

# Chapter 22

## THE REMOVAL OF MINERAL IMPURITIES FROM KAOLIN USING FLOTATION

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### ABSTRACT

The beneficiation of kaolin by flotation has been practiced on an industrial level since 1961. A brief history of industrial kaolin flotation is given, with a description of the various processing schemes used by the companies that practice kaolin flotation. Some of the areas where improvements could be made in the beneficiation of kaolin are given.

### INTRODUCTION

Kaolin clay, consisting mainly of the mineral kaolinite, is widely used as a white pigment. Its main uses include pigmented paper coatings, paints, fillers and extenders for paper, plastics, inks and miscellaneous other pigment applications. In the United States, kaolin production for 1988 was approximately 8.6 million metric tons with an estimated value of \$810 million. About 12% of the kaolin is processed with various beneficiation techniques into premium (high brightness) products that sell for about \$50 per ton above the equivalent standard grade (Ampian, 1989).

Although much of the kaolin produced is used in inert filling applications where the product specifications are not rigid, a significant quantity of the kaolin is processed into products where very tight quality specifications exist. These specifications put restrictive limits on such properties as clay-water viscosity, particle size distribution, brightness, color, and freedom from oversize particles.

This discussion will concentrate on one beneficiation process, flotation, used to improve the color and brightness of the kaolin pigment, and will review the advantages and disadvantages of the various flotation techniques used commercially. Other processes for impurity removal from kaolin have been discussed previously (Sennett et al., 1979).

### THE EFFECT OF DISCOLORING IMPURITIES

The brightness and color of the pigment are influenced to a degree by relatively small quantities of (1) discrete, colored impurities present in the kaolin and (2) iron hydroxide stains on the surface of the particles. Generally, flotation processes remove  $TiO_2$  from the kaolin which improves product brightness. Iron content is not much affected by flotation. Unlike many flotation processes where the desired component is concentrated in the froth, kaolin flotation is the reverse of this, i. e., the undesired component is removed in the froth and discarded.

While pure anatase  $TiO_2$  is a very white pigment with a brightness of approximately 100, the anatase present in the kaolin deposits has an intense reddish-brown color. This color is likely due to substitution of 2 to 5% iron (expressed as %  $Fe_2O_3$ ) for titanium in the crystal lattice of the anatase. As the anatase is removed from the kaolin, substantial brightness improvement of the remaining kaolin is obtained. Typical brightness values as a function of  $TiO_2$  for a kaolin from middle Georgia are shown in Figure 1. (Redrawn from Sennett et al., 1979).

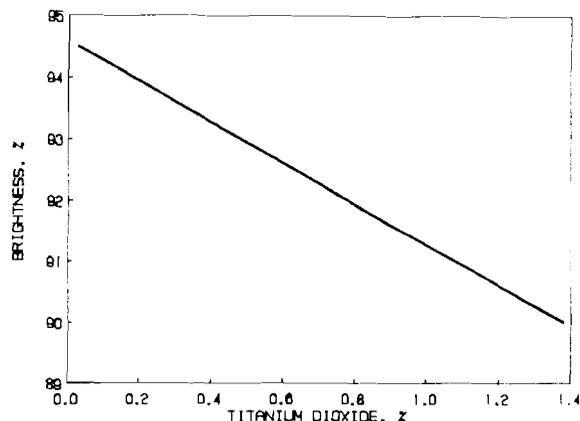


Figure 1 Relation of  $TiO_2$  to Brightness

Typical properties of a No. 1 paper grade kaolin (before TiO<sub>2</sub> removal by flotation) is shown in Table 1.

Table 1

PROPERTIES OF A COMMERCIAL COATING GRADE KAOLIN

Brightness	86.5 - 87.5
Particle size distribution:	
% + 25 mesh	0.003
% < 5 μm	100
2	92
1	76
.5	55
.2	21
Median size (μm)	.44
Chemical analysis: (%)	
Ignit. loss (1,000°C.)	13.8
Al <sub>2</sub> O <sub>3</sub>	38.5
SiO <sub>2</sub>	44.9
TiO <sub>2</sub>	1.6
Fe <sub>2</sub> O <sub>3</sub>	0.50
K <sub>2</sub> O	0.03
CaO	0.03
MgO	0.02
Na <sub>2</sub> O	0.35
SO <sub>3</sub>	0.1

Generally the flotation processes reduce the TiO<sub>2</sub> content of a No. 1 coating fraction to about 0.5% or less. At this level of titanium dioxide, a brightness of 90 or slightly higher may be obtained after reductive bleaching. Under ideal conditions additional TiO<sub>2</sub> may be removed and an even higher brightness can be obtained but no commercial products of higher brightness are available.

BRIEF HISTORY AND DESCRIPTION OF KAOLIN FLOTATION

Ultraflotation was the first successful anatase removal flotation process used with kaolin on a commercial scale. Production of a high brightness coating clay started in 1961 and the process, with modifications, is still being used today by Engelhard Corporation. This process uses a carrier mineral (calcium carbonate of controlled particle size) to aid in the separation of the anatase from the kaolin. This process uses standard subaeration flotation cells with tall oil and a high molecular weight sulfonate as a collector. An extender oil is also used. Flotation is carried out on kaolins after fractionation into suitable particle size ranges. This process has been well described elsewhere (Seeton, 1961; Greene et al., 1961; Wang, 1980; Chia, 1983).

Production of the premium brightness products was also started later (in 1966) by Anglo American Corporation, now ECC America, Inc. ECCA uses a patented process for the flotation beneficiation of kaolin. Standard subaeration flotation machines are used and oleic acid with an activator are the flotation reagents. The reagents are added in stages and flotation and conditioning times are reported to be 100 minutes. The feed to flotation is a "full fraction" kaolin, i. e., a crude kaolin with oversize particles removed but not yet further fractionated into the size distribution of the ultimate commercial products. Details of the process are given by Cundy, 1969, 1976, and Nott, 1978.

In 1981 Freeport Kaolin started producing premium brightness kaolin products based on the patented process (Young et al., 1985) named Titanium Removal/Extraction Process or "TREP". In 1985 Freeport Kaolin was acquired by Engelhard Corporation who continues to use this process as well as the older Ultraflotation technique. The TREP process uses special conditioning and column flotation for the removal of the anatase. The reagents used are an activator and oleic acid, and the full fraction feed slurry is oxidized prior to being conditioned and floated.

Other kaolin producers (Thiele Kaolin Company, J. M. Huber Corp., and Georgia Kaolin Company) also produce 90 brightness kaolins but it is not believed that flotation is used. A patent issued to Thiele Kaolin Company (Yoon et al., 1979) describes an interesting flotation process using a hydroxyamate collector but it is not believed that the described process is used commercially.

SPECIFIC FLOTATION PROCESSES

It is very difficult to make a detailed comparison of the various flotation processes used by domestic producers since kaolin manufacture is a highly competitive industry. Much of the technology is proprietary and details of significant improvements are not made public.

Engelhard.

Figure 2 is a flow chart for the Engelhard carrier mineral flotation process. As noted above, it has been described in more detail in the Denver Equipment Bulletin M4-B117. Since the original publication of the process, considerable improvements have been made. An aluminum-silicate hydrosol is the dispersant used by Engelhard for the Ultraflotation process (Mercade, 1967, 1978). In addition, the carrier flotation process has been studied in great detail by Dr. Somasundaran and his students (Wang et al., 1980, Chia et al., 1983).

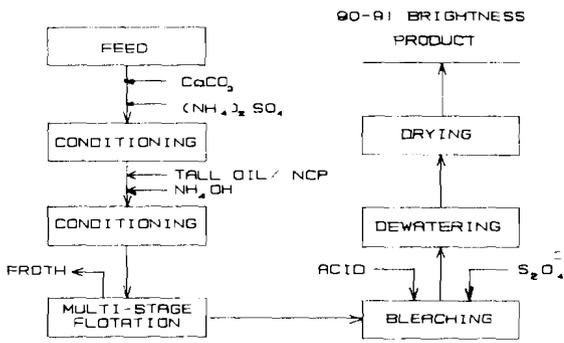


Figure 2 Ultraflotation Flowsheet

Figure 3 shows the TREP flotation process as initially developed by Freeport Kaolin. The process, when commercial production started in 1981, represented a significant improvement over previous processes in that a new type of conditioning was introduced (Bacon et al., 1984) and column flotation was carried out (Bacon, 1984). A further improvement over the then existing processes was that flotation could be carried out at higher solids, 35% or greater. As with carrier mineral flotation, process improvements have been made since its introduction.

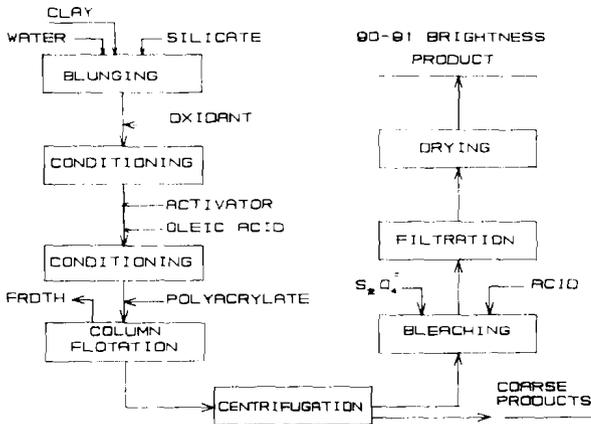


Figure 3 TREP Flowsheet

ECC America, Inc.

Figure 4 illustrates the flotation process described in patents issued to ECCA. As with the other flotation schemes, it is suspected that significant process improvements have been made since its commercialization.

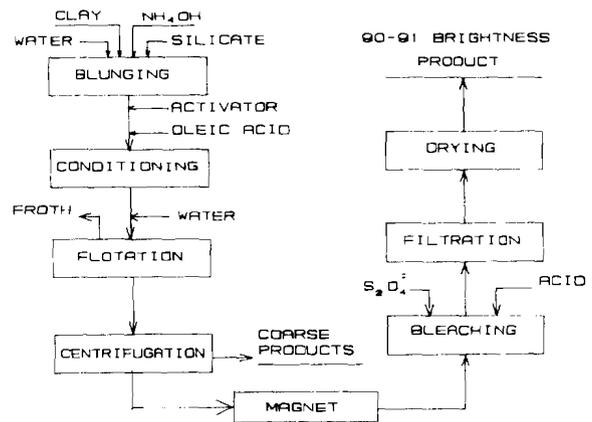


Figure 4 ECCA Flowsheet

Process Comparisons.

So that ready comparisons can be made between the various flotation processes, a summary of the process steps is given in Table 2.

PROBLEMS IN KAOLIN BENEFICIATION BY FLOTATION

Although several economic commercial flotation processes are being used, significant room for improvement in these processes exist. Specific problem areas in kaolin flotation include:

1. Variable response of kaolins from different sources. Although the in-ground raw material is typically at least 95% kaolinite, flotation response of different crudes can be very different and require in-process compensation by varying reagent use, conditioning energy, etc.
2. Conditioning energy requirements are high.
3. Flotation is carried out at low solids so that considerable water must later be removed to make a high solids slurry or dry kaolin product.
4. Flotation reagents must be substantially removed from the products since they might cause adverse effects in the products' subsequent use.
5. Existing flotation processes remove only a small amount of iron (that associated with the anatase impurity). Iron is a powerful discolorant and removal of even a small additional amount would give a further brightness improvement in the product.

Table 2

## COMPARISON CHART

## FLOTATION PROCESSES FOR ANATASE REMOVAL FROM KAOLIN

PROCESS		ULTRAFLOTATION	TREP	ECCA
Feed	Particle size	Sized fractions	Full	Full
	Dispersant	Hydrosol	Sodium silicate	Sodium silicate
	Pretreatment	CaCO <sub>3</sub> carrier (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Potassium persulfate	
Reagents	Activator		Calcium salts	Metal salts
	Collector	Tall oil Sulfonate	Oleic acid	Oleic acid
	Other	NH <sub>4</sub> OH		Pine oil
Conditioning	Energy input			
	Amount	> 85 kJ/kg	> 61 kJ/kg	> 61 kJ/kg
	Solids	25%	35%	40%
	pH	8 - 9	6 - 7	Alkaline
	Equipment	Denver, high energy	Patented design	High speed
Flotation	Solids	20 - 25%	35%	16%
	Equipment	Mechanical	Column	Mechanical
	pH	8 - 9	6.2 - 7.8	Alkaline
	Other		Na polyacrylate	
Product	Brightness	88	89	88
	Particle size	Coating fractions	Full fraction	Full fraction
	TiO <sub>2</sub>	0.5 - 1.0%	0.2 - 0.5%	0.5%
References		Green et al, 1961 Seeton, 1961 Mercade, 1967	Bacon, 1984 Bacon et al, 1984 Young et al, 1985	Cundy, 1969 Nott, 1978 Cundy, 1986

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