The subject invention relates to an improved method for concentrating very finely divided (or "slimmed") minerals and ores into components by froth flotation and relates, more particularly, to an improved method for conditioning minerals and ores of such character for froth flotation for the purpose of enhancing the degree of concentration thereof.

Froth flotation is a widely practiced process for separating multicomponent minerals and ores into components. The process is amenable to a large variety of minerals and ores and provides in many instances, a highly economical and efficacious method for concentrating components of minerals and ores.

There are, however, several limitations to the froth flotation process. One of the most serious drawbacks to the process is that very finely sized feed, viz., feed comprising particles passable through a 200 mesh screen, and particularly those of -10 microns or finer, are not effectively concentrated by froth flotation. Such very fine particles or slimes may be naturally occurring constituents of a mineral ore or may be artificially produced during the grinding of the mineral or ore to a suitable size for mineral liberation. It is well-known to those skilled in the art that certain materials will not float in a froth flotation process when ground to an exceedingly fine size, although they will float under the same conditions when provided in coarser grain size.

At any rate, those who have heretofore attempted to concentrate components of various slimed minerals and ores by froth flotation have met with little success and have, accordingly, advocated desliming prior to flotation, when possible, although this procedure adds to the processing costs and loss of valuable mineral. Further, it is general practice to desit, when possible, from grinding certain ores and minerals to a degree at which slimes are artificially produced.

In many instances slimes cannot be avoided and removed, when present, for economic or practical reasons. For example, kaolin clay is a naturally slimed mineral, consisting predominantly of particles 2 microns or finer, the clay being mechanically associated with very finely divided color body impurities which detract from the value and utility of the clay in many applications. Prior art efforts to beneficiate the clay by floating the color body impurities have met with mediocrec success at best unless the clay feed was prefractionated to reduce the quantity of fines. Certain relatively coarse grained minerals and ores, too, have defied effective froth flotation since they are not readily reduced to suitable flotation feed size without provision of fines when they are ground to overcome interlocking between dissimilar mineral genera to permit their flotation. As examples of ores which become slimed when ground for flotation feed may be cited magnetite-brucite ores and uraninite ores (from which concentration of uranium values are desired). Other examples are well-known to those skilled in the art.

The technical problem is replete with reports of prior results in beneficiating such slimed minerals and ores by froth flotation with prefractionation or desliming.

Accordingly, a principal object of the subject invention is the provision of an improved froth flotation technique wherein very finely divided or slimed minerals and ores are useful as feed material.

Another object of the invention is the provision of a froth flotation process whereby slimed minerals and ores may, without slime removal, be more effectively concentrated than by employment of prior art methods.

A more specific object of the present invention is the provision of an improved means for conditioning slimed minerals and ores for froth flotation in order to realize a higher degree of collection of the valuable constituents of said slimed minerals and ores.

These, and further objects and advantages, are realized in accordance with the instant invention wherein the conditioning of slimed minerals and ores for froth flotation is accomplished with two essential agents which, cooperatively, permit improved beneficiation of very finely divided feed.

Broadly stated, our invention contemplates a process for the froth flotation of very finely divided multicomponent mineral masses in which the finely divided or slimed feed is conditioned with (1) a reagent capable of selectively oiling a desired component of the feed for entry into the froth during the concentration step, and (2) a particular auxiliary mineral which is collector coated (oiled) in a manner such that it is also capable of entry into the froth during the concentration step, thereby enhancing or promoting the flotation of the selectively oilied fraction of the feed. The feed thus conditioned and in the form of an aqueous pulp is subjected to froth flotation thereby to produce a froth product which is a concentrate of the oilied water-repellent component of the feed in intimate association with the collector-coated water-repellent auxiliary mineral particles and a machine discharge product which is a concentrate of the component of the feed which has not been selectively oilied and is thus water-wettable.

Obviously, there must be an explanation why the use of oilied auxiliary solid particles improves the flotation of very finely divided components of a feed material, especially in view of many cases where, indeed, no separation at all is obtained with ordinary froth flotation procedures. The results we have obtained indicate that a probable explanation would be a marked affinity between oilied auxiliary mineral particles and the oilied component of the feed. On this basis, it appears likely that the oilied auxiliary particles form a nucleus for the attachment of the finely divided oilied fraction of the feed. These loaded carrier particles are obviously particularly amenable to froth flotation and separation from the water-wettable residual fraction of the feed. In other words, the loaded carrier particles are adapted to air-bubble attachment. Thus, the method of our invention comprises a novel concept in the flotation art that definitely extends its application to slimed minerals in the -10, -5 and -2 micron particle size ranges.

An interesting and surprising feature of our invention is that the auxiliary mineral we employ may contain significant quantities of particles 10 microns or finer. It has been previously brought out that conventional froth flotation procedures are not adapted to the efficient flotation of such fine particles.

The present invention, in its broadest aspect, is not limited to beneficiation of any species or genus of finely divided minerals or ores since its benefits are realized when employing a variety of minerals and ores in which the slime is of natural or artificial origin. Our method may be applied with equally good results to feed in which a valued component is concentrated in the froth product or machine discharge product or in which both froth and machine discharge products are valued materials.
The very finely divided or slimed minerals and ores to which our invention relates are those which consist essentially of particles finer than about 200 mesh and is applicable to feed of —10 microns, —5 or —2 microns.

Any finely divided mineral or ore may be beneficially conditioned for froth flotation in accordance with the present invention provided: (1) the components thereof which it is desired to separate are liberated from each other, and (2) one of said components must differ from the other to the extent that it contains a substantial amount of a component which is capable of being selectively coated with an oriented hydrophobic coating, the coating being held on the surface of particles of the component by chemical or physical forces or combinations thereof.

The method of our invention is subject to numerous variations, e.g., by appropriate choice of auxiliary mineral, the feed may be reagentized with the same reagents as used in reagentizing the particulate auxiliary mineral to render said mineral suitable as a conditioning material, and the reagentization of feed and auxiliary mineral in such a case may be performed concurrently or separately on the relative affinity for the reagents of the solids being treated. However, when the choice of auxiliary minerals is such that it cannot be collector coated by the reagent or reagents used to collect the desired component of the feed, then the reagentization of auxiliary mineral will be done independently of the reagentization of the feed.

In accordance with an embodiment of our invention, the froth product is separated into an auxiliary mineral component and a component of the feed which has been floated. In this case the recovered auxiliary particles may be reused in a subsequent conditioning treatment after reoiling when necessary.

In accordance with still another embodiment of our invention, the froth product or machine discharge product is reconcentrated.

Pursuant to still another embodiment of our invention, the composite froth product of a concentration step is used in one or a plurality of subsequent concentration steps as the particulate auxiliary mineral, after treating the composite froth product with additional quantities of reagents when necessary.

By application of our conditioning treatment, slimed ores and minerals may be more effectively concentrated than by prior art techniques and, in some instances, slimed ores and minerals, never heretofore concentrateable by froth flotation, may now be beneficiated with a good degree of efficiency.

More specifically, in accordance with the method of the instant invention, we initially select as a feed material a very finely divided multicomponent mineral or ore, viz., one which contains a preponderant amount of —200 mesh particles, and which is inherently capable of beneficntation by froth flotation by virtue of liberation of components which are to be separated and ability of one of the mechanically separable components to be selectively collector coated with an oriented water-repellent coating. The feed may have been subjected to previous treatment such as, for example, flotation, tabling, hydraulic classification, grinding, chemical treatment, etc.

The novel method of our invention can be applied to both metallic and nonmetallic ores and minerals and should be particularly beneficial in those cases in which difficulty is experienced in the flotation step due to the presence of slimes or fines. As a specific example of suitable feed for our flotation method may be cited kaolin clay which is discolored by titaniferous and, in some instances, ferruginous impurities. Kaolin clay in the form of a dispersed aqueous slip may be reagentized, in accordance with our invention, with a selective collector such as oleic acid or tall oil in an alkaline pulp, in conjunction with a collector-coated particulate auxiliary mineral, for flotation of the colored impurities in the clay. Another suitable feed material is uraninite ore which becomes artificially slimed when ground to liberate the uranium values; the slimed uraninite feed may likewise be reagentized with a negative ion collector such as amines, in conjunction with a collector-coated particulate auxiliary mineral such as calcite, for flotation of the uranium value in the ore.

As has been brought out hereinabove, reagentization of feed and auxiliary mineral particles to condition the feed for flotation by froth flotation may be carried out simultaneously or separately, depending on the nature of the feed and the auxiliary mineral.

We may reagentize the feed, auxiliary mineral or mixtures thereof in any suitable apparatus ordinarily used for reagentizing ores and minerals, such apparatus being well-known to those skilled in the art and being fully described in the literature. Ordinarily, the reagents will be added to the particulate solid when the solid is dispersed in any aqueous medium, utilizing a dispersant when necessary to overcome the tendency of the solid particles to flocculate. However, it is felt within the compass of our invention to reagentize the feed, auxiliary mineral or mixtures thereof simultaneously with the step of grinding the solids to a suitable grain size for the flotation process.

In those instances where the auxiliary mineral is of a character such that it may be reagentized with the same reagents utilized for treating the ore or mineral feed, the process is simple and requires merely the incorporation and intimate admixture of the auxiliary mineral with the feed material during the reagentizing step. The reagents employed must be calculated to provide not only for floating a fraction of the feed but also for floating the auxiliary mineral. In some instances, even when the reagents are the same for feed and auxiliary mineral, it will be desirable to reagentize feed and auxiliary mineral separately, preferably each in the form of a dispersed aqueous pulp, and then admix the reagentized materials; an instance where such practice is indicated is where the auxiliary mineral or feed has surface characteristics such as to preclude proper reagentizing of the other material.

In some instances, separate reagentization of feed and carrier is obviously mandatory. In such a case, the pre-ferred practice will be to prepare an aqueous pulp of dispersed feed reagentized with appropriate reagents, separately reagentize an aqueous pulp of the auxiliary mineral, admix the pulps and subject the admixed pulps to froth flotation.

The particle size of the particulate auxiliary material may vary within a wide range, which, of course, must lie within the range of material floatable in the presence of the reagentized feed, i.e., usually within the range of from about 14 mesh (Tyler standard) to 5 microns or finer. It has been our experience, however, that generally speaking particles somewhat finer than 325 mesh may be preferred to particles coarser than 325 mesh.

As an auxiliary mineral, we may employ any mineral of suitable size which is capable of being provided with an oriented hydrophobic surface coating, the coating being of a character such that the auxiliary mineral will be floatable in the presence of the particular reagentized feed pulp which is being beneficiated. Thus, the choice auxiliary mineral will depend, inter alia, on the pH employed in the flotation cell and the ionic nature of the collector reagent.

As examples of suitable particulate auxiliary minerals may be mentioned calcite, barite, kyanite, silica sand, anatase and fluorspar. Auxiliary minerals may be unicolored or multicomponent materials or may be mineral admixtures. Suitable reagents for floating the auxiliary minerals above-specific are described in Taggart Handbook of Mineral Dressing 16th edition (1960 edition) or may be experimentally determined. However, it will be readily apparent to those skilled in the froth flotation art that
any mineral which may be appropriately conditioned for flotation in the presence of the reagentized feed pulp is within the compass of our invention. The particular choice of reagents for the auxiliary mineral particles should be based on the nature of the solids in the feed pulp.

The optimum proportion of auxiliary mineral relative to feed solids may also vary within wide range, the minimum amount of auxiliary mineral weight basis, ordinarily being at least equal to and frequently exceeding the weight of the fraction of the feed which is to be floated. Moreover, the amount of auxiliary mineral may be substantial relative to the floated feed and may be equal or double or more the weight of the total feed. We have, for example, achieved a substantially equivalent degree of concentration of color body impurities from a gray sedimentary kaolin clay utilizing reagentized calcite as the carrier for said color body impurities, when calcite was used in amounts from 5 to 200% by weight of the clay feed.

In the reagentization of feed and auxiliary minerals, there may be used in addition to the hydrocarbon-containing collector, promoters, inhibitors and/or other appropriate flotation adjuvants. pH adjustors may be employed when their use is indicated.

Preferably, subsequent to the reagentization of the feed and the auxiliary mineral particles, the pulp is subjected to aeration (and usually mechanical agitation) in any suitable flotation cell. Additional reagents may be added during this step if required. As a result of the aeration, the color body impurities, collector coated, are carried upward into the froth in association with the reagentized particles of auxiliary mineral and the composted froth is separated from the tailings or machine discharge product.

The concentration may be accomplished in any suitable apparatus for the purpose, such apparatus being well-known in the art and forming no part of the subject invention. Appropriate frothers may be added when their use is indicated.

As in other flotation processes, product recovery and efficiency of concentration may be improved by reflotating either the froth or machine discharge products through the flotation cell.

When desired, the auxiliary mineral may be separated from the floated fraction of feed by any appropriate method. The choice of method will depend on many factors which include, inter alia, the relative grain size and specific gravity of the auxiliary mineral and the floated fraction of feed, and the physical and chemical surface characteristics of the solids.

In other situations it may be advantageous to employ an auxiliary mineral which is a desirable component when admixed with the floated feed material.

The method of our invention as applied to the beneficition of kaolin clay discolored with titanosiferous and ferruginous matter will be more fully illustrated in the following examples. It will be understood that these examples are given only for illustrative purposes and that our invention is not limited to the specific materials and quantities set forth therein since other finely divided minerals and ores may be used in lieu of kaolin clay with equally good results by judicious selection of reagents and operating conditions.

CRUDE KAOLIN SLIP PREPARATION

Twenty-five pounds (dry basis) of crude Georgia kaolin known as Klondyke Crude was stirred with about 100 pounds of water (Culligan softened) until practically all of the clay lumps were disintegrated. The slurry was screened to remove all plus 325 mesh grit. The degritted clay had a particle size distribution such that 98% by weight of the particles was —15 microns, 92% was —10 microns, 89% was —5 microns, 50% was —1.5 microns and 15% was —0.5 micron (all particle sizes referring to equivalent spherical diameters).

Example I

2925 grams (500 grams dry) of the —325 mesh crude kaolin slip (above-described) was pulped with water into a 1000 gallon laboratory Minerals Separation Airflow flotation machine to a concentration of about 10% solids.

The kaolin pulp was agitated without air for 1 minute with 0.3% (based on dry weight of clay) sodium silicate. While the machine was running, the following reagents were added to the pulp: ammonium sulfate, 5.0 pounds; ammonium hydroxide, 5.0 pounds; crude tall oil fatty acid, 5.0 pounds; neutral Calcium Petronate, 5.0 pounds; and American Cyanamid Reagent 801, 2.5 pounds. The neutral Calcium Petronate was supplied by Sonneborn Chemical Company and has the following analysis:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium sulfonate complex</td>
<td>41.0</td>
</tr>
<tr>
<td>Sodium sulfonate</td>
<td>Trace</td>
</tr>
<tr>
<td>Mineral oil</td>
<td>58.5</td>
</tr>
<tr>
<td>Water</td>
<td>0.5</td>
</tr>
<tr>
<td>Percent Ca in sulfonate complex</td>
<td>2.86</td>
</tr>
</tbody>
</table>

American Cyanamid Reagent 801 is a water-soluble petroleum sulfonate produced by American Cyanamid Company under their designation “801.” The quantity of reagents are pounds per ton of dry kaolin. The pulp was conditioned with the above reagents for 10 minutes with the air off and then air was admitted to the flotation machine and a froth removed for 10 minutes.

To the pulp remaining in the flotation machine the following reagents were added: ammonium hydroxide, 1.5 pounds; crude tall oil fatty acid, 1.2 pounds; neutral Calcium Petronate, 1.2 pounds; and American Cyanamid Reagent 801, 0.6 pounds. The reagent quantities are pounds per ton of dry clay. The pulp was further conditioned for 10 minutes without air and then subjected to froth flotation, removing a second froth product for 10 minutes. The two froth products were combined. The results of this experiment are given below, wherein brightness index refers to a brightness value obtained by TAPPI standard method T-646 m-54, 2 as described on pages 159A and 160A of the October 1954 issue of TAPPI (a monthly publication of the Technical Association of the Pulp and Paper Industry). The method measures the light reflectance of a clay sample and thus gives a quantitative indication of its brightness or whiteness.

<table>
<thead>
<tr>
<th>Product</th>
<th>Percent Weight</th>
<th>Percent Brightness Index</th>
<th>Percent T10b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flotation Froth Products</td>
<td>38.8</td>
<td>69.2</td>
<td>1.527</td>
</tr>
<tr>
<td>Flotation Machine Discharge Products</td>
<td>81.2</td>
<td>81.0</td>
<td>0.252</td>
</tr>
<tr>
<td>—225 Mesh Crude Kaolin Feed</td>
<td>100.0</td>
<td>78.8</td>
<td>1.78</td>
</tr>
</tbody>
</table>

*Calculated values.

Following are examples of flotation of colored impurities from kaolin clay using auxiliary minerals whereby the important advantages of the present invention are realized.

Example II

This example illustrates the embodiment of our invention in which the clay feed and auxiliary mineral are reagentized separately, each in the form of an aqueous pulp.

985 grams (200 grams dry) of the same crude Klondyke kaolin slip as used in Example I was pulped with water into a laboratory Fagergren flotation machine to a concentration of 10% solids. The kaolin pulp was
agitated (air off) with 0.3% (based on dry weight of clay) sodium silicate for 1 minute. While the machine was operating, the following reagents were added to the pulp: ammonium sulfate, 5.0 pounds; ammonium hydroxide, 7.5 pounds; crude tall oil fatty acid, 6.2 pounds; neutral Calcium Petronate, 6.2 pounds; and American Cyanamid Reagent 801, 3.1 pounds. Reagent quantites were pounds per ton of dry clay. After the reagents were added the pulp was conditioned for 5 minutes.

400 grams of —325 mesh natural calcite (Thompson Weimann & Company No. 1 white) was pulped with water to 68% solids and conditioned for 5 minutes in a paddle type agitator with the following reagents: caustic soda, 0.25 pound; and crude tall oil fatty acid, 4.0 pounds. Reagent quantities were all pounds per ton of calcite. The calcite was 98% by weight —40 microns, 36% —10 microns and 10% —3 microns.

The reagentized calcite was added to the reagentized kaolin pulp in the FAGGERGREN flotation machine and the whole conditioned together for an additional 2 minutes without aeration.

The reagentized kaolin-calcite pulp was transferred to a 1000 gram Minerals Separation AIRFLOW flotation machine and diluted with water to about 13% total solids. The diluted reagentized pulp was subjected to froth flotation removing a froth product for 5 minutes and the flotation machine discharged. The first froth product was repulped into the flotation machine and refloated for 5 minutes without additional reagents. The froth product was refloated to more times. The following metallurgical results were obtained.

<table>
<thead>
<tr>
<th>Products</th>
<th>Per cent Wt.</th>
<th>Per cent Bright-</th>
<th>Per cent TiO₂</th>
<th>Per cent CaCO₃</th>
<th>Per cent Fe₂O₃</th>
<th>Per cent TiO₂ Distr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>100.0</td>
<td>75.8</td>
<td>1.78</td>
<td>0.49</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 1</td>
<td>92.3</td>
<td>84.9</td>
<td>0.46</td>
<td>0.39</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 2</td>
<td>79.0</td>
<td>84.5</td>
<td>0.44</td>
<td>1.5</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 3</td>
<td>72.0</td>
<td>84.0</td>
<td>0.45</td>
<td>3.1</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 4</td>
<td>8.5</td>
<td>84.0</td>
<td>0.43</td>
<td>3.1</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Froth Prod.</td>
<td>4.5</td>
<td>20.44</td>
<td></td>
<td></td>
<td>0.31</td>
<td>27.0</td>
</tr>
<tr>
<td>Total Mach. Disc.</td>
<td>94.5</td>
<td>84.6</td>
<td>0.43</td>
<td>1.1</td>
<td>23.0</td>
<td></td>
</tr>
</tbody>
</table>

Note.—Metallurgical balance based on dry kaolin feed.

The compositied machine discharge product had a brightness value of 88.0% after being bleached with zinc hydrosulfite.

The results of this sample, as compared with the results of Example I (which was similar in all respects other than that the flotation was carried out in the absence of the added reagentized calcite) indicates that the presence of the reagentized calcite improved the beneficiation of the kaolin clay substantially, both with respect to the yield of beneficiated product, brightness index and titanium reduction. It will be noted that the brightness of the beneficiated product was 81.0% in Example I whereas by the method of invention the brightness was increased to 84.6% with an excellent weight recovery of 95.5%.

Example II

This example illustrates the embodiment of the instant invention wherein the feed and the auxiliary mineral particles are reagentized simultaneously in the form of an admixed aqueous pulp.

985 grams (200 dry) of —325 mesh crude kaolin slip (same as Example I) was pulped with water into a FAGGERGREN flotation machine to 10% solids. The kaolin pulp was agitated with 0.3% (based on dry weight of clay) sodium silicate for 1 minute. 400 grams of —325 mesh natural calcite was added to the agitated kaolin pulp and the whole diluted with water to about 20% solids. While the machine was operating the following reagents were added to the pulp: ammonium sulfate, 5.0 pounds; ammonium hydroxide, 6.3 pounds; crude tall oil fatty acid, 14.2 pounds; neutral Calcium Petronate, 6.2 pounds; and American Cyanamid Reagent 801, 3.1 pounds. Reagent quantities were pounds per ton of dry clay. After the addition of reagents the pulp was conditioned for 17 minutes. The reagentized pulp was transferred to a 1000 gram Minerals Separation AIRFLOW flotation machine and diluted with water to about 15% solids. The reagentized pulp was then subjected to flotation removing a froth product for 5 minutes. The remainder of the experiment was the same as Example II. The following metallurgical results were obtained.

<table>
<thead>
<tr>
<th>Products</th>
<th>Per cent Wt.</th>
<th>Per cent Bright-</th>
<th>Per cent TiO₂</th>
<th>Per cent CaCO₃</th>
<th>Per cent Fe₂O₃</th>
<th>Per cent TiO₂ Distr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>100.0</td>
<td>75.8</td>
<td>1.78</td>
<td>0.49</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 1</td>
<td>92.3</td>
<td>84.9</td>
<td>0.46</td>
<td>0.39</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 2</td>
<td>79.0</td>
<td>84.5</td>
<td>0.44</td>
<td>1.5</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 3</td>
<td>72.0</td>
<td>84.0</td>
<td>0.45</td>
<td>3.1</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 4</td>
<td>8.5</td>
<td>84.0</td>
<td>0.43</td>
<td>3.1</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Froth Prod.</td>
<td>4.5</td>
<td>20.44</td>
<td></td>
<td></td>
<td>0.31</td>
<td>27.0</td>
</tr>
<tr>
<td>Total Mach. Disc.</td>
<td>94.5</td>
<td>84.6</td>
<td>0.43</td>
<td>1.1</td>
<td>23.0</td>
<td></td>
</tr>
</tbody>
</table>

Note.—Metallurgical balance based on kaolin feed.

Example IV

This example was principally the same as Example II except the kaolin slip was composed of another type of kaolin from a different area and is commonly called "Georgia Gray Kaolin." The clay is characterized by a very low brightness index. Reagents and operating conditions were those detailed in Example II. The metallurgical results are shown below.

<table>
<thead>
<tr>
<th>Products</th>
<th>Per cent Wt.</th>
<th>Per cent Bright-</th>
<th>Per cent TiO₂</th>
<th>Per cent CaCO₃</th>
<th>Per cent Fe₂O₃</th>
<th>Per cent TiO₂ Distr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>100.0</td>
<td>75.8</td>
<td>1.78</td>
<td>0.49</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 1</td>
<td>92.3</td>
<td>84.9</td>
<td>0.46</td>
<td>0.39</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 2</td>
<td>79.0</td>
<td>84.5</td>
<td>0.44</td>
<td>1.5</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 3</td>
<td>72.0</td>
<td>84.0</td>
<td>0.45</td>
<td>3.1</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 4</td>
<td>8.5</td>
<td>84.0</td>
<td>0.43</td>
<td>3.1</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Froth Prod.</td>
<td>4.5</td>
<td>20.44</td>
<td></td>
<td></td>
<td>0.31</td>
<td>27.0</td>
</tr>
<tr>
<td>Total Mach. Disc.</td>
<td>94.5</td>
<td>84.6</td>
<td>0.43</td>
<td>1.1</td>
<td>23.0</td>
<td></td>
</tr>
</tbody>
</table>

Example V

This example was principally the same as Example II except the kaolin slip was composed of another kaolin from a different area and which has a higher brightness index level than the kaolin used in Example II. Reagents and operating conditions were those detailed in Example II. The results obtained are shown below.

<table>
<thead>
<tr>
<th>Products</th>
<th>Per cent Wt.</th>
<th>Per cent Bright-</th>
<th>Per cent TiO₂</th>
<th>Per cent CaCO₃</th>
<th>Per cent Fe₂O₃</th>
<th>Per cent TiO₂ Distr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>100.0</td>
<td>75.8</td>
<td>1.78</td>
<td>0.49</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 1</td>
<td>92.3</td>
<td>84.9</td>
<td>0.46</td>
<td>0.39</td>
<td>11.8</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 2</td>
<td>79.0</td>
<td>84.5</td>
<td>0.44</td>
<td>1.5</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 3</td>
<td>72.0</td>
<td>84.0</td>
<td>0.45</td>
<td>3.1</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Mach. Disc. 4</td>
<td>8.5</td>
<td>84.0</td>
<td>0.43</td>
<td>3.1</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Froth Prod.</td>
<td>4.5</td>
<td>20.44</td>
<td></td>
<td></td>
<td>0.31</td>
<td>27.0</td>
</tr>
<tr>
<td>Total Mach. Disc.</td>
<td>94.5</td>
<td>84.6</td>
<td>0.43</td>
<td>1.1</td>
<td>23.0</td>
<td></td>
</tr>
</tbody>
</table>

Example VI

This example illustrates the beneficiation of a fine fraction of discolored kaolin clay by froth flotation utilizing a reagentized calcite carrier in the conditioning step.

The clay feed in this experiment was a fractionated Georgia kaolin having a particle size distribution such that about 100% by weight of the particles had an equivalent spherical diameter of 3 microns or finer and about 50% by weight was 0.5 micron or finer.

985 grams of a slip of the clay containing 200 grams of clay were pulped with water into a laboratory FAGGERGREN flotation machine to a concentration of 10% solids. While the pulp was agitated (air off), the following reagents were added to the pulp: ammonium sulfate, 5.0 pounds; ammonium hydroxide, 5.0 pounds; crude tall oil fatty acid, 6.2 pounds; neutral Calcium Petronate, 6.2 pounds; and American Cyanamid Reagent 801, 2.1 pounds.
pounds. Reagent quantities were pounds per ton of dry clay. After the reagents were added the pulp was conditioned for 5 minutes.

600 grams of —325 mesh natural calcite having a particle size distribution such that 98% by weight of the particles was —40 microns, 36% of the particles was —10 microns, and 10% was —3 microns, was pulped with water to 68% solids level and conditioned for 2 minutes in a paddle type agitator with the following reagents: caustic soda, 0.25 pound; and crude tall oil fatty acidic, 4.0 pounds (all reagent quantities being in pounds per ton of dry calcite).

The reagentized calcite was added to the reagentized kaolin pulp in the Fagergren flotation machine and the whole conditioned together for an additional 20 minutes. The solids content of the composited pulp was 21%.

The reagentized kaolin-calcite pulp was transferred to a 1000 gram Minerals Separation Airflow flotation machine and diluted with water to about 17% total solids. The diluted reagentized pulp was subjected to froth flotation removing a froth product for 5 minutes. The flotation machine was discharged and the first froth product was repulped into the flotation machine and refloated without additional reagents for 10 minutes. The froth product was refloated two more times and the machine discharge products of all steps were composited.

The results of this experiment are summarized below:

<table>
<thead>
<tr>
<th></th>
<th>Percent Weight</th>
<th>Percent Brightness Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prefractionated Kaolin Feed</td>
<td>100.0</td>
<td>80.9</td>
</tr>
<tr>
<td>Flotation Froth Products</td>
<td>5.5</td>
<td>80.4</td>
</tr>
<tr>
<td>Flotation Machine Discharge Products</td>
<td>94.8</td>
<td>86.2</td>
</tr>
</tbody>
</table>

The machine discharge product was bleached with zinc hydrosulphite to a brightness of 90.2%.

The results of the example indicate that a very fine prefractionated clay may be brightened to a high level with outstanding recovery utilizing the method of our invention.

**Example VII**

This example is similar to Example III except that materially less calcite was used in conditioning the clay.

425 grams (dry basis) of the —325 mesh Klondyke kaolin slip was pulped with water into a Fagergren flotation machine to 10% solids and 30% of Thompson Wein Company No. 1 white calcite (based on the dry clay weight) added to the pulp. The pulp was conditioned for 17 minutes (air off) with the following reagents: ammonium sulfate, 5 pounds; ammonium hydroxide, 5 pounds; tall oil, 7.6 pounds; and 6.2 pounds of Calcium Petronate (all reagents expressed in pounds per ton of dry clay). The pH of the reagentized pulp was 9.2. The reagentized pulp was transferred to the Minerals Separation Airflow machine and subjected to a single float for 10 minutes. The percent recovery was 50.1%, based on the dry clay weight. The feed clay had a brightness of 78.8% and the beneficiated product had a brightness of 87.2% (which was increased by 89.6% by bleaching). The titania analysis of feed clay was 1.78 and beneficiated product was 0.37. The Fe₂O₃ analysis of feed was 0.33.

We have obtained beneficiation of kaolin using other carriers with similar and different collector reagents. As exemplified, such carrier materials may be cedum calcium fluoride, ground marble and ground silica sand, utilizing as the collector reagent the iron oxides in the case of marble and calcium fluoride and octadecylamine acetate in the case of the silica sand.

**We claim:**

1. The method for beneficiating a very finely divided multicomponent mineral mass including liberating components which comprises conditioning said mass for froth flotation with (1) a reagent capable of selectively oiling at least one component of said mass, and (2) collector-coated auxiliary mineral particles characterized further by being floatable in the presence of an aqueous pulp of said reagentized mass, and subjecting the thus conditioned mass in the form of an aqueous pulp thereof to froth flotation thereby to produce a froth product which is a concentrate of oil components of said mass in intimate association with said auxiliary mineral particles and a machine discharge product.

2. The method for beneficiating a very finely divided multicomponent mineral mass including liberating components which comprises forming an aqueous pulp of said mass, conditioning said aqueous pulp for froth flotation with (1) a reagent capable of selectively oiling at least one component of said mass, and (2) collector-coated auxiliary mineral particles which are characterized by being floatable in the presence of said aqueous pulp, and subjecting the thus conditioned aqueous pulp to froth flotation thereby to produce a froth product which is a concentrate of oil components of said mass in intimate association with said auxiliary mineral particles and a machine discharge product.

3. The method of claim 2 wherein said very finely divided mass is a naturally slimed ore.

4. The method of claim 2 wherein said finely divided mass is an artificially slimed ore.

5. The method of claim 2 wherein said very finely divided mass is a naturally slimed mineral aggregate.

6. The method of claim 2 wherein said very finely divided mass is an artificially slimed mineral aggregate.

7. The method of claim 2 wherein said very finely divided mineral mass consists essentially of —200 mesh particles.

8. The method of claim 2 wherein said auxiliary mineral particles are —325 mesh.

9. The method of claim 2 including the additional step of separating the auxiliary mineral particles from the oil component of said mass.

10. The method for beneficiating a multicomponent mineral mass including liberating components and being further characterized by consisting predominantly of particles finer than 200 mesh which comprises forming an aqueous pulp of said mass, conditioning said aqueous pulp for froth flotation with (1) a reagent capable of selectively oiling at least one component of said mass, and (2) auxiliary mineral particles having a water-repellent coating on the surface thereof and being further characterized by being floatable in the presence of said aqueous pulp of said auxiliary mineral particles being employed in an amount by weight at least equal to that of the component of said mass which is selectively oiling, and subjecting the thus conditioned aqueous pulp to froth flotation thereby to produce a froth product which is a concentrate of oil components of said mass in intimate association with said auxiliary mineral particles and a machine discharge product.

11. The method for beneficiating a very finely divided multicomponent mineral mass including liberating components which comprises forming an aqueous pulp of said mass in intimate association with particles of an auxiliary mineral, conditioning said aqueous pulp for froth flotation with a collector reagent capable of selectively oiling certain components of said mineral mass whereby residual components of said mineral are water-wettable, said reagent also being capable of oiling said particles of auxiliary mineral, and subjecting the thus conditioned pulp to froth flotation thereby to produce a froth product which is a concentrate of oil components of said mineral mass in intimate association with particles of said auxiliary mineral and a machine discharge product consisting of water-wettable residual components of said mass.

12. The method for improving the brightness of kaolin clay having color body impurities mechanically associated therewith comprising forming a dispersed aqueous pulp of said clay, conditioning said aqueous pulp for froth flotation with (1) a collector reagent capable of selectively
2,990,958

oiling said color body impurities, and (2) collector-coated particles of an auxiliary mineral, said particles being further characterized by being floatable in said pulp, and subjecting the thus conditioned aqueous pulp to froth flotation thereby producing a froth product which is a concentrate of said color body impurities in intimate association with said auxiliary mineral particles and a machine discharge product which is a concentrate of clay of enhanced brightness.

13. The method for beneficiating kaolin clay discolored with mechanically associated color body impurities which comprises forming a dispersed aqueous pulp of said clay, conditioning said aqueous pulp with a reagent reagent capable of selectively oiling said color body impurities, separately forming an aqueous pulp of particles of an auxiliary mineral, reagentizing said auxiliary mineral pulp with a reagent capable of collecting said particles of auxiliary mineral when admixed with said aqueous clay pulp, admixing said reagentized pulps, subjecting the admixed reagentized pulps to froth flotation, thereby producing a froth product which is a concentrate of oil color body impurities originally in said clay in intimate association with particles of said auxiliary material and a machine discharge product which is a concentrate of clay of enhanced brightness.

14. The method for beneficiating kaolin clay discolored with mechanically associated color body impurities which comprises forming a dispersed aqueous pulp of said clay and particles of an auxiliary mineral, conditioning said aqueous pulp for froth flotation in the presence of a collector reagent capable of selectively oiling color body impurities in said clay and also capable of collecting said particles of auxiliary mineral, and subjecting the thus conditioned aqueous pulp to froth flotation thereby producing a froth product which is a concentrate of said color body impurities in intimate association with said particles of auxiliary material and a machine discharge product which is a concentrate of clay of enhanced brightness.

15. The method for removing a mechanically separable color body impurity comprising a titaniferous mineral from kaolin clay which comprises forming a dispersed aqueous pulp of said clay, conditioning said aqueous pulp for froth flotation with (1) a negative ion collector reagent selective to the color body impurity in said kaolin clay, and (2) collector-coated particles of an auxiliary mineral capable of floating in said aqueous pulp, and subjecting the thus conditioned aqueous pulp to froth flotation in an alkaline circuit thereby producing a froth product which is a concentrate of said color body impurities in intimate association with particles of said auxiliary mineral and a machine discharge product which is a concentrate of beneficiated clay.

16. The method of claim 15 wherein said kaolin clay and said auxiliary mineral are concurrently reagentized.

17. The method of claim 15 wherein said kaolin clay and said auxiliary mineral are separately reagentized.

18. The method of claim 15 wherein said kaolin clay and said auxiliary mineral are concurrently reagentized in the form of an admixed aqueous pulp thereof with a higher fatty acid collector.

19. The method of claim 15 wherein said kaolin clay and said auxiliary mineral are separately reagentized, each with a higher fatty acid collector.

20. The method of claim 15 wherein said aqueous pulp is conditioned for froth flotation with at least one material selected from the group consisting of neutral hydrocarbon oils and water-insoluble oil-soluble petroleum sulfonates.

21. The method of claim 15 wherein said aqueous pulp is conditioned for froth flotation with at least one material selected from the group consisting of neutral hydrocarbon oils and water-insoluble oil-soluble petroleum sulfonates and with ammonium sulfate.

22. The method for removing a mechanically associated color body impurity comprising a titaniferous mineral from kaolin clay which comprises forming a dispersed aqueous pulp of said clay, conditioning said aqueous pulp for froth flotation with (1) a higher fatty acid collector reagent selective to said color body impurity, (2) particles of an auxiliary mineral collector coated with a higher fatty acid and (3) at least one material selected from the group consisting of neutral hydrocarbon oils and water-insoluble oil-soluble petroleum sulfonates, and subjecting the thus conditioned aqueous pulp to froth flotation in an alkaline circuit thereby producing a froth product which is a concentrate of said color body impurities in intimate association with particles of said auxiliary material and a machine discharge product which is a concentrate of beneficiated clay.

23. The method of claim 22 wherein said kaolin clay and said particles of auxiliary mineral are concurrently reagentized in the form of an admixed aqueous pulp thereof.

24. The method of claim 22 wherein said kaolin clay and said particles of auxiliary mineral are separately reagentized, each in the form of an aqueous pulp, and the reagentized aqueous pulps are admixed.

25. The method of claim 22 wherein said particles of auxiliary mineral are finer than 325 mesh.

26. The method of claim 12 wherein said auxiliary mineral is calcium carbonate and it is employed in amount of 5% to 200%, based on the weight of said clay.

27. The method of claim 12 wherein said dispersed aqueous pulp of clay is formed by dispersing clay in sodium silicate solution.

References Cited in the file of this patent
UNITED STATES PATENTS

2,569,680 Leek ------------------- Oct. 2, 1951
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,990,958
July 4, 1961

Ernest W. Greene et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 69, for "with" read -- without --; column 4, line 63, after "choice" insert -- of --; column 7, lines 10 and 11, for "Thompson Weinman & Company" read -- Thompson Weinman Company --; line 30, for "to" read -- two --.

Signed and sealed this 14th day of November 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents
USCOMM-DC