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Kaolin Flotation: Beyond the Classical

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Recovery of fine particles has been considered to be a major limitation of the classical flotation process. However, the beneficiation of kaolin, a naturally occurring fine ore, via flotation has been practiced over the last 40 years. Kaolin is valued as a white pigment, and therefore, the goal in kaolin flotation circuits is to remove the colored impurities to result in an acceptable brightness product. Kaolin flotation originated with a novel carrier flotation process, and later on carrierless flotation techniques were developed. The collector chemistry utilized to beneficiate kaolin is based on fatty acids, and recently hydroxamates have been successfully used. The purpose of this paper is to cover the flotation practice in the kaolin industry in terms of the history and the reagent schemes.

INTRODUCTION

Kaolin clay, consisting largely of the mineral kaolinite, is widely used as a white pigment. In the United States, for example, pigment kaolin production was nearly 7,514,000 tons in 1997 (CCPA, 1997). The estimated revenue for this production volume was close to $1.6 billion.

Although much of the kaolin is used as an inert filler where product specifications are not very rigid, a large quantity of kaolin is converted to products where very restrictive specifications apply. These specifications set severe limits on such properties as viscosity in a water suspension, particle size distribution, color, and brightness. The term "brightness" refers to the reflectance of the pigment to blue light (TAPPI). Because even the brightest commercial kaolins have a somewhat yellowish color, the blue reflectance (or brightness) is a reasonably good measure of their nearness to a perfectly white material.

There are several beneficiation techniques, such as size classification methods, magnetic separation, flotation, selective flocculation, and bleaching, which are used in the kaolin industry for removal of colored impurities that result in improving the brightness of kaolin. This paper will focus solely on one beneficiation method—flotation—used to

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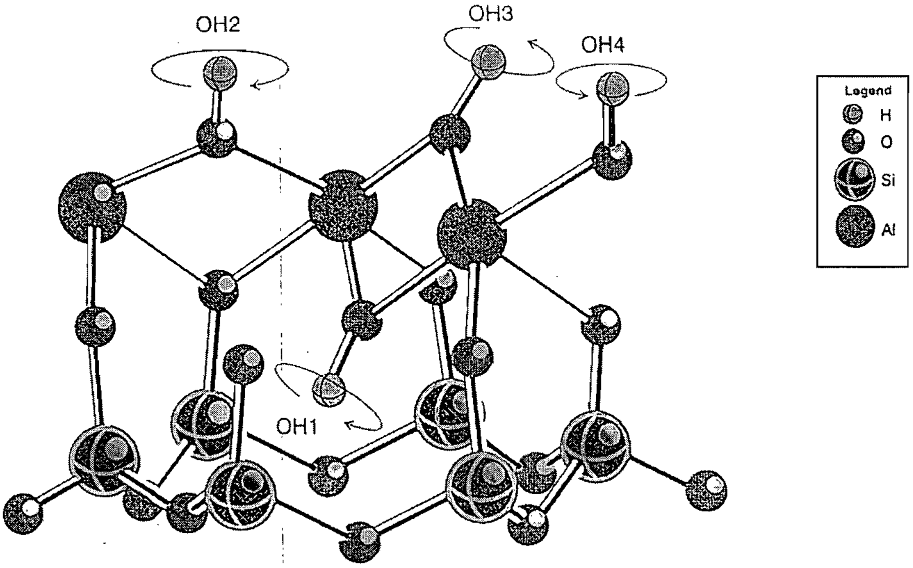

FIGURE 1 The structure of the mineral kaolinite (after Grim, 1962)

improve the color and brightness of Georgia kaolin and will review the advantages and problems associated with it.

KAOLINITE STRUCTURE AND SOURCES

The mineral kaolinite is an aluminum silicate and can be represented by the formula $(OH)_8Si_4Al_4O_{10}$. The formula is frequently written as $Al_2O_3.2SiO_2.2H_2O$, which, although perhaps easier to remember, implies the presence of water of hydration that does not occur in kaolinite. Pure kaolinite has the composition, expressed as oxides, 46.54% SiO_2, 39.50% Al_2O_3 and 13.96% H_2O. In actual fact, commercial kaolins differ somewhat from the above analysis because of the presence of accessory minerals and possible substitutions of other elements within the crystal lattice. The structure of the mineral kaolinite is shown in Figure 1.

Kaolinite is a common mineral and is an almost universal component of the fine-particle fraction of all soils. There are however, a number of areas of the world where kaolinite exists in sufficient concentration to be commercially exploited (Patterson and Murray, 1975). The two main producing areas of pigment kaolinite are the Cornwall area of England and the fall line of Georgia and South Carolina in the United States. Recently, Brazil is on the way to becoming a major resource and supplier of kaolin.

The kaolin of Cornwall originates from in-situ weathering of granitic rock, while the Georgia–South Carolina and Brazilian kaolins are sedimentary deposits. As a result of the different modes of origin, the two types of kaolin present quite different problems in beneficiation for color improvement. This paper will focus only on flotation methods currently in practice in Georgia for removal of colored impurities.

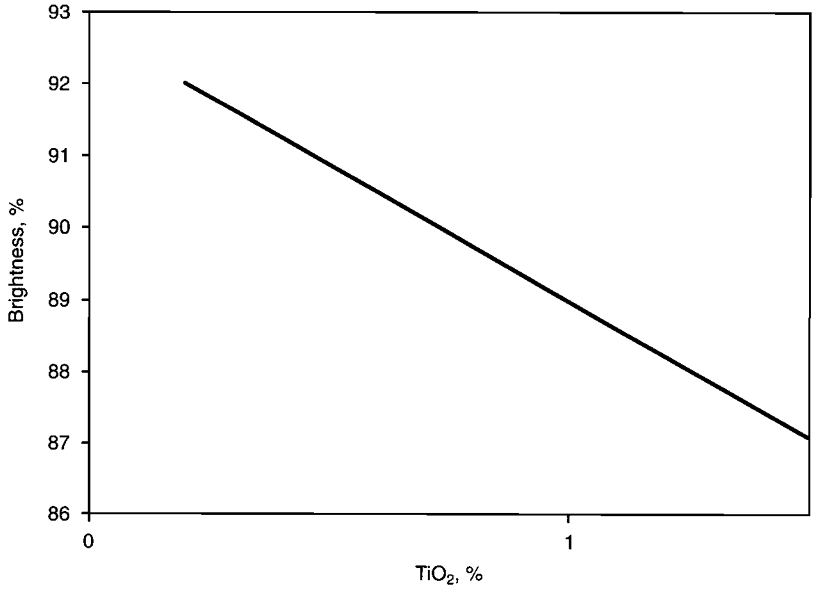

FIGURE 2 Relation of TiO_2 to brightness

THE NATURE OF COLORING IMPURITIES

In the late 1950s, it became apparent to kaolin producers that there would be a considerable market for kaolin pigments of greater than 87 brightness. Since pure kaolinite should be white, brightness value of 95 or better should be possible if discoloring impurities could be removed. It may be mentioned here that the brightness scale is calibrated with respect to pure $MgCO_3$, which has been arbitrarily assigned a value of 100.

Research showed that anatase titanium dioxide is one of the major colored impurities in the kaolins of the southeastern United States. Although commercial, synthetic, pigment anatase is pure white with a brightness close to 100, the anatase occurring in kaolin is beige to dark reddish brown. The color of the anatase is due to substitution of other cations such as Fe within its lattice that are generally present at levels of less than 5%.

As anatase titanium dioxide is removed from kaolin, the brightness of the remaining kaolin is improved as shown in Figure 2. All titanium removal processes give the brightness vs. TiO_2 content relationship shown in Figure 2. However, the curve may be displaced slightly when kaolins from different sources are treated. In addition to the titanium dioxide in the anatase form, there is also some present in the rutile form. The rutile titanium dioxide occurs mostly in coarse particles. Because, in the normal wet processing of kaolin, the extreme coarse particle fraction is discarded, the rutile is not a significant discoloring impurity in the final product.

In addition to rutile and anatase, many other minerals are found associated with Georgia kaolins. These include goethite, graphite, kyanite, marcasite, muscovite, pyrite, quartz, siderite, smectite (-montmorillonite), tourmaline, staurolite, and zircon. Many of these minerals are potential discoloring agents for clay, but they normally occur in very small quantity or in the coarse particles.

The removal of colored impurities by flotation entails the problems associated with fine particle flotation.

WHY FINE PARTICLE SIZE IS A PROBLEM IN FLOTATION

Fine particles or slimes (less than 10 microns) may be naturally occurring constituents of a mineral or ore or may be artificially produced during the grinding of the mineral or ore to a suitable size for mineral liberation. 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 that detract from the value and utility of the clay in its pigmentary applications. Therefore the beneficiation of kaolin entails using methods that are effective in the fine-particle range.

It has been observed 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. The loss in floatability of fine particles has been attributed to the difference in the physico-chemical properties of the fines compared to the coarse (Fuerstenau, 1980). First, the small mass and momentum of the fine particles cause these to report to the froth either due to entrainment in the liquid or mechanical entrapment within the particles being floated. Secondly, the large specific surface area of fine particles results in excessive collector consumption. Thirdly, surface and electrochemical properties of fine particles tend to be different from the properties of coarse particles of the same material. The higher solubility or leaching of cations from fines owing to the high specific surface energy may lead to unwanted activation of nonfloatable minerals and thus loss of selectivity.

REMOVAL OF COLORED IMPURITIES BY FLOTATION

A lot of effort has been put into improving the flotation response of fine feeds over the last several years. There are no general flotation methods that have been developed for beneficiation of fine particles. Each industry has developed its own way of dealing with the problem of flotation of fine particles. In this section the different flotation processes used for beneficiation of kaolin are described in a chronological order.

Ultraflotation

Carrier mineral flotation or "ultraflotation" was the first successful anatase-removal process used with kaolin on a large scale at Engelhard Corporation and was put into commercial operation in 1961 (Greene et al., 1961). In this process the conditioning of kaolin is accomplished with two essential agents, tall oil and calcium carbonate, which cooperatively permit improved beneficiation of the very finely divided feed. The schematic of the carrier flotation process is shown in Figure 3. The tall-oil reagentized carrier mineral captures some of the very fine particle impurity, which then can be floated using standard subaeration cells, because the carrier mineral is relatively coarse in particle size as compared to both the clay and the anatase to be removed. Calcite form of calcium carbonate is a satisfactory carrier mineral because of its low cost, excellent flotation response, being readily available, and ease of removal from the froth.

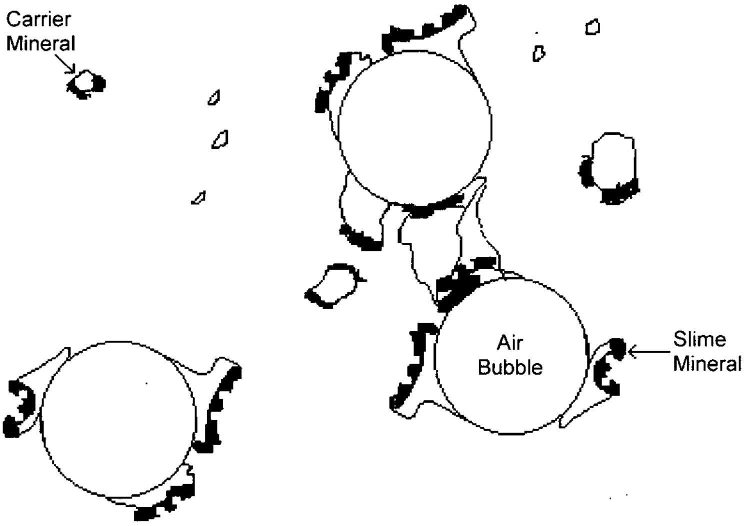

FIGURE 3 Schematic of ultraflotation (after Fuerstenau, 1980)

Wang and Somasundaran (1983) clarified the cooperation between tall oil and calcium carbonate in ultraflotation. According to them the "piggyback phenomenon" of attachment of anatase onto calcite is due to hydrophobic bonding between the oleate layers adsorbed on the mineral surfaces. This conclusion is based on electrokinetic measurements showing that both anatase and calcite are negatively charged in the presence of oleate collectors. This thus rules out the possibility of electrostatic interaction between the two minerals.

Wang and Somasundaran (1983) also provided an explanation for the beneficial effect of high-speed agitation during conditioning in the ultraflotation process. The collector adsorption on kaolinite is relatively weak as compared to its adsorption on calcite and anatase. Therefore, upon high shear agitation, the collector coating on kaolinite is prevented while it remains intact on the other minerals, which will enhance the selectivity of the flotation process. Experimental evidence for this explanation is that, in the presence of sodium oleate, the zeta potential of kaolinite decreases with increasing agitation while that of anatase is not affected.

Several major improvements have been made to the ultraflotation process since its inception, including the dispersant type, throughput, and the type of crudes processed. Mercade (1967) developed a novel hydrosol dispersant prepared by addition of alum to sodium silicate that is believed to quench higher chain silicate oligomers and thereby result in a more robust dispersion of the crude for the flotation process. At present, ultraflotation products have a TiO_2 of less than 0.8% depending upon the crude used.

ECCI Process

English China Clay International (ECCI) developed the first carrierless flotation process for removal of titaniferous impurities (Cundy, 1969). The two essential features of this process are high-energy scrubbing of the kaolin slurry at 40–60% solids and the presence of activator ions such as calcium. The scrubbing action, according to Cundy, consists of cleaning the minerals of their contaminants and is derived from relatively high solids under high-speed agitation. It is, however, more likely that this process facilitates liberation of the colored impurities from kaolin and thus prepares the slurry for conditioning with the oleic acid in the presence of calcium ions. Again, as with the ultraflotation process, the high-speed agitation probably leads to surface coating of only the anatase particles and thus selectivity in flotation. The collector-coated anatase particles may be selectively coagulated under the high-speed agitation, which effectively increases the particle size and allows flotation.

In the ECCI process, the kaolin crude is conditioned with oleic acid and calcium salts under alkaline conditions. The flotation solids are reduced to 15–20%, and standard subaeration flotation cells are used to remove the colored impurities.

Titanium Removal and Extraction Process (TREP)

The TREP was developed at Freeport Kaolin (now Engelhard Corporation) and is a carrierless flotation that uses oleic acid as a conditioning reagent in the presence of a calcium activator under acidic conditions (Young et al., 1985).

A major improvement of the TREP over the previous kaolin flotation processes was flotation at the same high solids as during conditioning, i.e., in excess of 25%. This lends to the benefit of higher throughput and lower dewatering costs. The other unique features of the TREP compared to previous flotation methods are indigenously developed high-intensity conditioner (Bacon and Brooks, 1984) and column-like flotation cell (Bacon, 1984). In the TREP conditioner the temperature of the conditioned slurry reached is in excess of 200°F. The conditioned product is then treated with a deflocculant prior to being floated in the column flotation cell described in the patent by Bacon (1984). A typical TREP is described below (Young et al., 1985).

A coarse-grained Middle Georgia crude with a particle size distribution of less than 50–65% of less than 2 microns is treated with 1–3 #/t N brand silicate dispersing agent and then passed through a 250-mesh screen to remove mica, sand, and other coarse particles. The clay slurry is pH adjusted to 6.5 to 7.0 with aqueous NaOH. The nearly neutral slurry is then allowed to stand for approximately 15 to 24 hours before use. The slurry can be pretreated with an oxidizing agent such as oxone since the storage time allows it time to operate on the oxidizable impurities. The pH of the aged slurry is generally 6.5 to 6.8 and is the preferred pH range for conditioning. It may be mentioned, however, that slurries having a pH value as low as 6.1 have been conditioned satisfactorily. The conditioning of the slurry is done in the TREP conditioner using 0.5 #/t $CaCl_2$ and 5 #/t oleic acid for 20 minutes. The addition of the calcium chloride decreases the pH of the conditioner feed to 4.0 or so, and the pH after conditioning is in the range of 6.1 to 6.3. The conditioning under acidic pH distinguishes the TREP from the ECCI process.

Sodium polyacrylate is added in the amount of 4 #/t as an after-conditioning dispersant. This is allowed to mix into the slurry for a few minutes before frothing begins in the column cell. As frothing continues, the pH is raised to a maximum value of 7.8, if necessary, to improve the removal of impurities.

TABLE 1 Effect of TREP on beneficiation of kaolin (Young et al., 1985)

Sample	% TiO_2	GEB
Feed	1.76	84.7
TREP product	0.53	89.1

TABLE 2 Effect of polyacrylate dispersant added prior to conditioning on flotation (Young et al., 1985). The N-brand sodium silicate has a modulus of 3.22.

Sample	Dispersant Type	Dosage (#/ton)	Product % TiO_2	GEB	%TiO_2 Removal
Feed		—	1.83	85.6	—
TREP product	"N" brand sodium silicate	2.3	0.53	90.9	71.0
TREP product	"N" brand sodium silicate	2.3	1.50	87.0	18.0
	Na Polyacrylate	1.7			

TABLE 3 The efficiency of various dispersants added after conditioning on flotation in the TREP (Young et al., 1985)

Sample	Dispersant	Dispersant Dosage, #/t	% TiO_2	GEB	TiO_2 removed
Feed	—	—	1.76	84.7	—
TREP product	None	—	1.12	86.0	36.4
TREP product	TSPP/Na_2CO_3	2	1.06	86.8	39.8
TREP product	Na silicate	2	0.95	87.3	46.0
TREP product	Na polyacrylate	2	0.53	89.1	69.9

After the impurities are removed, the unfractionated product is flocculated with 10% H_2SO_4 and bleached with 15 lbs/ton K-Brite (a commercial form of sodium dithionite). The unfractionated products are filtered and microwave dried.

The TAPPI brightness is measured on a Technidyne S-4 Brightness Tester, and the TiO_2 analysis is determined by X-ray fluorescence. A typical result of a TREP experiment is given in Table 1, where GEB is the GE Brightness.

The TREP is sensitive to the dispersant added prior to conditioning and flotation. Young et al. showed that organic dispersants such as polyacrylates or inorganic dispersants such as sodium polyphosphates added prior to conditioning inhibit flotation (see Table 2).

The results dramatically show that the addition of a polyacrylate dispersant prior to conditioning is very detrimental to TiO_2 removal. The polyacrylate salt added before conditioning provides only one fourth of the TiO_2 removal obtained otherwise. However, the conditioner product could be best dispersed for flotation with polyacrylate rather than an inorganic dispersant as illustrated in Table 3.

These results show that the polyacrylate dispersant added to the conditioned product results in almost two-fold TiO_2 removal during flotation compared to no dispersant. Further, the inorganic dispersants offer only a marginal improvement over no dispersant addition prior to flotation.

Hydroxamate Flotation

The above-mentioned flotation processes are based on the use of the fatty acid or tall-oil type of collectors that require the use of divalent or trivalent activator cations. The presence of activator ions makes the process sometimes difficult to control because of the necessity to maintain a proper balance between the amounts of collector and activator added. For example, an excessive use of activators can induce coagulation of the clay particles and makes the separation difficult. Further, activators may also cause the flotation of the clay particles themselves rather than the colored impurities, resulting in a poor separation efficiency and a loss of clay recovery. It is therefore desirable to have a collector for colored impurities that does not require activators.

Hydroxamates, (R-C(O)-NH-OM), where R is an alkyl, aryl, or alkylaryl group and M represent an alkali or alkaline metal or hydrogen, are a class of chelating chemicals and thus they adsorb by chemisorption. Chemisorption has been suggested to be a successful approach to improve the flotation of fine particles due to the following reasons (Fuerstenau, 1980):

1. specific chemical interactions between the collector ion or molecule and metallic cation sites on the surface; and
2. the residual concentration of collector in chemisorbing systems is low, which obviates the excessive collector consumption.

Fuerstenau and Pradip (1980) present an excellent review of the hydroxamate collectors. Yoon and Hilderbrand (1986) first patented a successful kaolin flotation process based on hydroxamate collectors. The hydroxamate collectors can be used effectively at pH values above 6, at which the dispersion of clay is readily achieved. The amounts of these reagents required for flotation are considerably less than those typically used in the conventional tall oil flotation process. Also, the hydroxamate collectors possess frothing properties so that no frothers may be necessary for flotation.

Cytec patented a feasible manufacturing process (1990) for hydroxamates and the product reagent S6493 is currently used by Thiele Kaolin. The hydroxamate collector is supplied as a water-in-oil microemulsion. Hydroxamates can be used to condition solids as high as 70% wt% and the flotation solids can be between 15–45% solids.

The flotation with hydroxamate collectors consists of the similar prior basic steps as described with the other processes such as dispersing the clay slurry and conditioning with the collector. The distinguishing features with the hydroxamate collectors are relative insensitivity to the dispersant type for dispersing clay slurry and high solids during conditioning and flotation (Yoon and Hilderbrand, 1986). The conditioning pH is generally maintained between 8–10, because at lower pH values the process is not that efficient and a pH higher than 10 results in excessive frothing, which may inhibit effective separation. In many flotation systems that use hydroxamate as collectors, the optimum pH has been shown to be between pH 9–9.5, which is similar to the pK_a of hydroxamic acid (Fuerstenau and Pradip, 1980). The results (Table 4) indicate that kaolin is no exception.

TABLE 4 Effect of conditioning pH on flotation of anatase from a Middle Georgia crude (Yoon and Hilderbrand, 1986)

Sample	pH	% TiO_2	Clay yield, wt%
Feed	—	1.45	100
Float product	6.2	1.08	94.6
"	6.8	0.95	93.8
"	7.4	0.84	94.7
"	8.2	0.82	91.2
"	8.9	0.71	89.4
"	9.6	0.66	93.2

TABLE 5 Effect of blended hydroxamate and tall oil versus the individual collectors on TiO_2 removal and clay yield (Shi and Yordan, 1996)

Collector	Dosage, #/t	%TiO_2 product	Yield of Clay, %	Amount of TiO_2 removed by flotation	Coefficient of separation
Tall Oil (Westvaco L-5)	3.0	0.30	64.9	81.0	0.46
Cytec S6493 hydroxamate	2.0	0.28	86.0	81.9	0.68
Tall Oil (Westvaco L-5)	1.0				
Cytec S6493 hydroxamate	1.0	0.31	86.6	80.0	0.67

Two variations on the usage of hydroxamates in flotation have been developed at Thiele Kaolin. These consist of:

- synergistic effect of cocollector chemistry comprising of oleic acid and hydroxamate (Shi and Yordan, 1996); and
- pretreating the crude with hydroxamate in clay-water system prior to addition of the deflocculant (Norris and Yordan, 1997).

The blended cocollector system serves to reduce the dosage of hydroxamate significantly while maintaining similar level of TiO_2 removal and clay yield. The industrial implication is a lower collector cost since the hydroxamates are more expensive than the tall oil. Table 5 illustrates that the cocollector of hydroxamate and tall oil removes the same amount of anatase as the individual collectors. However, the efficiency of the cocollector system is the same (measured by the coefficient of separation) of the hydroxamate chemistry while using only half of the dosage of alkyl hydroxamates and only one third of the dosage of tall oil.

The coefficient of separation (C.S.) is an index used to measure the flotation process performance (Wang and Somasundaran, 1980) and is defined as:

$$\text{C.S.} = (\%\text{Yield of Clay} + \%\text{ of } TiO_2 \text{ removed by flotation} - 100)/100$$

Thus the C.S. varies from 0 for no separation to 1 for perfect separation. According to Norris and Yordan (1997), the C.S. varies from 0.3 to 0.75 in the case of beneficiation of kaolin by froth flotation.

TABLE 6 Effect of order of addition of deflocculant and hydroxamate collector on beneficiation of East Georgia crude (After Norris and Yordan, 1997)

Reagents	#/t	pH	%TiO_2 removed by flotation	% yield of clay	C.S.
Sodium silicate	9	8.6	60.7	67.3	0.28
Soda ash	2				
S6493	4				
S6493	4	8.0	80.0	82.2	0.62
SHMP	4				
Soda ash	3				

SHMP = Sodium hexametaphosphate

The cocollector usage circumvents the use of activators such as the divalent salts normally required with oleic acid (Shi and Yordan, 1996). This is an interesting phenomenon and merits further investigation.

The advantage of prior addition of hydroxamate to condition the kaolin is that any type of deflocculant can be used on this slurry (Norris and Yordan, 1997). This provides flexibility in the choice of the dispersant for the floatation feed. All the flotation schemes described so far utilize the coarse-grained, Middle Georgia crude. The patent of Norris and Yordan (1997) also shows the prior addition of hydroxamate provides improved effectiveness when conditioning fine-grained, East Georgia crudes as illustrated in Table 6.

SUMMARY

A review of the current flotation practice in the kaolin industry certainly shows that the kaolin industry has been at the forefront of adapting the flotation technology to fine-particle processing. Still there are many technological challenges that need to be addressed and include:

- variable response of kaolins from different sources;
- high conditioning energy requirements;
- low flotation solids, which entails a large amount of water removal; and
- higher iron removal.

A fundamental understanding of the industrial practice is certainly needed to refine the existing processes as well as develop new reagent schemes. The move to specific collector chemistry such as hydroxamates has shown a lot of promise in designing robust flotation processes. The hydroxamate collector is relatively insensitive to the dispersant type and pH, which offers a lot of forgiveness during processing. The downside is the higher chemical cost of the reagent.

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