration of the rougher slip of clay from the froth flotation cells.

Still another advantage of the process of the invention is that a purified slip of unfractionated kaolin clay may be obtained at a solids content of 20 percent or above. At these solid contents, the slip may be fractionated in a centrifuge to recover a desired fine size fraction of kaolin. When an unfractionated kaolin clay is purified by froth flotation, the slip of purified clay is too dilute to charge to a centrifuge. For this reason, among others, it has been the practice to fractionate a clay before flotation. Among other difficulties or limitations, the procedure does not result in a beneficiated coarse size fraction of clay.

When a valuable slimed mineral is recovered in the float product, it may be obtained as a higher grade concentrate than would be obtained by rougher froth flotation with a deflocculated pulp at the same solids content. This is because of the reduced entrainment of gangue when separation takes place in the nonturbulent pulp.

It was surprising that a conditioned slimed ore pulp could be concentrated without aeration and froth flotation. Slimed ore pulps are more difficult to concentrate than coarser ore pulps

and the latter invariably require aeration and agitation for air-bubble attachment and collection. It was therefore unexpected that a conditioned deflocculated slimed pulp could be concentrated without the aeration and agitation considered essential when beneficiating the coarser pulps.

It may be reasonably concluded from these results that the conditioning step has a unique effect when it is carried out with a slimed deflocculated pulp containing an emulsified polar-nonpolar reagent. Present experience indicates that conditioning of slimed fluid pulps at high solids results in sufficient solution of air and activation of the hydrophobic particles to float the particles without subsequent agitation and aeration in a flotation cell. To the best of my knowledge this unique effect has never been recognized or appreciated prior to my invention or discovery. Heretofore, the slimed, conditioned pulps were always diluted with a substantial proportion of water before separation was carried out, thereby negating the inherent ability of the selectively filmed particles to float as a result of the conditioning treatment per se.

PRIOR ART

The process of the invention is similar to selective oil agglomeration processes in that in both processes mineral species are separated as a result of agitating a mixture of minerals in water containing organic reagents. However, the parameters of my process are fundamentally different; consequently, the agglomerates or floccules are formed in a different manner and are very different in character. Thus, oil agglomeration, as described for example in U. S. Pat. Nos. 763,259–60 and 777,273–4 to Catermole, requires the use of large quantities of oils, e.g., 100 lb./ton of ore. The agglomerates are dense strongly bonded masses, typically one-fourth inch in diameter. The process of the invention utilizes very small quantities of emulsified reagents, sufficient merely to film the solids with a monolayer. For example, my process generally utilizes from about 5 to 10 lb./ton organic reagents per ton of clay. Under the conditions employed in my process, the filmed particles are collected in the form of a fluffy mass of loosely bonded aggregates which usually float as a unitary layer.

As another distinguishing feature, prior art agglomeration processes generally depend upon the expenditure of power to compact the particles into the desired dense coherent agglomerates. This is not true of the process of the invention because in my process the only agitation required is that necessary to mix the ingredients and film the particles.

Further, in my process reagents are emulsified and macroscopic oil globules are absent. Prior art oil agglomeration processes depend upon the bridging action of macroscopic oil globules during collection.

As pointed out above, my process differs fundamentally from froth flotation in that quiescent settling is used in lieu of air injection and agitation. Significantly, my process produces best results when the aqueous slurries contain reagents which minimize and preferably eliminate the formation of a froth or foam on the surface of the pulp during the conditioning step. The formation of such froth undesirably favors entrainment of water-wetted particles.

DETAILED DESCRIPTION

The process of the invention is applicable to the treatment of minus 200 to 325 mesh mineral masses containing a preponderating amount of slimes (minus 10 micron particles). To respond to the process, the minus 10 micron particles must be a mixture composed in part of particles which may be coated with a polar-nonpolar compound such as soap and also containing particles which remain water-avid when a deflocculated pulp of the mixture is treated with the polar-nonpolar reagent.

The invention is of especial benefit in the treatment of kaolin clays which contain discrete, finely disseminated colored titaniferous impurities. The invention will therefore be described with particular emphasis on clay purification, although it will be understood that the process of the invention is applicable to the concentration of other slimed mineral mixtures and ores.

The titaniferous impurities in sedimentary kaolin clays is generally mustard-color and is believed to be a form of the mineral anatase (TiO_2). Typically the fine size fractions of sedimentary kaolins contain 1 to 2 percent by weight TiO_2, the quantity being sufficient, however, to reduce substantially the brightness of the clay. To obtain high brightness kaolin clay pigments from such fine clay, the TiO_2 content should normally be reduced to 1 percent, preferably less.

Dispersed slips of fine size fractions of kaolin from hydraulic classifiers are a suitable starting material in carrying out the process of the invention. The slips must contain sodium silicate as a dispersant and a wetting agent for the clay particles. Combinations of ammonium carbonate or sodium carbonate and sodium silicate may be used. Hydrosols obtained by adding small quantities of salts of polyvalent metals to dilute sodium silicate are useful. Clay as mined may be used after blunging and dispersing in water. Coarse size fractions of kaolin may also be treated.

The dispersed clay slips must be fluid and watery in consistency and sufficient water must be used to provide a slip of such nature.

As applied to the purification of kaolin clay, the process of the invention entails the selective coating of titaniferous impurities with a water-repellent film without causing macroscopic oil globules to form and while minimizing the formation of foam in the slip of discolored clay. Titania particles in a deflocculated clay slip may be filmed selectively with dispersed or emulsified soaps of fatty acids, such as oleic acid, resin acids, or mixtures of fatty and resin acids (e.g., tall oil). The fatty or resin acid is preferably saponified at least partially before adding it to the deflocculated clay slip. Ammonium hydroxide is a preferred saponifying agent. However, it is within the scope of the invention to saponify the fatty acid mixture in situ in an alkaline deflocculated slip. Oil soluble petroleum sulfonates (anionic) have a desirable effect on the collection of some impurities when used with fatty acids. Preferably, the sulfonate is emulsified by the fatty acid soap and the emulsion is incorporated into the deflocculated clay slip. To curtail foam, an emulsifiable light hydrocarbon oil such as fuel oil or mineral oil is generally incorporated. Alternatively, foam suppressants such as oxalate salts, e.g., ammonium oxalate, may be used. However, when very small quantities of soap are used, e.g., less than about 5 lb./ton, foam formation during conditioning may be minimal without recourse to the use of foam suppressants.

To promote filming, the pH of the dispersed clay slip should be mildly alkaline before filming reagents are added. A pH within the range of 8 to 9 is recommended. Ammonium hydroxide and sodium hydroxide solutions are suitable.

The incorporation of auxiliary finely divided hydrophobic particles such as fatty acid-coated calcite or fatty acid-coated polymeric particles generally aids in the collection of the titania particles. These particles may be coated simultaneously with the titania particles by incorporating them into the deflocculated clay slip before soap and oil are added. The added particles are preferably finer than 325 mesh although minus 100 mesh particles may be used. Especially preferred are particles substantially all of which are finer than 10 microns. The added particles are employed in amount within the range of 5 to 200 percent, preferably 15 to 30 percent, of the clay weight. Any solid which is capable of being filmed with a hydrophobic coating compatible with the other constituents in the slip may be used. Preferably the solid is one capable of being filmed with the same reagent(s) used to film the colored impurities. The solid additive may be a normally hydrophilic mineral such as calcite or barytes or a normally hydrophobic material such as sulfur, talc or wax. Nonmineral solids such as plastics, e.g. (poly)vinyl chloride, polyacrylates and nylon, may be used. Synthetic inorganic solids such as precipitated calcium carbonate and barium sulfate are suita-

ble. The auxiliary solid should have low oil absorption properties to minimize reagent consumption and to avoid difficulties in filming the finely-divided colored titaniferous impurities.

Total solids during the conditioning step may be from 10 to 40 percent by weight, preferably 15 to 25 percent. At solids below 15 percent, excessive water consumption is required. Above 30 percent solids, the pulp may be too viscous for the filmed particles to rise and float when the pulp is held under quiescent conditions. Maximum solids will vary with the particle size and the surface characteristics of the slimed solids.

The conditioning step is carried out by agitating the slip without bubbling air into the slip until selective filming of ore minerals and auxiliary particles takes place. The filming of the slimed particles requires a high energy input and the temperature of the slip normally increases. In a typical conditioning operation the temperature undergoes an increase of about 10° F. to 50° F., usually 15° F. to 25° F. An increase in temperature up to and including the boiling point is within the scope of the invention. The temperature rise as a result of the conditioning step will of course vary for a given power input with the initial temperature of the slip, ambient temperature, the heat transfer properties of the vessel, and with the solids of the slip in the conditioner. In some cases, the slip temperature may not increase.

Using a Denver agitator (impeller-type) with slips at clay solids levels of about 15 to 20 percent by weight, a conditioning time is usually within the range of about 15 to 30 minutes. Employing high shear agitators, e.g., a Waring Blendor, much shorter times, e.g., a few minutes, are used. When too much energy is applied, the slimed particles may compact into hard dense spherical agglomerates. Obviously conditioning should stop before this takes place.

The slip or pulp usually has the appearance of a homogeneous creamy suspension after the conditioning is complete. Foam should be minimal.

To effect the collection of the impurities, the creamy suspension is maintained under nonturbulent conditions until the hydrophobic floccules rise and float. Mild agitation may be carried out well under the surface of the conditioned slip to prevent sedimentation of the deflocculated solids or to facilitate withdrawal of the deflocculated slip when the process is carried out on a continuous basis. The agitation, however, should not be severe enough to cause a vortex or to whip air into the slip.

As settling progresses, the rapid upward movement of a layer of flocculated particles may be observed. As the particles move upwardly in the slip the definition between the layer of hydrophobic floccules and the deflocculated aqueous slip becomes more striking. When the coated particles reach the water-air interface they form a lightweight spongy layer that is free from hard, dense agglomerates. Apparent movement within the slip ceases. Below the floated layer is an opaque creamy slip, which in the case of clay, is usually appreciably whiter than the slip of conditioned clay. Unless the slip has been agitated during the settling period, sedimentated particles may be observed at the bottom of the slip.

The floated layer may be separated from the deflocculated slip by various means. The technique employed will depend on the equipment that is available. Employing an upright settling cylinder, the deflocculated slip may be drained from a port near the lower portion of the cylinder. When this system is used, agitation of the floated layer should be minimized or avoided because it may result in removing air from the float and the floated material will sink and report with the slip while the slip is being withdrawn. Alternatively, the floated layer may be removed from the surface of the deflocculated slip. As a further variation, the separation may be carried out on a continuous basis with the floated layer being scraped from the surface and the slip being withdrawn adjacent the base of the slip. The apparatus may include means to remove sediment simultaneously. An apparatus suitable for effecting the separation on a continuous basis is the Komline-Sanderson SR type unit, described in Bulletin No. 129, 8/67, "Flotation Clarification and Recovery Practice," Komline-Sanderson Engineering Corporation, Peapack, New Jersey.

In some cases, separation may be effected by filtration or screening. This separation method is especially applicable when relatively coarse particles, e.g., plus 325 mesh particles, were added to the pulp to aid in the collection of slimes.

It is also within the scope of the invention to stir the slip mildly after the float has formed. As mentioned, this will remove occluded air from the floated layer and cause it to settle. In this case, the fluid aqueous slip may be removed from the hydrophobic settled mass by decantation.

The tailing product (deflocculated slip) is lower in solids than the original treated slip. Slips containing 15 to 25 percent solids typically contain 13 to 22 percent solids after the float product is removed. A representative float product may contain about 50% solids. The invention is not limited, however, to the production of concentrates at these specific solids levels since they have been mentioned for illustrative purposes only. The TiO_2 analysis of clay in the tailing of a rougher separation is generally about 50 percent of that of the starting clay. In some cases appreciably more than 50 percent of the titania impurity is removed during a single (rougher) quiescent settling operation.

The deflocculated slip (tailing) from the rougher stratification treatment may be treated in various ways to remove residual impurities or solid additive and organic reagents.

A preferred method for cleaning the deflocculated tailing from the rougher concentration is to recondition (agitate) the slip without removal or addition of reagents and maintain the reconditioned slip under quiescent conditions until solids flocculate and float. This may be carried out a plurality of times. By cleaning a clay tailing in this manner, the slip of purified clay may be produced at solids levels of 15 to 25 percent. In contrast, purified clays from commercial cleaner froth flotation cells generally are obtained as slips containing from 3 to 10 percent clay solids. In some cases it may be beneficial to dilute deflocculated slips from the rougher beneficiation step before the slips are cleaned by reconditioning them without addition of reagents and then maintaining the slips under quiescent conditions until floats form.

As an alternative, the tailing may be diluted and agitated and aerated in a froth flotation cell. Residual conditioning reagents and impurities report as a froth.

In some cases, oxidation of residual organic flotation reagents in the rougher slip of clay suffices to impart the desired whiteness and brightness to clay without subjecting the clay from the rougher treatment to further cleaning. If desired, the clay slip may be treated with an oxidizing agent after it has been cleaned by any of the methods described hereinabove. When treating gray kaolin clays the oxidation treatment is of especial benefit because it also brightens the gray clay substantially when the treatment is carried out in conjunction with a subsequent treatment with a reducing bleach reagent, as described in U. S. Pat. No. 3,353,668 to James B. Duke.

To increase the recovery of a mineral such as clay which is concentrated in the trailing, the floated layer from the rougher cleaning may be diluted, reconditioned and the reconditioned pulp maintained under quiescent conditions. The underflow (e.g., the aqueous clay slip) is then separated. If desired, the underflow may be combined with the clay clip from the rougher cleaning and the mixture subjected to further beneficiation. Clay recoveries of 98 to 99 percent have been obtained in this manner.

A slip of purified clay may be flocced, thickened, bleached and dried by means well within the skill of the art. By carrying out the rougher and cleaner operations at high solids (e.g., 15 percent and above), the clay may be bleached without removing water.

In an embodiment of this invention whole (unfractionated) kaolin is purified and the purified slip of clay is fractionated to recover a fine and/or coarse size fraction by centrifuging. The kaolin is blunged and dispersed in the usual manner, wet-degritted to remove plus 325 mesh (Tyler) particles, and the

degritted slip is conditioned with soap and, preferably emulsified light oil. The conditioned slip is given a rougher purification, in accordance with this invention, by quiescent settling and separation of the slip from the float which contains the colored impurities. This conditioning and separation is carried out at a solids content within the range of 20 percent to 40% and may be repeated with the slip of purified clay from the rougher concentration until a deflocculated slip containing clay of desired purity is obtained at a solids content above 20 percent. Clay recovery may be improved by diluting the float with water, conditioning, quiescent settling and recovering the tailing. The purified clay in the form of a deflocculated slip at 20 to 30 percent clay solids is then fractionated in the centrifuge in the usual manner.

The invention has been described with especial reference to the purification of clay in an alkaline deflocculated slip using a soap to coat discrete colored impurities in the clay. Other slimed mineral masses to which the present separation method may be applicable included slimed oxidized and sulfide ores as well as mixtures of sulfide and oxidized minerals. Examples of slimed mineral mixtures included talc ores, phosphatic slimes, slimed manganese ores and slimed iron ores (oxide and sulfide ores). Oiling reagents similar to those used to coat titaniferous impurities are suitable for collecting oxides of transition metals and effecting their separation from silica and silicate minerals in an alkaline deflocculated pulp containing sodium silicate to depress silica and silicates.

Cationic reagents may be used when silica or silicate minerals are to be rendered hydrophobic and separated, for example, from oxide or carbonate minerals. In all cases, the pulps must be well deflocculated before selective filming takes place.

Following are examples illustrating embodiments of the present invention and some of its advantages. In the examples, all proportions are expressed on a weight basis.

Brightness values refer to values obtained with a G.E. Recording Spectrophotometer by TAPPI Standard Method T–646 m–54. These values are indicative of the titania contents of clay products.

EXAMPLE I

This example illustrates the preparation, in accordance with this invention, of a 91.6 percent bleached brightness kaolin clay at a 90 percent weight recovery from an 84.3 percent brightness fine size fraction of a white clay from Washington County, Georgia. Minus 325 mesh plastic particles, tall oil soap, petroleum sulfonate and hydrocarbon oil were used to collect the colored impurities.

A sample of the crude was blunged, dispersed with sodium carbonate and sodium silicate, degritted by sedimentation and fractionated in a Tolhurst centrifuge to provide a slip of dispersed fine clay at least 80 percent by weight of which was finer than 2.0 microns.

A 2,500 gm. sample of the dispersed slip at 20 percent solids and containing 500 gm. clay (dry weight) basis bas placed in a Denver conditioner. The agitator was started and 50 gm. of powdered polyvinyl chloride resin ("QYNV") was added. The plastic contained particles predominantly within the range of 1 to 3 microns.

Forty-five ml. of 5 percent ammonium sulfate solution was added while the agitator was in operation, bringing pH to 7.5. Over a period of 1½ minutes, there was added an emulsion made by agitating a mixture of 20 ml. of a 2.5 percent solution of ammonium hydroxide and 67 drops of a 50/50 (weight basis) mixture of the tall oil acids (68–73 percent fatty acids and 25–27 percent rosin acids) and a solution of calcium petroleum sulfonate in mineral oil ("Calcium Petronate"). After the emulsion had been added, the pH was 8.4. Forty-five drops of fuel oil ("Eureka M") was gradually added over a period of 6½ minutes with agitation. After all of the reagents had been added the agitation was continued for an additional 25 minutes. At the end of this period, the slip temperature was 100° F.

The warm creamy slip was placed in a clear plastic container with a drain and valve near the bottom. The container was secured at a 45° angle and allowed to stand without agitation for 5 minutes. A spongy brownish-yellow layer formed above a milky-appearing, fluid slip of dispersed clay. The dispersed clay slip was drained by opening the valve in the container. Without adding water or other reagents the clay slip was agitated in the Denver conditioner for a minute and placed in another clear plastic container provided with a valve. The slip was maintained under quiescent conditions for 5 minutes. The bottom fluid layer was drained and then recleaned by the steps used in the first cleaning step. The resulting slip of purified clay had a solids content of 17 percent.

The clay obtained by the rougher and two cleaner settling steps had a brightness of 89.7 percent and represented a 90 percent clay recovery. The beneficiated clay was bleached to 91.6 percent brightness by treatment with 9 lb./ton zinc hydrosulfite at a pH of 3.

Thus, 90 percent of the impure 84.3 percent brightness white clay was recovered in the form of a 17 percent solids slip of purified clay having an unbleached brightness of 89.7 percent and a bleached brightness of 91.6 percent.

By processing the floated layer containing the impurities, clay recovery could be improved.

EXAMPLE II

This example illustrates the preparation by the process of the invention of a 91.3 percent unbleached brightness kaolin clay at an excellent recovery from another sample of the impure Washington County kaolin clay. Minus 325 mesh calcite, tall oil soap, petroleum sulfonate and oil were used to collect the impurities.

A sample of crushed kaolin clay was blunged in deionized water at 40 percent solids in a Denver agitator. The pH of the resulting blunged clay was 4.1. To disperse the blunged clay, a 5 percent solution of sodium hydroxide was added with agitation for 15 minutes, bringing the pH to 5.2. Following this, a 5 percent solution of soda ash was added in amount of 2.2 lb./ton and the mixture was agitated for 30 minutes. The pH was 7.4 at this point. A dilute hydrosol containing 6.0 lb./ton "N" sodium silicate solution and 0.6 lb./ton alum was added. The slip was then agitated for 20 minutes. The resulting dispersed slip had a pH of 7.8 and was at about 22 percent solids.

To degrit and fractionate the slip, it was allowed to settle for 5 minutes and the supernatant was fractionated on a Tolhurst centrifuge under conditions calculated to produce an aqueous effluent containing clay particles of which at least 80 percent by weight were finer than 2 microns, equivalent spherical diameter.

A 2,110 gm. portion of the slip of fractionated 84.3 percent brightness kaolin clay at 22 percent clay solids (470 gm. dry fractionated clay) was placed in a Denver agitator. While the agitator was in operation, 100 gm. of minus 325 mesh calcite classified to a mean particle size below 5 microns was added and the slip was agitated for 1 minute. A dilute ammonium soap dispersion obtained by agitating about 50 drops of the refined tall acids, 50 drops of "Calcium Petronate" and 20 ml. of 2.5 percent ammonium hydroxide solution was added to the slip over a period of 1½ minutes while the slip was being agitated. The amount of reagents added corresponded to 4.5 lb./ton of tall oil acids and 4.5 lb./ton of the sulfonate solution. After agitation was continued for 5 minutes, "Eureka M" oil was added in amount of 8 lb./ton. The pulp was conditioned for a total of 60 minutes.

The warm conditioned pulp was immediately transferred to the plastic cylinder. The cylinder with contents was allowed to stand in a room at about 75° F. for 5 minutes without agitating the slip or moving the cylinder. A fluffy material resembling natural sponge formed on the top of the slip. This layer, which contained the oiled impurities and calcite, readily broke down into a uniform paste when gently pressed between the fingers.

The clay slip was separated from the top layer by opening a drain at the bottom of the cylinder and the slip was returned to the Denver agitator. Without diluting it, the slip was mixed in the Denver conditioner for 1 minute without aeration. The slip was then maintained under quiescent conditions, resulting in the formation of a yellow fluffy scum substantially smaller in volume than the layer in the original stratification step and similar in appearance and texture. The clay slip was drained and the agitation and settling were repeated one more time.

The resulting purified clay slip had a solid content of about 20 percent and represented an 87 percent recovery of the clay in the original fractionated clay slip.

A sample of the slip was dried overnight at 220° F. and tested for brightness by the TAPPI procedure. Unbleached brightness was 91.3 percent. SInce the original fractionated clay had a brightness of 84.3 percent before stratification, the clay had increased 7.0 percent in brightness as a result of the treatment. TiO_2 content of the fine size fraction of kaolin clay was reduced from 2.7 percent to 0.26 percent.

EXAMPLE III

Following is an illustration of the process of the invention carried out without addition of an auxiliary solid to aid in the separation of titaniferous impurities from a fine size fraction of kaolin clay.

A sample of white Georgia kaolin was blunged in water, dispersed with soda ash and a hydrosol formed by adding a dilute solution of alum to a dilute solution of "N" sodium silicate, as in the previous example. The clay was degritted and fractionated to at least 80 percent minus 2 microns. The slip of fine size clay was at about 22 percent solids and had a pH of 7.8. The clay in the slip analyzed about 2.69 percent TiO_2.

A 500 gm. charge of the 22 percent solids slip was added to a large Waring Blender and brought to a pH of about 8 by adding ammonium hydroxide solution. A 5 percent aqueous solution of ammonium sulfate was then added, followed by the incorporation of the emulsion described in Example I. The emulsion was employed in proportion corresponding to 2 lb./ton NH_4OH, 4.5 lb./ton of tall oil acids and 4.5 lb./ton "-Calcium Petronate.": After addition of the emulsion the Waring Blendor was covered and run at high speed for 1 minute. "Eureka M" oil was added in amount of 8 lb./ton over a period of 6 minutes while the Waring Blendor, was in operation. The agitation was continued for 10 minutes after all of the oil had been added. Total conditioning time was 18 minutes. As a result of conditioning, pulp temperature increased from 70° F. (before any conditioning) to 151° F. after conditioning was complete.

As soon as the motor of the Waring Blendor was shut off, the hot pulp was poured into a 8-inch diameter plastic cylinder provided with a drain near the base. With the drain closed the cylinder and contents were maintained stationary and without agitation.

A very dark foamy layer, about ½ inch deep, formed on the surface of the pulp. After the pulp had been allowed to settle for 5 minutes, the drain was opened and the clay slip was withdrawn without removing the dark foamy layer. The clay slip was returned to the Waring Blendor which was closed and operated at high speed for 1 minute. The contents were returned to another cylinder with a drain. After standing in the cylinder for 5 minutes, the clay slip was drained. The agitation and draining was repeated one more time.

The clay slip from the second cleaner step was at about 17 percent solids and contained 90% of the fine size fraction of kaolin clay that was processed. Chemical analysis of the purified clay indicated that it contained 0.97 percent TiO_2. Since the fractionated clay from which the purified clay was obtained analyzed 2.69 percent TiO_2, about two-thirds of the titania was removed by the treatment. The purified clay was bleached by treating it sequentially with potassium permanganate and zinc hydrosulfite, as described in U. S. Pat. No. 3,353,668 to Duke.

EXAMPLE IV

Example I was repeated with another sample of the dispersed slip of fractionated Washington County clay crude using 150 gm. minus 325 mesh barytes instead of 50 gm. powdered (poly)vinyl chloride resin. Conditioning reagents for the 20 percent solids slip (500 gm. dry clay) were: minus 10 micron barytes, 150 gm.; 5 percent solution of ammonium sulfate, 45 ml.; an emulsified mixture containing 20 ml. 2.5 percent ammonium hydroxide solution, 103 drops of a 50/50 mixture of the tall oil acids of Example I and "Calcium Petronate" and then 77 drops "Eureka M" oil. Conditioning time after all reagents had been added was 25 minutes. Slip temperature was originally 73° F. After conditioning the temperature was 102° F.

The conditioned slip was placed in the transparent container which was maintained at an angle of 45°, as in Example I. After 5 minutes, concentration of the colored impurities took place, as evidenced by the presence of a lower milky white layer and a top spongy layer. The procedure was repeated twice, with a 1 minute conditioning time as in Example II. The lower layer from the second cleaning was at 16.7 percent solids and contained 87 percent of the clay. The clay bleached to a brightness of 89.6 percent with zinc hydrosulfite and contained 0.42 percent TiO_2.

EXAMPLE V

Still in accordance with the present invention, a 79.2 percent brightness fine size fraction of gray Georgia kaolin clay was brightened to 90.5 percent with a 97 percent clay recovery. TiO_2 content was reduced from about 1.5 percent to 0.51 percent.

The details are as follows: The clay was blunged, dispersed with sodium carbonate and "N" sodium silicate solution, degritted and fractionated as in Example I. The slip of 90 percent minus 2 micron fractionated clay was conditioned at 20 percent solids with 30 percent by weight "Drikalite," based on the clay weight, ammonium sulfate, and an emulsion of water, ammonia, tall oil acids and "Calcium Petronate" using proportions of reagents employed in Example I. Total conditioning time was 17 minutes. The conditioned slip was immediately transferred to a glass beaker and allowed to stand until layers formed. The clay slip was separated from the floated layer by siphoning and the latter was diluted, conditioned for 1 minute and allowed to settle. The deflocculated clay slip was combined with the deflocculated clay slip from the first settling. The resulting slip was conditioned for 1 minute in the Denver cell and allowed to settle. After floated matter was removed, the slip of beneficiated clay was flocced with sulfuric acid, thickened, treated with dilute potassium permanganate solution at 180° F. and a pH of 2.5. Following this the slip was bleached with zinc hydrosulfite, filtered, dried and pulverized. The resulting clay had a brightness of 90.5 percent.

EXAMPLE VI

This example illustrates the treatment of kaolin clay by the method of this invention to provide purified clay at a sufficiently high solids content (27.8 percent) to charge to a centrifuge for particle size fractionation.

Pulverized Washington County crude (2,340 gm. "as is" clay basis) was agitated in 2,660 ml. water in a Fagergren agitator for 15 minutes to form a slip containing 40 percent solids. The slip was dispersed by adding 80 ml. of a 5 percent aqueous solution of sodium carbonate, agitating for 15 minutes, and then adding 120 ml. of a hydrosol obtained by mixing 80 ml. of "O" sodium silicate solution diluted to 5 percent with water and 40 ml. of a 1 percent alum solution. After the hydrosol was added, the slip was agitated for 15 minutes.

The slip was degritted by sedimentation to remove plus 325 mesh grit. The degritted slip contained 27.8 percent solids and the clay analyzed 1.86 percent TiO_2 (weight).

The degritted slip was returned to a Fagergren flotation cell. To a 1500 g. charge of the degritted slip there was added over a period of 1½ minutes an emulsion containing 60 ml. of 2.5 percent ammonium hydroxide solution and 300 drops of a 50/50 (w/w) mixture of the tall oil acids and "Calcium Petronate." Over a period of 1 minute, 90 ml. of a 5 percent solution of ammonium sulfate was added. The slip was intensively agitated for 30 minutes with the air inlet closed.

After the agitation was terminated, the slip was placed in the 8 inch plastic cylinder at a 45° angle and allowed to stand for 5 minutes. The clay slip was drained from below. The clay slip was agitated again for 1 minute, returned to the settling cylinder, maintained quiescent for 5 minutes and clay drained from the floated impurities. This was repeated one more time, producing a 27.8 percent solids slip of purified clay at a sufficiently high solids level to be fractionated on a centrifuge.

The purified slip of clay was fed to a laboratory model Bird centrifuge which as operated under conditions calculated to produce as an overflow a fine size fraction of purified kaolin clay in which at least 80 percent by weight of the particles were finer than 2.0 microns, equivalent spherical diameter. The fine size fraction, representing 63 percent of the clay charged to the centrifuge, was found to analyze 0.33 percent TiO_2. The slip was at 23.8 percent solids.

The purified clay in the slip had an unbleached brightness of 86.6 percent. The use of 12 lb./ton zinc hydrosulfite bleach resulted in a 90.0 percent bleached brightness clay product.

EXAMPLE VII

In accordance with the present invention, pyrolusite in a finely disseminated low grade manganese ore from Chile was concentrated from silica and silicates along with calcite which was subsequently separated from the manganese by froth flotation.

The starting ore analyzed 22.3 percent Mn, 4.8 percent SiO_2 and 24.64 percent CaO.

The details of the procedure used to separate pyrolusite and calcite from the silica and silicate gangue are as follows.

The ore was crushed to minus 10 mesh and wet-ground to 98 percent minus 200 mesh at 50 percent solids. The ground ore was diluted with water to 25 percent solids and potassium ferrocyanide (0.2 lb./ton) was added to depress ferruginous gangue. The pulp was deflocculated by adding soda ash (1.0 lb./ton) and then incorporating a hydrosol obtained by adding a dilute alum solution to a dilute solution of "0" sodium silicate. The hydrosol was used in proportion corresponding to 8.0 lb./ton sodium silicate solution and 0.8 lb./ton alum. The deflocculated pulp was then conditioned at 25 percent solids with 9.0 lb./ton ammonium sulfate as a 5 percent solution and with an emulsion containing tall oil acids (2.0 lb./ton) "Calcium Petronate" (4.5 lb./ton) and ammonium hydroxide (2.0 lb./ton). Following this, "Eureka M" oil was added in amount of 8.0 lb./ton. Conditioning time was 25 minutes.

The charge was placed in the plastic container which was maintained at a 45° angle for 3 minutes. The deflocculated slip was drained from the dark floated layer. The floated layer was diluted with water and the mixture was conditioned for 3 minutes, returned to the plastic container and allowed to settle at the 45° angle for 3 minutes. The deflocculated slip was drained and the float material, a concentrate of a mixture of calcite and pyrolusite was recovered.

I claim:

1. A process for concentrating slimed oxide mineral particles from slimed siliceous mineral particles in a mixture thereof which consists essentially of forming said mixture into an alkaline deflocculated slip containing sodium silicate, subjecting said slip to intensive mechanical agitation in the presence of a dispersed fatty acid soap without forming discrete oil globules and substantial froth until oxide particles are rendered hydrophobic and thereby flocculate, without diluting said slip substantially, maintaining it quiescent without bubbling air therein until said flocculated hydrophobic oxide particles rise to the surface of the deflocculated slip and float in the form of a layer of loosely-bonded agglomerates, and separating said deflocculated slip from said layer of agglomerates.

2. The method of claim 1 wherein said slimed oxide particles are composed of an oxide of a transition metal.

3. The process of claim 1 wherein said slimed siliceous particles are kaolin clay and said slimed oxide particles are a colored titania impurity in the clay.

4. The process of claim 3 wherein the slip of kaolin clay containing colored titania impurity undergoes an increase in temperature of at least 10° F. during said agitation.

5. The method of claim 3 wherein the slip is subjected to said intensive agitation and is maintained quiescent at a clay solids content within the range of 15 to 25 percent.

6. The method of claim 3 wherein said slip of deflocculated clay that has been separated from said layer of agglomerates is subjected to high shear agitation without being diluted and, after the agitation has been terminated, the slip is maintained quiescent without aeration until residual titaniferous particles rise and form a floated layer, and the slip is separated from the floated layer.

7. A method for removing colored titaniferous impurities from a fine size fraction of kaolin clay which consists essentially of providing a deflocculated alkaline aqueous slip of said clay containing sodium silicate and added alkali, agitating said slip with a high energy input at a total solids level in excess of 15 percent with a fatty acid soap and a substantial quantity of minus 325 mesh particles different from said clay and capable of being rendered hydrophobic until the temperature of the slip increases by at least 10° F. and the particles of impurity and added minus 325 mesh particles are coated with soap, discontinuing the agitation, without diluting the slip maintaining it under conditions sufficiently quiescent for the slip to stratify into an upper sponge-like layer containing soap-coated particles, which layer floats on a deflocculated slip of purified clay, and separating the deflocculated slip from said sponge-like layer.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,670,883 Dated June 20, 1972

Inventor(s) Samuel R. Weir

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1 - line 69, "of other mineral matter Georgia." should read -- of other mineral matter. --.

Column 9 - line 10, "The resulting purified clay slip had a solid content . . ." should read -- The resulting purified clay slip had a solids content . . . --.

Column 11 - line 36, "4.8 percent SiO_2" should read -- 4.81 percent SiO_2 --.

Signed and sealed this 24th day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

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