KAOLIN CLAY BENEFICIATION

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Filed June 1, 1965, Ser. No. 467,902
6 Claims. (Cl. 269—166)

This application is a continuation-in-part of applicant's copending application Serial No. 205,786, now abandoned, filed June 27, 1962, entitled "Microdows of Hardness and each Figure on a Cube Face of Fluorite. In this Process Synthetic Organic Polymeric Particles are Used, their Surface Portions of which are Substantially Homogeneous Physically. This is Particularly Important Where There May be a Hydrolytic Adsorption of Organic Acids on Highly Surface-Active Materials. According to this invention, the variation of adsorptive characteristics due to presence of different faces on crystals and the differing activities of those different faces are avoided and, accordingly, a particularly delicate differential separation of desirable from undesirable fractions in clay is obtained.

One object of this invention is to provide an improved process of flotation whereby to separate materials of different surface characteristics.

Another object of this invention is to provide the flotation process for differential separation of extremely finely divided (in the range of 15 to 5 micron diameter size) particles.

Yet another object of this invention is to provide a process whereby to separate impurities from clay and so improve its color.

Still another object of this invention is to provide a process for purifying kaolin clays by flotation and bleaching.

These objects and effects of this invention will be apparent to those skilled in the art on study of the accompanying specification, examples and drawing, which drawing forms a part of this specification and, in which:

The drawing is a schematic representation of an overall plant process for practicing the invention.

While foams are stable by virtue of the ability of their bubble walls to meet mechanical shocks by increase of surface tension on local extension and a fall of surface tension on local contraction with the change of tension being of sufficient duration to outlast small, sudden disturbances by changes in surface concentration of surface active agents, such is not the best surface for separation of finely divided particles as occur in clays. According to this invention, there are provided in the foam or bubble column non-waxy water-insoluble accessory particles whose surfaces are homogeneous. These particles render the foam, of which the bubble column is formed, mechanically stable and also provide to the particles of clay passing through the walls of such foam or bubble column surfaces which have predetermined constant chemical characteristics not affected by minor changes in the composition of the interface between gas and liquid in that foam.

The use of relatively non-polar water-insoluble accessory collector particles, made of materials as in the following example and also such solid, non-waxy polymers as polyethylene, polypropylene, polyethylene, polyvinyl chloride, polyacrylate, polymethacrylates, polyamides, polymethylene polyesters and phenol polyesters in the presence of mineral oils, is covered according to this invention.

The following specific examples are exemplary of the process and other teachings of this invention:

EXAMPLE 1

The following general procedure is followed in each of the examples hereinbelow, except as otherwise noted.

Step 1—200 grams of a high color crude kaolin clay is blended with 100 grams of water in a laboratory Waring blender for 5 minutes. This crude has a size distribution of

62.68% minus 2 microns
12.15% plus 5 microns

and a chemical analysis (by weight) of

39% Al2O3
45% SiO2
0.7% Fe2O3
1.3% TiO2

In this process synthetic organic polymeric particles are used, the surface portions of which particles are substantially homogeneous physically. This is particularly important where there may be a hydrolytic adsorption of organic acids on highly surface-active materials. According to this invention, the variation of adsorptive characteristics due to presence of different faces on crystals and the differing activities of those different faces are avoided and, accordingly, a particularly delicate differential separation of desirable from undesirable fractions in clay is obtained.

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12.15% plus 5 microns

and a chemical analysis (by weight) of

39% Al2O3
45% SiO2
0.7% Fe2O3
1.3% TiO2
and a G.E. brightness, when dry, of 82.0. Such brightness is determined by drying at 90° C. to a moisture content of 1% by weight and then testing the brightness as taught at pages 96-97 of “Kaolin Clays and Their Industrial Uses,” J. M. Huber Corporation, New York, 1955.

Step 2.—The slip is then screened progressively through Tyler 180, 170 and 325 mesh.

Step 3.—To this 67% solids slip, reagents as below described are then added:

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Amount, grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂SO₄ as 20% aqueous solution</td>
<td>0.5</td>
</tr>
<tr>
<td>NH₄OH as 20% aqueous solution</td>
<td>0.75</td>
</tr>
<tr>
<td>Cyanamid 710 (tall oil)</td>
<td>0.62</td>
</tr>
<tr>
<td>Calcium petroate</td>
<td>0.62</td>
</tr>
<tr>
<td>Cyanamid A01 (water-soluble petroleum sulfonate)</td>
<td>0.31</td>
</tr>
</tbody>
</table>

The resulting slip is added to a laboratory Fagergren machine powered with a 1/4 horsepower motor and having a 4-inch outside diameter stator cage within which a smaller rotating cage or impeller rotates at a speed controllably variable from 1200 to 2500 r.p.m. 0.6 gram of sodium metasilicate is added to the speeded Fagergren machine as an aqueous solution 10 grams in volume. The resulting mass is admixed for 5 minutes.

Step 4.—A 68% solid slip of the following was made and blended 5 minutes in a "Lightnin" laboratory stirrer:

<table>
<thead>
<tr>
<th>Grams</th>
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</thead>
<tbody>
<tr>
<td>Caustic soda (as 3.35 grams of aqueous solution)</td>
</tr>
<tr>
<td>Cyanamid 710</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Polyethylene</td>
</tr>
</tbody>
</table>

The polyethylene is in the form of solid spheres of a specific gravity of about 0.93 and a size distribution of:

- 90% minus 100 mesh (Tyler 180 mesh series),
- 50% minus 200 mesh (Tyler 170 mesh series),
- 10% minus 400 mesh (Tyler 325 mesh series).

The resulting accessory solid particle pulp is added to the operating Fagergren machine and admixed therewith for 2 minutes.

Step 5.—To the mixture of slips in the Fagergren machine, sufficient water to make a total of 2,000 ml of water is added; mixing is continued for 1 minute; the air inlet for aeration of the pulp through the hollow impeller is then opened for 5 minutes. A 1.5-inch high bubble column froth is then formed above the pulp body. The clay slip is floated for 5 minutes at a low speed (1,500 r.p.m.) of the impeller of the Fagergren machine.

Step 6.—The weight of the solids carried from the machine in the froth during the first 2½ minutes of the flotation period of Step 5 (the first float fraction) was 142.8 grams. These solids had a color distinctly darker than that of the feed. The weight of solids carried from the machine in the froth during the second 2½ minutes of the flotation period (the second float fraction) was 147.4 grams. The pH of the liquor of the pulp body was 9.4. 106 grams of the residue from the froth flotation treatment was tested for G.E. brightness as above described for Step 1 and provided a G.E. brightness of 84. This 84 brightness fraction treated for 30 minutes at 60° C. with 0.5% sodium hydrosulfite and 0.5% aluminum sulfate (as in U.S. Patent No. 2,539,594 to I. Williams) provided a bleached clay with a G.E. brightness, determined in the same manner as above described, of 87.0. The polyethylene particles in the float fraction are readily separated from the minor portion of the clay therein by gravity separation in water, were recovered and were re-used as in Step 4 above in treating another portion of the feed.

EXAMPLE II

Steps 1–5 were as in Example I, except that:

(a) In Step 1, 200 grams of a dark or low color crude kaolin clay was used. It had a G.E. brightness of 70 and a size distribution as follows:
- 69–74% minus 2 microns
- 8–11% plus 5 microns
and a chemical analysis of:
- 37.15% Al₂O₃
- 44.27% SiO₂
- 0.78% Fe₂O₃
- 1.80% TiO₂

(b) In Step 4, 20 grams of polyvinyl chloride beads of globular shape, a specific gravity of 1.4, and with a particle size of 90% minus 200 mesh, 10% minus 800 mesh was used as accessory particles in place of the polyethylene particles used in Example I. The pH of the liquor in the flotation machine was 9.1.

Step 6.—The first float fraction had a dark color and weighed 34 grams; the second float fraction weighed 42.4 grams. The residue of 117 grams free of polyvinyl chloride particles was recovered and had a G.E. brightness, determined as in Example I, of 72.0. The accessory particles were readily recovered from the float fraction for reuse as in Step 4 for treating another fresh portion of the feed by settling of the clay particles to the bottom and skimming off the polyvinyl particles from the top of a hydraulic classifier to which the float fraction was fed.

EXAMPLE III

Steps 1–5 were as in Example II, except that:

(a) In Step 1, 200 grams of light color crude was used; such crude had a G.E. brightness of 83, a size distribution of 90 to 94% minus 2 microns and 0 to 1% plus 5 microns, and a chemical analysis as follows:
- 57% Al₂O₃
- 43% SiO₂
- 0.34% Fe₂O₃
- 1.6% TiO₂

Step 6.—Flotation according to Step 6 produced a first dark colored float fraction the solids of which weighed 30.5 grams, the solids in the second float fraction weighing 43.9 grams. The residue had no polyvinyl chloride particles therein. The pH of the float liquor was controlled at 9.2 by addition of less than 1 cc. of 0.84 NH₄HSO₄. The G.E. brightness of the product was 84.5. The accessory particles were readily recovered as in Example II.

EXAMPLE IV

Steps 1–5 were as in Example I, except as follows:

(a) Step 1 used 200 grams of the same crude as in Example I with a G.E. brightness of 82.

(b) Step 4 used a reaction mixture of the following composition:

<table>
<thead>
<tr>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caustic soda (0.3 gram of aqueous solution)</td>
</tr>
<tr>
<td>Cyanamid 710</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Nylon particles</td>
</tr>
</tbody>
</table>

These nylon particles were made as follows: 50 grams of “Zytel” nylon 66 melting powder pellets was dissolved in 340 grams of formic acid at 90° C. Nylon fibrils were precipitated by pouring 50 grams of this formic acid solution into 3 liters of distilled water in an operating Waring blender of one-gallon capacity; the operating blender setting was at 90 volts, low speed; the rate of addition of the formic acid solution equaled 4 grams of solution per minute.

The precipitate was thereafter washed and filtered. The particles had a specific gravity of 1.14, an average molecular weight of 12,000, and were round-sectioned smooth-surfaced fibrils of 10 to 500 microns in length and a length/diameter ratio of from 10:1 to 50:1.

Step 6.—The pH of the liquor in the pulp body below
the bubble column was 9.2. The solids in the first float fraction—that obtained from the first 2/3 minutes of the flotation period—was dark colored and weighed 22.1 grams. The solids in the second float fraction—that obtained from the second 2/3 minute portion of the float period—produced solids weighing 31.5 grams. The residue was free of nylon particles and a 101-gram sample of said residue had a G.E. brightness (tested as above) of 85.5. The accessory nylon particles were readily separated by sedimentation from the clay particles in the float fraction and were re-used in treatment of a second portion of clay particles in a reaction mixture as in Step 4 of the example.

The residue was bleached by the same process as in Example I; the bleached product had a G.E. brightness of 88.

Similar result was obtained by using 20 grams of "Dacron" (amorphous polyethylene terephthalate) particles of 93% minus 100 mesh size in place of the nylon fibrils abscised. These particles were fibrils of the same general size and shape as the nylon fibrils but all minus 100 mesh in size.

EXAMPLE V

Steps 1–5 were as in Example IV, except that:

(a) Step 1 used 200 grams of low color crude of Example II with a G.E. brightness of 70.5.

Step 6.—The pH of the flotation pulp body liquor was 9.6 and was lowered to 9.2 by addition of H2SO4. The first float fraction solids were dark in color and weighed 69.4 grams; the second float fraction solids weighed 20 grams. A 153-gram sample of the residue had a G.E. brightness of 73.0. Bleaching of this residue as in Example IV produced a G.E. brightness of 83.5.

Similar results were obtained by using 20 grams of "Colfoam" hollow unicellular colorless microspheres of urea formaldehyde (with alpha cellulose dispersed therein, probably in a substantially molecular state of subdivision). Such material has a true specific gravity of 1.5 but the microspheres, which have an average particle size range of from 2 to 60 microns, have an average specific gravity well below 1.0.

EXAMPLE VI

Steps 1–5 were as in Example I, except that:

(a) In Step 1, 200 grams of a low color clay as in Example II with a G.E. brightness of 72 was used.

(b) In Step 4, the reaction mixture used was:

<table>
<thead>
<tr>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caustic soda (6 grams of solution)</td>
</tr>
<tr>
<td>Cyanamid 710</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Caclite #1 (—325 mesh)</td>
</tr>
</tbody>
</table>

The calcite used was Thompson Weinman & Co. No. 1 White.

Step 6.—The weight of froth fraction solids recovered in the first half of the flotation period was 291 grams. In the latter half of the flotation period 188 grams of solids was recovered. The G.E. brightness of the residue, when dried, was 73.5. The residue had a very substantial portion of calcite therein.

EXAMPLE VII

Steps 1–5 were as in Example VI, except that:

(a) In Step 1, 200 grams of high color crude clay as in Example I with a G.E. brightness of 82 was used.

Step 6.—The first half of the flotation period yielded 182 grams of solid, composed of calcite and clay. The second half of the flotation period yielded 304 grams of solid. A 122-gram sample of the residue had a G.E. brightness of 84.5 and much calcite therein.

EXAMPLE VIII

Steps 1–5 were as in Example VI, except that:

(a) In Step 1, 200 grams of dark color crude clay as in Example II was used;

(b) In Step 4, no accessory particles were used.

Step 6.—The initial pulp pH was 9.4; it was controlled to 9.2. The following results were obtained. The solids which were carried off as "float" during the first half of the flotation period weighed 38 grams; the solids which came over as "float" in the latter half of the flotation period weighed 35.4 grams. A 127-gram sample of the residue from the flotation treatment, when dry, had a G.E. brightness of 70.0.

EXAMPLE IX

Steps 1–5 were as in Example I, except that:

(a) In Step 1, 200 grams of a fractionated crude clay as in Example III having a G.E. brightness of 80.5 was used as feed;

(b) In Step 4, 10 grams of white Vinyon rayon (a copolymer of 88% to 90% vinyl chloride and remainder vinyl acetate, approximate molecular weight of 20,000 and specific gravity of 1.2) in the form of cylindrical, smooth-surfaced fibrils of about 10 to 15 microns diameter (1.5 denier rayon) and 300 to 1500 micron length, providing a length/diameter ratio of from 20:1 to 150:1, was formed by chopping 1.5 denier thread thereof in water with a weight ratio of rayon to water of 20:1. The resulting fibrils were mixed with 0.4 gram of Cyanamid 710 reagent, 0.34 gram of NaOH, 200 grams of water and 0.5 gram of white mineral oil. This reagentized collector particle mixture was admixed with the pulp in Step 1 in the Fagergren machine. The pH of the pulp in the Fagergren machine was 7.9.

Step 6.—Flotation according to Step 6 of Example I produced a first dark colored float fraction and a second float fraction of lighter color; the solid residue of the float, weighing 93% of the initial feed, had a G.E. brightness of 82.0. Bleaching of this residue by the same process as in Example I gave a bleached product with a G.E. brightness of 97.5.

EXAMPLE X

Steps 1–5 were as in Example I, except that:

(a) In Step 1, 200 grams of a dark colored crude clay as in Example II having a G.E. brightness of 72.0 was used as feed.

(b) In Step 4, a reagentized mixture of collector particles was made by blending the following with water:

<table>
<thead>
<tr>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caustic soda</td>
</tr>
<tr>
<td>Cyanamid 710</td>
</tr>
<tr>
<td>Vinyon fibrils (as in Example IX)</td>
</tr>
</tbody>
</table>

This reagentized collector particle mixture was admixed with the pulp of Step 1 in the Fagergren machine. The pH of the pulp liquor in the Fagergren machine was controlled at 9.2.

Step 6.—The weight of the solids in the froth fraction recovered in the first half of the flotation period (the first float fraction) was 25.4 grams; the second float fraction weighed 23.6 grams. The G.E. brightness of the residue (determined as in Example I) was 74.5. Bleaching of this residue by the same process as in Example I provided a bleached product with a G.E. brightness of 80.0.

EXAMPLE XI

Steps 1–5 were as in Example I, except that 200 grams of a dark colored crude clay as in Example II, having a G.E. brightness of 72.0, was used as feed.

In Step 4, a reagentized mixture of collector particles was made by blending with water:

<table>
<thead>
<tr>
<th>Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanamid 710</td>
</tr>
<tr>
<td>Caustic soda</td>
</tr>
<tr>
<td>White mineral oil</td>
</tr>
</tbody>
</table>
Resinox RS 6852 consisted of colorless oleophilic particles in the minus 200 mesh particle size range. It is a phenol-formaldehyde resin made by the Monsanto Chemical Company and has a specific gravity of 1.3. The particles are roundish pebble like in shape and free of sharp edges. This reagentized collector particle mixture was admixed with the pulp of Step 1 in the Fagergren machine. The pH of the pulp liquor was 8.1.

Step 6.—The weight of solids in the froth fraction recovered in the first half of the flotation period (the first float fraction) was 22.8 grams; the second float fraction weighed 47.1 grams. The machine discharge (sink) fraction weighed 150.1 grams, was free of “Resinox” and had a G.E. brightness of 73.5. Bleaching of this residue by the same process as in Example 1 provided a bleached product with a G.E. brightness of 80.5. This procedure effected considerable separation of TiO₂ content of the low color crude as shown below.

<table>
<thead>
<tr>
<th>Crude Feed</th>
<th>Fraction 1</th>
<th>Fraction 2</th>
<th>Fraction 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ (%)</td>
<td>1.80</td>
<td>0.78</td>
<td>0.76</td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
<td>44.27</td>
<td>37.15</td>
<td>37.06</td>
</tr>
<tr>
<td>SiO₂ (%)</td>
<td>37.15</td>
<td>37.06</td>
<td>37.06</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
<td>74.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As shown by Example VIII, the flotation procedure used did not, per se, significantly improve the brightness of the clay treated. The Examples I through V, IX, X, XI and XII are all to show that, on using only 20 grams of the reagentized accessory particles according to this invention, better recoveries and results are obtained than on use of 200 grams of particles with surfaces wherein the feature of homogeneity is absent, as in Examples VI and VII.

A plant operation according to the process of this invention is diagrammatically shown in the drawing. In such operation, the steps comprise treating a finely divided mineral mass composed of particles of relatively different surface characteristics, such as a kaolin clay feed with color impurities therein, by first admixing said mass with a frother and a collector agent or agents for froth flotation in an aqueous medium, the collector agent being a reagent capable of selectively coating the colored clay particles—which have one surface characteristic—with an oleophilic coating. Water-insoluble, non-waxy synthetic polymeric accessory particles of homogeneous surface oil adsorption characteristics and selected from the group consisting of polyethylene, polyvinyl chloride, nylon, polyethylene terephthalates, urea, formaldehydes, polypropylenes, polystyrenes, polycarbonates, polyethylene Vectra, and phenol polystyrels, said particles being floatable in an aqueous slurry of said kaolin, and then

(a) treating said kaolin clay for froth flotation in an aqueous medium with

(i) a reagent capable of selectively coating particles of one surface characteristic with an oleophilic coating and

(ii) non-waxy water-insoluble polymeric accessory particles of homogeneous surface oil adsorption characteristics and selected from the group consisting of polyethylene, polyvinyl chloride, nylon, polyethylene terephthalates, urea, formaldehydes, polypropylenes, polystyrenes, polycarbonates, polyethylene Vectra, and phenol polystyrels, said particles being floatable in an aqueous slurry of said kaolin, and then

(b) subjecting the thus-treated kaolin to froth flotation producing

(i) a froth product which contains said accessory particles and particles of said one surface characteristic and

(ii) a sink product containing kaolin clay brighter than the initial kaolin clay.

2. The process of claim 1 wherein said accessory particles are recovered from the froth product.

3. The process of claim 1 wherein said accessory particles have an average particle size diameter in the range of 50 to 200 microns and a specific gravity of less than 1.7.

4. The process of claim 3 wherein said accessory particles are polyethylene beads.

5. The process of claim 3 wherein said accessory particles are nylon fibrils.

6. The process of claim 3 wherein said accessory particles are polyvinyl chloride beads.

References Cited by the Examiner

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<table>
<thead>
<tr>
<th>No.</th>
<th>Date</th>
<th>Inventor</th>
<th>Title</th>
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<tr>
<td>2,569,680</td>
<td>10/1951</td>
<td>Leek</td>
<td>209—5</td>
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<td>154—46</td>
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<td>1/1963</td>
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<td>209—166</td>
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<table>
<thead>
<tr>
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<tr>
<td>118,433</td>
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HARRY B. THORNTON, Primary Examiner.

R. HALPER, Assistant Examiner.