

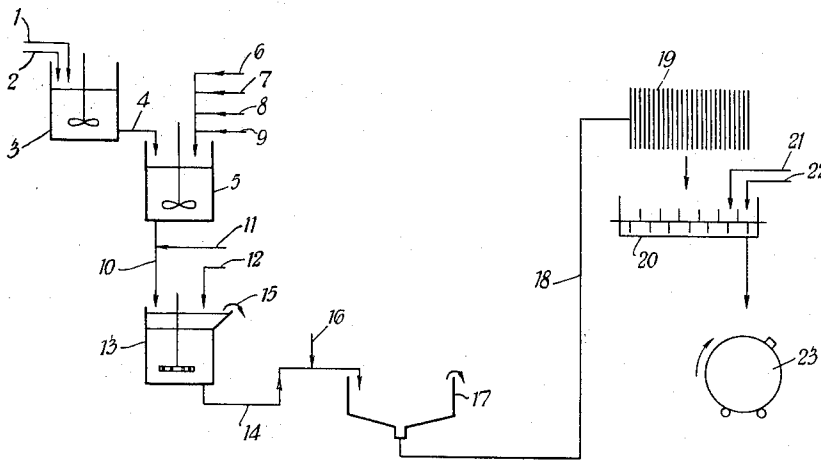
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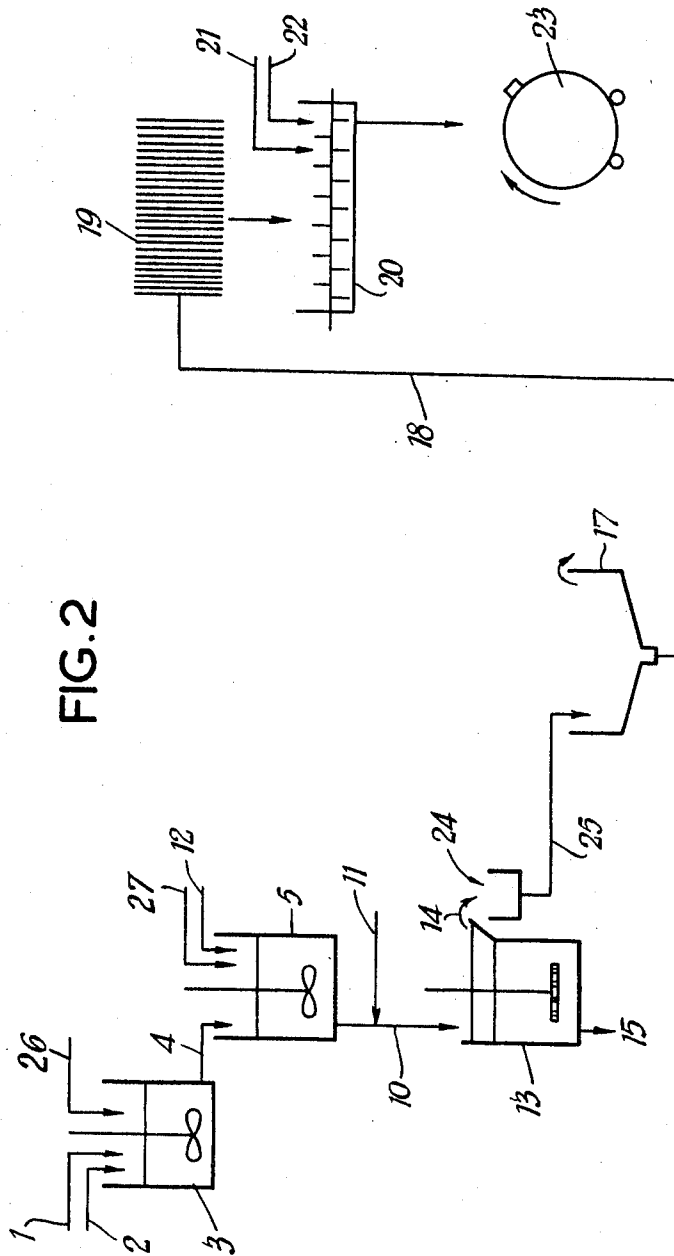
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[54] **GRINDING TREATMENT OF CLAY**
6 Claims, 2 Drawing Figs.
 [52] U.S. Cl. **241/4,**
241/16, 241/20, 241/30

ABSTRACT: A forth flotation process for the removal of mineral impurities from a crude clay wherein the flotation reagents are removed from the purified clay particles by agitation of a slurry of the clay with a particulate grinding material consisting of particles of a size in the range from one-half inch to 100 mesh B. S. sieve. The weight ratio of particulate grinding material to clay is in the range 2:1 to 5:1, and the agitation is continued for a time sufficient to dissipate in the slurry at least 100 horsepower hours of energy per long ton of clay.





GRINDING TREATMENT OF CLAY

This application is a continuation-in-part of Ser. No. 732,386, filed May 27, 1968 and now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the treatment of clay and, more particularly but not exclusively, is concerned with the treatment of kaolinitic clays.

Owing to an increasing demand for high quality white clays for use in the paper coating industry, it is desirable to be able to use deposits of inferior quality kaolinitic clays and to improve their brightness by an economic process. Various processes for improving the brightness of inferior quality kaolinitic clays have been tried, for example flotation or calcination, with varying degrees of success. Some processes are effective on some kaolinitic clays and not on others; and some processes produce kaolinitic clays which although having improved brightness have other unsuitable characteristics, for example calcined kaolinitic clays have a high brightness but are abrasive.

If a froth flotation process, such as is described in U.S. Pat. Specification No. 2,990,958 or No. 3,450,257 (U.K. Specification No. 1,103,585,) is used to treat a clay feedstock containing mineral impurities, it is possible to obtain useful increases in brightness on many types of clay feedstocks. However, with the products of a froth flotation process, and particularly with those clay feedstocks where large quantities of reagents are required, the full potential of the process is not reached because the froth flotation reagents, e.g. oleic acid, are adsorbed by the clay and (a) give rise to frothing difficulties in the subsequent processing of the clay, (b) reduce the gain in clay brightness which would otherwise be obtained, and (c) reduce the gloss of a paper coated with a paper coating composition containing the clay. The reduction in the gain in the brightness of a clay, and the reduction in the gloss of a paper coated with a paper coating composition containing a clay, on which there is adsorbed one or more of the reagents used in a froth flotation process can be demonstrated simply by comparing the properties of a clay before and after the adsorption of a froth flotation reagent thereupon. For example, a sample of clay comprising 65 percent by weight of particles smaller than 2 microns equivalent spherical diameter had a brightness of 82 units and when incorporated in a paper coating composition and coated onto paper under standard conditions gave a sheet gloss of 40 T.A.P.P.I. gloss units, whilst another sample of the same clay to which had been added 6 lbs. of oleic acid per ton of clay had a brightness of 80.5 units and when incorporated in a paper coating composition and coated onto paper under the same standard conditions gave a sheet gloss of 34 T.A.P.P.I. gloss units. It is therefore an object of the present invention to provide an improved froth flotation process for the treatment of a clay in which either the product of the process does not have deposited thereon significant amounts of one or more of the reagents used in the process or the effects of such reagents are nullified.

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a process for increasing the brightness of a clay feedstock, which process comprises the steps of:

- a. subjecting the clay feedstock, after conditioning and in the form of a reagentized aqueous slurry, to a froth flotation process so as to separate mineral impurities from said clay feedstock and to form a suspension of purified clay in a reagentized aqueous liquor,
- b. adjusting the concentration of the suspension of purified clay in the reagentized aqueous liquor, if necessary, to a solids content of at least 20 percent by weight,
- c. mixing the suspension of purified clay with a particulate grinding material in a volume ratio of particulate grinding material to suspension in the range 0.5:1 to 1.5:1, the particulate grinding material consisting of particles of a size in the range from $\frac{1}{2}$ inch to 100 mesh B.S. sieve,

- d. agitating the mixture resulting from step (c) for a time sufficient to dissipate therein at least 100 horsepower hours of energy per long ton of clay, and
- e. separating the particulate grinding material and the clay.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of the invention is particularly useful for treating feedstocks of kaolinitic clays intended for use in the paper coating industry. Such clays will normally have an initial particle size distribution such that at least 5 percent, but generally not more than 60 percent, by weight thereof consists of particles larger than 10 microns equivalent spherical diameter (e.s.d.).

The froth flotation process of step (a) can be carried out in a conventional manner, but advantageously is carried out according to one of procedures A and B described below:

PROCEDURE A

the clay feedstock is formed into an aqueous slurry having a solids content of at least 30 percent by weight, preferably from 35 to 50 percent by weight, and then conditioned at said solids content by agitating the slurry for a time sufficient to dissipate therein at least 20 horsepower hours of energy per long ton of clay. During or before the conditioning of the clay there is mixed with the aqueous clay slurry, a deflocculant, an alkali to raise the pH of the aqueous clay slurry to an alkaline value, a collector for the mineral impurities, and an activator. After conditioning of the clay, there is added to the clay slurry a frothing agent. The reagentized aqueous clay slurry thus formed is then introduced, preferably after dilution to a solids content in the range 15 percent to 30 percent by weight, into a froth flotation cell having a central, internal, submerged impeller wherein it is subjected to a froth flotation process. The purified clay is collected as the machine discharge product.

The deflocculant used in this procedure can be, for example, sodium silicate which is advantageously used in an amount varying from 1.0 to 12.0 lbs. per ton of clay.

The alkali used to raise the pH of the aqueous clay slurry to an alkaline value can be ammonium hydroxide although other similar materials may alternatively be used. In the case of the ammonium hydroxide there will generally be used from 1.0 to 12.0 lbs. per long ton of clay.

The collector for the mineral impurities can be, for example a fatty acid containing from 8 to 20 carbon atoms. Preferred collectors are oleic acid and lauric acid, and in the case of oleic acid there will generally be used from 1.5 to 7.5 lbs. of oleic acid per long ton of clay.

The frothing agent can be, for example, pine oil or a methyl or ethyl ether or polypropylene glycol.

The activator can be, for example, a water-soluble salt of a heavy metal or an alkaline earth metal including magnesium, for example lead acetate or calcium chloride.

PROCEDURE B

The clay feedstock is formed into an aqueous slurry having a solids content of at least 20 percent by weight, preferably from 35 to 50 percent by weight, and there is then added to the aqueous clay slurry a mineral acid to reduce the pH to 4.0 or below. A cationic collector is added to the aqueous clay slurry together with a frothing agent. The reagentized aqueous clay slurry thus formed is then conditioned at the solids content of at least 20 percent by weight, by agitating the slurry for a time, preferably but not essentially sufficient to dissipate therein at least 20 horsepower hours of energy per long ton of clay. The reagentized and conditioned aqueous clay slurry is then subjected to a froth flotation process, preferably after dilution where necessary to a solids content in the range 15 to 30 percent by weight, in a froth flotation cell having a central internal, submerged impeller. The froth containing the purified clay is collected and sprayed with water under pressure to destroy the froth and leave the purified clay in a flocculated state.

The cationic collector employed is advantageously an aliphatic amine having from 8 to 20 carbon atoms or an acetate or hydrochloride of such an amine, and is advantageously used in an amount in the range of from 0.2 to 2.0 lbs. of collector per long ton of clay.

The frothing agent can be, for example, pine oil or a methyl or ethyl ether of polypropylene glycol which is employed in an amount which is approximately the same as the amount of collector employed.

In both Procedures A and B above the froth flotation cell can be, for example, the Denver Sub-A machine shown on page 12-64 of the "Handbook of Mineral Dressing-Ores and Industrial Minerals" by Taggart.

At the end of the froth flotation process of step (a) the purified clay is generally recovered in the form of a suspension, in a reagentized aqueous liquor, having a solids content of less than 30 percent by weight. If the solids content is less than 20 percent by weight, the suspension must be concentrated to at least 20 percent. Preferably the suspension is concentrated to a solids content of at least 65 percent by weight to remove a major portion of the reagentized liquor. This can be achieved by first decanting the suspension, in the case of an anionic flotation process after treatment with a mineral acid to flocculate the clay, to obtain a thickened suspension and then filtering the thickened suspension to obtain a filter cake having a solids content of at least 65 percent by weight.

The clay suspension is re-slurried, if necessary, optionally with a nonmucilaginous dispersing agent, to a solids content in excess of 20 percent, generally from 25 percent to 50 percent by weight and preferably to a solids content of at least 35 percent by weight. There can then be added to the slurry a nonmucilaginous dispersing agent, preferably a water-soluble salt having a macromolecular anion with an average molecular weight in the range 100 to 10,000, for example a polyphosphate, e.g. that sold under the Trade Mark CALGON, tetrasodium pyrophosphate, a sodium salt of a polysilicic acid or a sodium, potassium or ammonium salt of a polyacrylic acid. When a nonmucilaginous dispersing agent is not used the solids content of the slurry preferably does not exceed 40 percent by weight. When a nonmucilaginous dispersing agent is used, the solids content of the slurry may be as high as 65 percent or more by weight. Generally, the amount of nonmucilaginous dispersing agent used will normally lie in the range of from 0.2 to 0.5 percent by weight, based on the weight of clay.

The aqueous clay slurry is then mixed with a particulate grinding material in a volume ratio of particulate grinding material to clay suspension in the range of from 0.5:1 to 1.5:1, the particulate grinding material consisting of particles ranging in size from ½ inch to 100 mesh B.S. sieve. Preferably, the grinding material consists of particles ranging in size from a No. 10 mesh B.S. sieve to a No. 30 mesh B.S. sieve. The particulate grinding material can, with advantage, be for example sand or a calcined china clay. Advantageously, the weight ratio of the particulate grinding material to the clay is in the range 2:1 to 5:1, most preferably about 4:1.

The mixture of aqueous clay slurry and grinding material is then agitated or a time sufficient to dissipate therein at least 100 horsepower hours of energy, per long ton of clay.

When the grinding process has been completed the clay is separated from the particulate grinding material, for example by sieving.

In order to obtain the significant improvements in brightness which are achieved by the present invention, it is essential that the products of the froth flotation process are ground in the manner described herein, since it has been found that other grinding processes do not achieve any significant improvement in the brightness of the clay product over and above that which could be obtained by treating the froth flotation product by a chemical bleaching process.

The invention is further illustrated by the following Examples in which reference is made to FIGS. 1 and 2 of the accompanying drawings which show schematically two installations for carrying out a process in accordance with the invention.

EXAMPLES 1

In this Example the installation shown in FIG. 1 was employed.

A first sample of an impure china clay comprising 60 percent by weight of particles smaller than 2 microns equivalent spherical diameter and having a percentage reflectance to violet light of 458 millimicrons wavelength of 81.0 units was subjected to the froth flotation process described below. The impure clay 1 was mixed with water 2 in a vessel 3 to give an aqueous slurry containing 38 percent by weight of solids. The aqueous slurry was fed via a conduit 4 to a vessel 5 wherein it was admixed with oleic acid 6, which was added in an amount of 4.5 lbs. of oleic acid per long ton of clay, ammonium hydroxide 7, which was added in an amount of 3.5 lbs of ammonium hydroxide per long ton of clay, lead acetate 8, which was added in amount of 1.4 lbs. of lead acetate per long ton of clay, and sodium silicate 9, which was added in an amount of 6.0 lbs. of sodium silicate per long ton of clay. The reagentized aqueous clay slurry was then conditioned by agitating for 12 minutes under conditions which resulted in the dissipation therein of 23 horsepower hours of energy per long ton of clay. At the end of the conditioning period water was added at 11 to dilute the reagentized slurry to a solids content of 18 percent by weight and the slurry then introduced into a froth flotation cell 13 having a width of 36 inches and provided with a central, internal submerged impeller of diameter 18 inches which was arranged to rotate at a peripheral speed of 1,050 feet per minute. 1.5 lbs. of pine oil per long ton of clay was then added as a frothing agent 12. The resulting mixture was subjected to a froth flotation process for a period of 60 minutes and the machine discharge product containing purified china clay was then bleached with zinc hydrosulphite and refined.

The foregoing procedure was repeated on a second sample of the same impure china clay except that, at the end of the froth flotation process and before bleaching, the machine discharge product was fed by a conduit 14 to a thicker 17, a mineral acid being added at 16 in order to flocculate the clay. The flocs were allowed to settle and the supernatant water decanted off. The thickened clay was then fed via a pipe 18 to a filter press 19 wherein it was compacted to form a filter cake having a solids content of about 70 percent by weight. The filter cake was reslurried in a vessel 20 with water 21 and 0.3 percent by weight of tetrasodium pyrophosphate 22 to give a slurry containing 45 percent by weight of solids. This slurry was then fed to a grinding apparatus 23 comprising a rubber lined cylinder wherein it was mixed with granules of a calcined china clay, having a size intermediate a No. 10 mesh B.S. sieve and a No. 30 mesh B.S. sieve, in the volume ratio of 0.95 volumes of calcined china clay granules to one volume of the suspension of china clay corresponding to a weight ratio of four parts by weight of calcined china clay granules to one part by weight of china clay from the froth flotation process. The cylinder 23 was sealed, placed on rollers and rotated at 61 r.p.m. for a time sufficient to dissipate in the slurry 250 horsepower hours of energy per long ton of clay. At the end of the grinding operation the china clay from the froth flotation process and the coarser calcined china clay used as grinding material were separated by sieving.

Finally, a third sample of the same impure china clay was treated in a similar way except that, after carrying out the froth flotation process and before bleaching, the clay was subjected to a ball milling process. In this process, the machine discharge product was concentrated and formed into a slurry having a solids content of 45 percent by weight using the same procedure as described above. To the slurry there was added 0.3 percent by weight of tetrasodium pyrophosphate and the resulting dispersion introduced into a rubber-lined cylinder containing flint pebbles of diameter ranging between 1½ inch to ¾ inch. The volume ratio of flint pebbles to china clay suspension was 0.95:1, the weight of the charge of flint pebbles being four times the weight of china clay in the suspension. The rubber-lined cylinder was then sealed, placed on rollers and rotated at 61 r.p.m. for a time sufficient to dissipate in

the slurry 250 horsepower hours of energy per long ton of clay. Thereafter the flint pebbles and china clay were separated.

The percentage reflectance to violet light of 458 millimicrons wavelength of the three clay samples, the gloss of a paper coated with a paper coating composition containing the clay samples, were measured and are recorded in Tables 1A and 1B below.

TABLE 1A

	Brightness % reflectance to violet light of 458 m μ wavelength	Increase in brightness	Percent- age of particles smaller than 2 μ
First Sample:			
a. Feed to process	81.0	—	60
b. Froth flotation product	87.0	6.0	
c. Bleached product	87.5	6.5	
d. Refined product ⁽¹⁾	89.0	8.0	90
Second Sample:			
a. Feed to process	81.0	—	60
b. Froth flotation product	87.0	6	
c. Ground product	89.6	8.6	
d. Bleached and refined product ⁽¹⁾⁽⁸⁸⁾	91.0	10.0	90
Third Sample:			
a. Feed to Process	81.0	—	60
b. Froth flotation product	87.0	6	
c. Ball milled product	87.8	6.8	
d. Bleached and refined product ⁽¹⁾	89.3	8.3	90

(1) The refined product was obtained by particle size separation using a centrifuge. In the case of the first sample there was a 48% recovery, in the case of the second sample there was a 95% recovery, and in the case of the third sample there was a 79% recovery.

TABLE 1B

	Gloss of paper coated with paper coating composition employing clay samples ⁽²⁾
First Sample	59 TAPPI Gloss Units
Second Sample	68 TAPPI Gloss Units
Third Sample	62 TAPPI Gloss Units

(2) Standard sheets of paper were coated to a weight of 10 g.s.m. with a paper coating composition comprising the following ingredients:

Clay Sample	100 parts by weight
Starch	10 parts by weight
Styrene-butadiene latex	10 parts by weight
Water	40 parts by weight
CALCON (Trade Mark)	0.3% by weight based on weight of clay.

EXAMPLE 2

In this Example the installation shown in FIG. 2 was employed.

A coarse residue china clay 1 containing, as impurities, mica, quartz and feldspar, was admixed with water 2 in a vessel 3 to give an aqueous slurry containing 40 percent by weight of solids. Sufficient dilute hydrochloric acid 26 was added to reduce the pH of the slurry to 3.0. The aqueous slurry was then transferred to a vessel 5 and admixed therein with oc-

tadecylamine acetate 27, which was added at the rate of 0.8 lbs. per long ton of clay, and pine oil 12, which was added at the rate of 0.8 lbs. per long ton of clay. The reagentized aqueous slurry was then conditioned by agitating for a period of 12 minutes under conditions which resulted in there being dissipated in the slurry 24 horsepower hours of energy per long ton of clay. At the end of the conditioning period water 11 was added to dilute the slurry to 25 percent by weight of solids, the slurry then being fed to a froth flotation cell 13 similar to that used in Example 1. The cell was run for 60 minutes and the froth 14, which comprises kaolinitic clay and mica substantially free from abrasive material, was continuously removed, further additions of water being made at intervals to maintain a substantially constant level of pulp in the cell. The collected froth was sprayed with high pressure water jets 24 in order to suppress the froth and release the product in the form of a flocculated suspension.

The product of the process was divided into three samples, the first of which received no further treatment and the second and third of which were subjected to a grinding process, as described below, for lengths of time sufficient to dissipate therein 80 and 160 horsepower hours of energy per long ton of clay, respectively. More particularly, the second and third samples were treated in the following way:

The flocculated suspension was first concentrated by transferring it via conduit 25 to a thickener 17 wherein the flocs were allowed to settle under gravity, the supernatant water being decanted off. The thickened suspension was then transferred by means of a conduit 18 to a filter press 19 wherein it was compacted to form a filter cake having a solids content of about 70 percent by weight. The filter cake produced in this way was then reslurried with water containing 0.3 percent by weight of tetrasodium pyrophosphate to give a slurry containing 40 percent by weight of solids. 1,880 ml. of this suspension were then introduced into a rubber-lined cylinder 23 of 6.6 litres capacity together with 4,000 g. of granules of the calcined china clay used in Example 1 to give a volume ratio of particulate grinding material to clay/water suspension of 0.81:1, the weight ratio of particulate grinding material to clay mineral being 4:1. The cylinder 23 was then sealed, placed on rollers, and rotated for a time sufficient to dissipate therein a specified amount of energy. Samples of (1) the original coarse china clay, (2) the unground froth flotation product, (3) the froth flotation product ground at 80 horsepower hours of energy per ton of clay, and (4) the froth flotation product ground at 160 horsepower hours of energy per long ton of clay, were then tested (a) for the weight per cent of particles having an equivalent spherical diameter smaller than 2 microns, (b) for the weight per cent of particles having an equivalent spherical diameter greater than 10 microns, (c) for brightness in terms of the percentage reflectance to violet light of 458 millimicrons wavelength before and after bleaching with zinc dithionite, and (d) for abrasiveness. The results obtained are set out in table 2A below:

TABLE 2A

Sample No.	1	2	3	4
Wt.% — 2 microns	6	7	23	34
Wt.% + 10 microns	42	34	11	7
Brightness				
(unbleached)	77.1	78.6	81.7	82.9
Brightness				
(bleached)	78.2	79.8	82.9	85.0
Abrasiveness ⁽¹⁾	185	76	53	53

(1) The abrasiveness was measured by the Valley Abrasion test, and the higher figures represent a higher degree of abrasiveness.

A mineralogical analysis was also made by X-ray diffraction, the results obtained being recorded in table 2B.

TABLE 2B

Sample No.	1	2	3	4
Mineral	% by weight			
Kaolinite	72	77	77	77
Mica	25	23	23	23
Quartz	2	0	0	0
Feldspar	1	0	0	0

EXAMPLE 3

A residue china clay containing, as impurities, mica, quartz and feldspar and having a particle size distribution such that 6 percent by weight consisted of particles smaller than 2 microns equivalent spherical diameter and 45 percent by weight particles larger than 10 microns equivalent spherical diameter was fed to a plane similar to that shown in FIG. 2 in the form of an aqueous suspension comprising 25 percent by weight of dry china clay. To this suspension there were added a cationic flotation collector, ARMAC HT manufactured by Armour & Co., at a dose of 0.3 lb. of the collector per long ton of dry clay, and sufficient sulfuric acid to lower the pH to about 3; and the mixture was conditioned in a stirred tank. Pine oil was then added as a frother at a dose of 0.3 lb of pine oil per long ton of dry clay and the mixture was subjected to continuous froth flotation in four stages, the feed to each successive stage being the machine discharge product from the previous stage. The froth from the flotation cells in all four stages was collected and sprayed with fine jets of water and the machine discharge product from the cell or cells in the fourth stage was discarded as waste.

The froth product was thickened by gravity in a tank and then filter pressed to give a cake containing 69 percent by weight of dry china clay. The filter cake was then mixed with sufficient water to give a suspension containing 27 percent by weight of solids and no dispersing agent was added. 340 gallons of this suspension and 43 cwt. of silica sand consisting of particles having sizes in the range 16 to 30 mesh B.S. sieve were loaded into a sand grinding mill and agitated for a time sufficient to dissipate in the suspension 150 horsepower hours of energy per long ton of dry clay. The weight ratio of dry sand to dry water suspension was 0.54:1. The suspension of ground clay was then separated from the sand by sieving.

Samples of the feed to the flotation plant, the froth product and the sand ground froth product were tested for percent reflectance to light of 458 and 574 millimicrons wavelengths and for particle size distribution. In order to determine the susceptibility of the samples to chemical bleaching each was treated in aqueous solution at pH 2.8 with sodium dithionite, the dose of sodium dithionite in each case corresponding to 4 lb. of the dithionite per long ton of dry clay. The bleached clay was then filtered, washed and dried at 80° C. and the percent reflectance to light of 458 and 574 millimicrons wavelength was determined. The results obtained are shown in table 3 below.

TABLE 3

	Feed	Froth	Sand ground product
% by wt. smaller than 2 microns e.s.d.	6	8	30
% by wt. larger than 10 microns e.s.d.	45	36	8
% reflectance to light of 458 m μ (unbleached)	77.0	78.4	82.7
% reflectance to light of 574 m μ (unbleached)	82.5	84.8	87.5
% of reflectance to light of 458 m μ (bleached)	77.7	80.2	84.1
% reflectance to light of 574 m μ (bleached)	82.7	84.2	87.9

A further quantity of the same residue china clay was treated in an identical manner except that, after the froth product had been thickened by gravity in a tank and then filter pressed, the filter cake was mixed with a smaller quantity of water and no dispersing agent to give a suspension containing 45 percent by weight of solids. 340 imperial gallons of this suspension were mixed with 43 cwt. of the same silica sand but it was discovered that the resultant mixture was too viscous to be agitated in the same grinding mill.

EXAMPLE 4

A residue china clay containing, as impurities, mica, quartz and feldspar and having a particle size distribution such that 9 percent by weight consisted of particles smaller than 2 microns equivalent spherical diameter and 39 percent by weight of particles larger than 10 microns equivalent spherical diameter was fed to a froth flotation plant in the form of an aqueous suspension comprising 25 percent by weight of the dry china clay. To this suspension there were added 0.3 lb. of ARMAC HT per long ton of dry china clay and sufficient sulfuric acid to lower the pH to 2.6. The mixture was conditioned in a stirred tank. There was then added 0.4 lb of a frother comprising a methyl ether of polypropylene glycol per long ton of dry china clay and the mixture was subjected to continuous froth flotation in four stages, the feed to each successive stage being the machine discharge product from the previous stage. The froth from the flotation cells in all four stages was collected and sprayed with fine jets of water and the machine discharge product from the fourth stage cell was discarded as waste.

The froth product was thickened by gravity in a tank to give a suspension containing 32 percent by weight of solids. This suspension was then diluted with clean water to 21 percent by weight of solids and the diluted suspension was mixed with silica sand consisting of particles having sizes in the ranges 16 to 30 mesh B.S. sieve in the proportion of 16 cwt. of sand to 135 imperial gallons of suspension. The weight ratio of dry sand to dry china clay was therefore 5.5:1 and the volume ratio of sand to china clay/water suspension was 0.50:1. The mixture was agitated in a sand grinding mill for a time sufficient to dissipate to the suspension 165 horsepower hours of energy per long ton of dry china clay. The suspension of ground clay was then separated from the sand by sieving.

Samples of the feed to the flotation plant, the front product and the sand-ground froth product were tested for percentage reflectance to light of 458 and 574 millimicrons wavelengths and for particle size distribution. In order to determine the susceptibility of the samples to chemical bleaching, each was treated in aqueous solution at pH 2.8 with sodium dithionite. The dose of sodium dithionite in each case corresponded to 4 lbs. of dithionite per long ton of dry china clay. The bleached clay was then filtered, washed and dried at 80° C. and the percentage reflectance to light of 458 and 574 millimicrons wavelength was determined. The results are shown in table 4 below

TABLE 4

	Feed	Froth	Sand ground product
% by weight smaller than 2 microns e.s.d.	9	11	31
% by weight larger than 10 microns e.s.d.	39	33	7
% reflectance to light of 458 m μ (unbleached)	76.9	78.8	82.1
% reflectance to light of 574 m μ (unbleached)	82.2	84.9	87.9
% of reflectance to light of 458 m μ (bleached)	77.5	79.2	83.3
% reflectance to light of 574 m μ (bleached)	82.3	84.6	87.9

EXAMPLE 5

A residue china clay containing, as impurities mica, quartz and feldspar and having a particle size distribution such that 5 percent by weight consisted of particles smaller than 2 microns equivalent spherical diameter and 55 percent by weight of particles larger than 10 microns equivalent spherical diameter was fed to a flotation plant in the form of an aqueous suspension comprising 25 percent by weight of the dry china clay. To this suspension there were added 0.3 lb. of ARMAE HT per long ton of dry china clay and sufficient sulfuric acid to lower the pH to 2.6. The mixture was conditioned in a stirred tank. There was then added 0.4 lb. of the same frother as in Example 3 per long ton of dry china clay and the mixture was subjected to continuous froth flotation in four stages, the feed to each successive stage being the machine discharge product from the previous stage. The froth from the flotation cells in all four stages was collected and sprayed with fine jets of water and the machine discharge product from the fourth stage cell was discarded as waste.

The froth product was thickened by gravity in a tank and filter pressed to give a cake containing 69 percent by weight of dry china clay. The filter cake was then divided into portions the first of which was diluted with water containing 0.45 percent by weight of sodium silicate dispersant based on the weight of dry china clay to give a suspension comprising 51 percent by weight of solids. The second was diluted with water containing the same quantity of sodium silicate to give a suspension comprising 60 percent by weight of solids and the third was mixed with the same quantity of water so that the final solids content of the suspension was still nearly 69 percent by weight. The first suspension was mixed with silica sand consisting of particles having sizes in the range 16 to 30 mesh B.S. sieve in the proportion 1 cwt. of sand to 7 imperial gallons of suspension. The weight ratio of dry sand to dry china clay was therefore 2.1:1 and the volume ratio of the sand to china clay/water suspension was 0.61:1. The mixture was agitated in a sand grinding mill for a time sufficient to dissipate in the suspension 105 horsepower hours of energy per long ton of dry china clay.

The second suspension was mixed with the same sand in the same proportions by volume but the weight ratio of dry sand to dry china clay was now 1.6:1. The mixture was agitated in a sand grinding mill for a time sufficient to dissipate in the suspension 135 horsepower hours of energy per long ton of dry china clay.

The third suspension was also mixed with the same sand in the same proportions but the mixture was found to be so viscous that it was impossible to agitate it in the sand grinding mill.

The first and second suspensions were separated from the sand by sieving and samples of the feed to the flotation plant, the froth product and the sand ground products 1 and 2 from the first and second suspension respectively were tested for percentage reflectance to light of 458 and 574 millimicrons wavelength and for particle size distribution. In order to determine the susceptibility of the samples to chemical bleaching each was treated in aqueous solution at pH 2.8 with sodium dithionite. The dose of sodium dithionite in each case corresponding to 4 lbs. of the dithionite per long ton of dry clay. The bleached clay was then filtered, washed and dried at 80° C. and the percentage reflectance to light of 458 and 574 millimicrons wavelength was determined. The results are shown in table 5 below:

TABLE 5

	Feed	Froth	Sand ground product 1.	Sand ground product 2.
% by weight smaller than 2 microns e.s.d.	5	7	23	33

Table 5—Continued

5	% by weight larger than 10 microns e.s.d.	55	48	18	12
	% reflectance to light of 458 m μ (unbleached)	73.8	76.1	79.3	79.7
	% reflectance to light of 574 m μ (unbleached)	78.8	80.7	84.0	84.8
10	% reflectance to light of 458 m μ (bleached)	74.0	77.4	81.2	81.8
	% reflectance to light of 574 m μ (bleached)	78.6	81.1	84.6	84.7

As previously noted, the clay product of the process of the present invention is of particular value for use in the paper coating industry.

20 I claim:

1. A process for increasing the brightness of a crude clay, which process comprises the steps of:

- 25 i. conditioning the crude clay and thereafter subjecting the crude clay in the form of a reagentized aqueous slurry to a froth flotation process so as to separate mineral impurities from said crude clay and to form a suspension of purified clay in a reagentized aqueous liquor,
- 30 ii. concentrating the suspension of purified clay in the reagentized aqueous liquor to a solids content of at least 65 percent by weight to remove therefrom a major proportion of the reagentized liquor,
- 35 iii. forming the concentrated suspension of purified clay into an aqueous slurry having a solids content in the range of from 25 percent to 50 percent by weight and containing a nonmucilaginous dispersing agent,
- 40 iv. mixing the aqueous slurry of purified clay containing the nonmucilaginous dispersing agent with a particulate grinding material in a weight ratio of particulate grinding material to clay in the range 2:1 to 5:1, the particulate grinding material consisting of particles ranging in size from $\frac{1}{2}$ inches to 100 mesh B.S. Sieve,
- 45 v. agitating the mixture resulting from step (iv) for a time sufficient to dissipate therein at least 100 horsepower hours of energy per long ton of clay, and
- 50 vi. separating the particulate grinding material and clay.

2. A process according to claim 1, wherein the particulate grinding material consists of particles ranging in size from a No. 10 mesh B.S. sieve to a No. 30 mesh B.S. sieve.

3. A process according to claim 2, wherein said mixture resulting from step (d) is agitated for a time sufficient to dissipate therein at least 150 horsepower hours of energy per ton of clay.

4. In a process for increasing the brightness of a clay feedstock wherein the clay feedstock is conditioned and then subjected in the form of a reagentized aqueous slurry to a froth flotation process so as to form a suspension of purified clay in a reagentized aqueous liquor, the improvement which comprises the steps of

- 55 a. adjusting the concentration of the suspension of purified clay in a reagentized aqueous liquor to a solids content of at least 20 percent by weight,
- 60 b. mixing the aqueous suspension of purified clay with a particulate grinding material in a volume ratio of particulate grinding material to clay/water suspension in the range 0.5 to 1.5:1, the particulate grinding material consisting of particles of a size in the range from $\frac{1}{2}$ inches to 100 mesh B.S. sieve,
- 65 c. agitating the mixture resulting from step (b) for a time sufficient to dissipate therein at least 100 horsepower hours of energy per ton of clay, and
- 70 d. separating the particulate grinding material and the clay.

5. A process according to claim 4, wherein the suspension of purified clay in a reagentized aqueous liquor is concentrated to a solids content of at least 65 percent by weight to

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remove a major proportion of the reagentized aqueous liquor and is thereafter formed into an aqueous slurry having a solids content in the range from 20 to 65 percent by weight and containing a nonmucilaginous dispersing agent, prior to mixing in the particulate grinding material in step (b).

6. A process according to claim 4, wherein the suspension

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of purified clay in a reagentized aqueous liquor is concentrated to a solids content of at least 65 percent by weight to remove a major proportion of the reagentized aqueous liquor and is thereafter formed into an aqueous slurry having a solids content in the range from 20 to 40 percent by weight, prior to mixing with the particulate grinding material in step (b).

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