Kaolin: processing, properties and applications

M.S. Prasad[a], K.J. Reid[a] and H.H. Murray[b]

[a]*Mineral Resources Research Center, University of Minnesota, Minneapolis, MN 55455, USA*
[b]*Department of Geology, Indiana University, Bloomington, IN 47405, USA*

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ABSTRACT

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Kaolins are white raw materials, their essential constituent being fine grained white clay, which are amenable for beneficiation that make them ideal for an assortment of industrial applications. Kaolin deposits can be classified into two types, primary (residual) and secondary (sedimentary). The main commercially important kaolin resources at the present time are the primary deposits of Cornwall in England and the sedimentary deposits in Georgia and South Carolina in the USA
This review outlines the geology and occurrence of kaolins in the world and the state of the art in processing high-quality kaolins. The physical and chemical characteristics of kaolin are also reviewed with respect to their use for specific applications in paper, ceramics and refractories, plastics, rubber, adhesives and paint industries.
The market outlook for world kaolin is outlined with respect to product specifications, markets and prices and the competition from other fillers such as calcium carbonate.

INTRODUCTION

The name kaolin is derived from the Chinese term "Kauling" meaning high ridge, the name for a hill near Jauchau Fu, China, where this material was mined centuries ago for ceramics. The main constituent, kaolinite, is a hydrous aluminum silicate of the approximate composition $2H_2O \cdot Al_2O_3 \cdot 2SiO_2$. Structurally, kaolinite consists of alumina octahedral sheets and silica tetrahedral sheets stacked alternately and has the theoretical formula $(OH)_8Si_4Al_4O_{10}$ and the theoretical composition 46.54% SiO_2, 39.5% Al_2O_3, 13.96% H_2O. The shape of a perfectly ordered kaolinite crystal is pseudo-hexagonal, but ordering may range from a high degree, to a poorly ordered crystal where shape is non-determinant. The arrangement of atoms in the kaolinite group is shown in Figs. 1A and B. In the silica layer the Si and O atoms are linked to form six membered rings, similar to those of cristobalite and tridymite (Fig. 1A). In the gibbsite layer (Fig. 1B), the Al atoms are in six fold coordination with O or (OH), but the O atoms from a hexagonal ring of
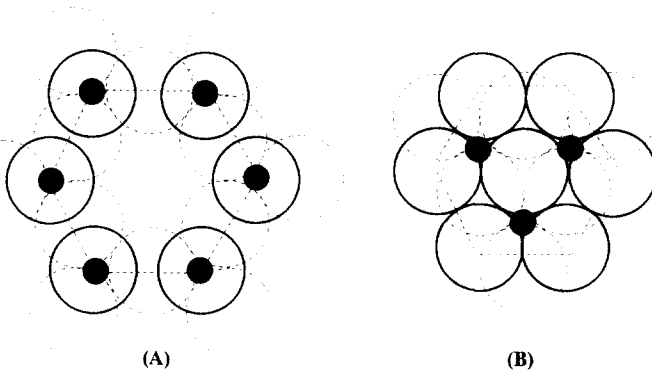
Fig. 1. Structure of kaolinite: (A) silica layer, (B) gibbsite layer (Wells, 1984).
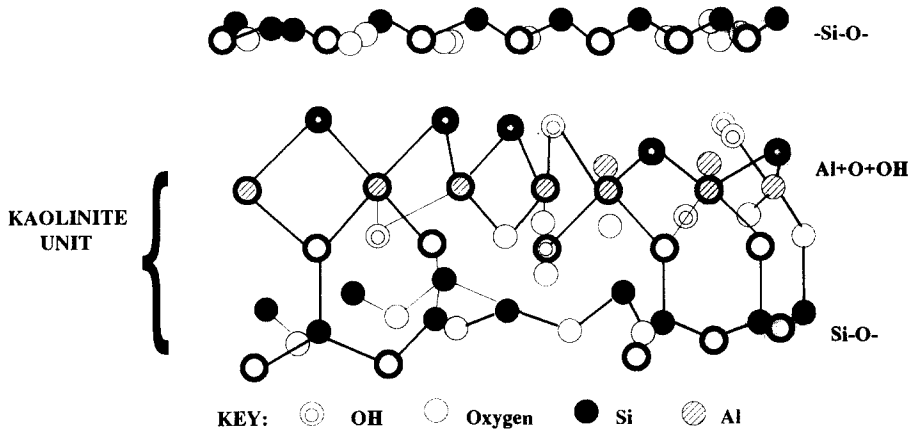

KEY: ◎ OH   ○ Oxygen   ● Si   ⧄ Al

Fig. 2. Structure of kaolinite, front elevation (Wells, 1984).

approximately the same size as the Si–O hexagonal rings. These two sheets, if superimposed "fit" almost exactly, forming a compound layer with the O atoms referred to as common atoms forming the link between the layers. The composite layer is shown in Fig. 2.

Kaolin is one of the most versatile industrial materials. It is chemically inert over a relatively wide pH range, is white in color and has good covering power when used as a pigment or extender. Kaolin is soft and non-abrasive, and has a low conductivity of heat and electricity. Some uses of kaolin, such as in paper coating, or fillers for paints and plastics require very rigid specifications including particle size, color and brightness and viscosity whereas other uses require no specifications, for example in cement where the chemical composition is most important. The paper industry consumes the largest amount of kaolin where it is used both as a filler and as a coating material on the paper surface to improve the quality of printing.

MINERALOGY, CLASSIFICATION AND OCCURRENCES

Mineralogy

The term "kaolin" is also used as a group name for minerals including kaolinite, nacrite, deckite and halloysite. Many authors, however, use the term kaolinite group. With the exception of the hydrated form of halloysite, all of these minerals have essentially the same composition. They differ in the mode of their structural arrangement. Kaolinite normally occurs as crystals ranging in size from a fraction of a micron up to several hundred microns across. Halloysite has the same composition as kaolinite with an additional sheet of oriented water molecules between the layers. In certain ceramic applications, halloysite has some advantages, but in most other cases its presence is neutral or disadvantageous. The presence of iron and titanium oxide minerals are disadvantageous as they impair whiteness and reduce brightness. The presence of excess silica in the form of quartz or cristobalite generally introduces abrasion problems in paper applications. The presence of micas and feldspar may influence the rheological, brightness and abrasion characteristics. The viscosity of the kaolin slurry is also affected by the presence of smectite.

Classification

Kaolins are generally classified as primary or secondary deposits. Primary kaolins are formed by the alterations of crystalline rocks such as granite and are found in the location where they were formed. Secondary kaolin deposits are sedimentary in nature and are formed by the erosion of primary deposits. As the eroded materials are washed down stream, separation takes place by gravity and particle size. The finer and lighter kaolin particles are carried farther and eventually deposit in lakes, estuaries, and lagoons where secondary deposits may be formed. In primary deposits, kaolin commonly makes up 15–30% of the total ore. The remainder of the ore consists of unaltered granite including quartz, muscovite, and feldspar. Secondary deposits contain far more kaolinite, with the Georgia deposits containing 85–95% kaolin. In this case, the contaminants include quartz, muscovite, smectite, anatase, pyrite, and graphite. Additional differences exist among the two deposit types. Primary clays are usually coarse, and contain far less anatase and iron oxide than secondary clays. There are also substantial differences among secondary clays depending on the exact nature of the deposit. As an example, kaolin samples from middle Georgia, between Macon and Sandersville, are coarser, contain more vermicular stacks, and different levels of anatase and iron oxide than kaolin samples obtained in East Georgia near Wrens. Because of this, many different techniques have been developed to beneficiate kaolin. Certain tech-

niques are used for some clays, while completely different processing schemes may be required for other clays.

Major occurrences

Kaolin deposits in the Georgia–South Carolina belt were derived from granitic and phyllitic rocks on the Piedmont plateau and were altered by weathering over a long period of geologic time (Fig. 3). The deposits are generally 85–95% kaolinite, the remainder being mainly quartz with minor amounts of muscovite, biotite, smectite, ilmenite, anatase, rutile, leucoxene, goethite and traces of zircon, tourmaline, kyanite and graphite (Bates, 1964).

The English kaolins occur in southwest England in Cornwall and are residual deposits, having formed by the hydrothermal and weathering alteration of Permian granites which are widely exposed in Cornwall and Devon (Fig. 4). The kaolin content of the commercial deposits in St. Austell range from 10 to 40%. The major nonclay mineral is quartz along with other minor accessory minerals (Kerler, 1963; Bristow, 1969, 1977; Patterson and Murray, 1975).

In Brazil, the secondary kaolin deposits exist along Jari River in the State of Amapa and along the Capim river in Para. They were derived from the weathering of the granites on the Guyana Shield (de Souza Santos, 1972). The kaolinite content in the deposit is comparable to Georgia deposits, comprising 80–90%.

The other major deposits of commercial interest are the primary deposits in Czechoslovakia formed as a result of weathering of crystalline rocks of the
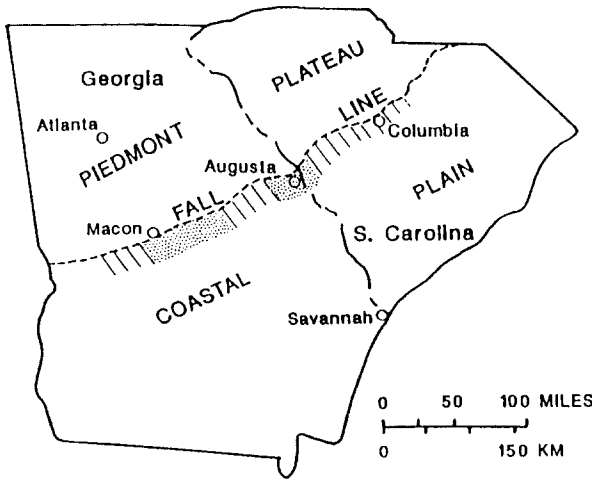

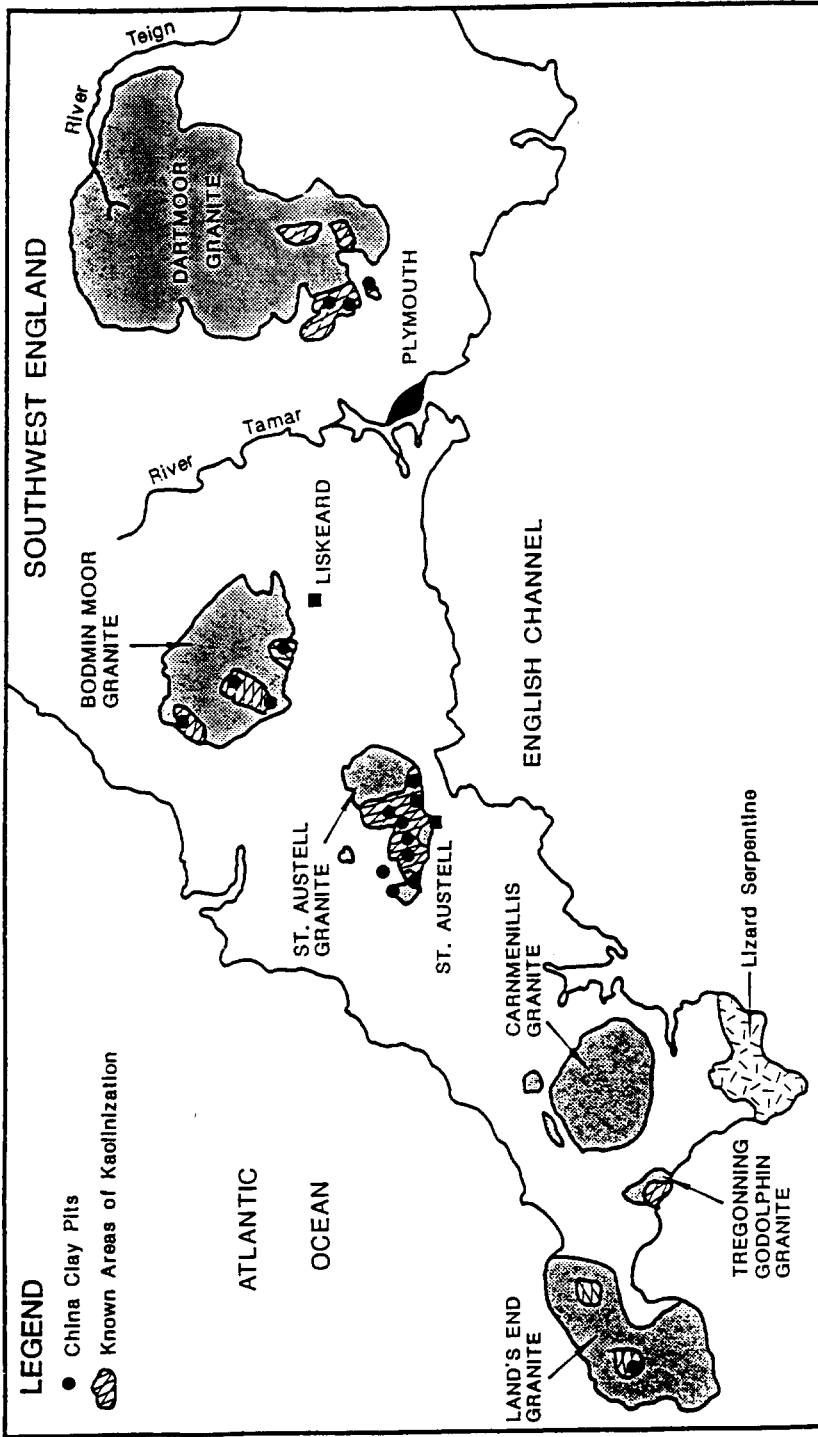Fig. 3. Location of kaolin deposits in the southeastern United States (Murray, 1984).

Fig. 4. China clay deposits of southwestern England (Guillet and Kriens, 1984).

Bohemian Massif (Kuzvart, 1969), the German deposits (Störr, 1975) in Bavaria and Saxony, the Ukraine deposits in USSR (Petrov, 1969), the deposits of primary origin near Pittong (Gaskin, 1969) and the secondary deposits of late Cretaceous age in Australia, near Weipa (Hill, 1988).

WORLD KAOLIN PRODUCTION AND CONSUMPTION

Production

Kaolin occurs in most of the countries in the world. However, there are very few deposits which are of good quality and sufficiently large in quantity to support a large kaolin operation. The world production of kaolin is given in Table 1 and it is noticed that the production of processed kaolin is dominated by the United States of America, the United Kingdom and the Soviet Union. Countries such as Czechoslovakia, Brazil and South Korea also produce substantial amounts of quality kaolins and are continuously increasing their production. The world production of kaolin showed a gradual improvement from 22.8 million tons in 1984 to 28.4 million tons in 1988. Production levels in USA and UK have shown substantial growth in the last five years whereas the production in Eastern European countries has remained relatively stable.

United States
The exceptional quality of the major kaolin deposits in the Georgia–South Carolina belt, coupled with the technical and financial strength of the major producing companies give the US producers a major position in international markets for the highest quality kaolins used in the paper industry. According

TABLE 1

World production of kaolin (× 1000 ST) (Sarkis, 1988)

Country	1984	1985	1986	1987	1988[a]
United States	7953	7793	8549	8827	9891
United Kingdom	3296	3472	3211	3372	3750
Soviet Union	3100	3200	3300	3300	3300
Czechoslovakia	736	720	768	768	756
Brazil (processed)	536	578	750	750	849
Republic of Korea	795	726	695	695	917
Other countries	5239	6334	8658	8658 26455	8691
Total	22,751	24,606	25,765	26,455	28,365

[a]Reported figures.

to the USBM statistical production data (Table 1), the total US kaolin production stood at 9.89 million tons in 1988 which showed a 28% increase as compared to 7.95 million tons in 1984. Of this amount, 82% is produced in Georgia, 8% in South Carolina followed by 2.8% in Arkansas. Other important producing states are California and Alabama producing respectively 143,100 and 48,911 tons in 1988. The total US production in 1988 amounted to about 35% of the total world production. The Georgia and South Carolina Kaolin belt extends over a strip of land about 25 miles wide and 150 miles long from Aiken, South Carolina to Andersonville, Georgia. The deposits of the belt are extremely pure and large, with an average kaolin content of 90% in the crude with minor amounts of quartz and mica as impurities. Ultimate kaolin reserves in the belt are very large and only the most attractive deposits are currently being mined.

United Kingdom

The main world source of kaolin other than the US, is the United Kingdom. The total production of kaolin in 1988 amounted to 3.75 million tons which represents 13.2% of the world production. The English deposits are primary unlike the secondary deposits of Georgia and they are mined by wet methods. Nine or ten tons of waste material is produced for each ton of kaolin recovered.

Other sources

The third largest producer of kaolin world-wide is the Soviet Union whose production was estimated at 3,300,000 tons in 1989. Production is concentrated mainly in the central Asiatic provinces, however, little of this kaolin enters world trade.

Another growing producer of kaolin is Brazil. Brazilian production in 1988 was only 849,000 tons, but this was almost entirely composed of high quality paper grade clays. The deposit currently being mined is extremely high grade, containing an average of 98% kaolin and is large enough to last 500 years at the current rate of extraction. The development of this deposit is one of the main reasons for the current growth of the Brazilian paper industry.

A potential large scale producer of high quality coating clays is Australia. Although current Australian kaolin production is only about 200,000 tons a year, deposits are of high grade and expansion seems likely.

Other significant world producers include Germany, France, South Korea, India and Czechoslovakia.

Consumption

The consumption of kaolin is not documented in many countries and it is difficult to produce exact figures for world kaolin consumption. However, based on the production, imports and exports by different regions of the world,

Roskill (1988) prepared the estimated consumption of kaolin as shown in Table 2. It is observed that the consumption of kaolin has shown a gradual increase from 17.1 million tons in 1982 to 20.8 million tons in 1986. The gradual increase in the consumption is noticed in all the regions and for the North American region, the increase was greatest at 41%.

The consumption of kaolin in the USA by end use is given in Table 3. It is apparent that the highest proportion of the kaolin consumption is in the paper industry which accounts for 60% of the total 9.9 million. There are two

TABLE 2

Estimated world consumption of kaolin ($\times 1000$ ST). (Roskill, 1988)

Region	1982	1983	1984	1985	1986
North America	4878	5630	6301	6191	6917
Western Europe	4946	4479	5112	5302	5313
Asia/Australia	1727	1744	1916	2076	2239
Latin America	1035	1056	982	1228	1144
Africa/Middle East	461	440	511	464	469
East European Countries	4148	4249	4448	4607	4723
Total	17,196	17,598	19,271	19,876	20,805

TABLE 3

Kaolin consumption in the US, 1988 (Sarkis, 1988)

Use	Total (ST)
Domestic	
Paper coating	2,737,396
Paper filling	1,631,224
Ceramics and refractories	1,324,565
Fiberglass and other installations	508,246
Bricks (unprocessed)	410,326
Paint	324,465
Rubber	224,197
Sanitary ware	26,847
Plastics	61,332
Other uses	850,966
Exports	
Paper coating	1,208,145
Paper filling	325,602
Rubber	98,093
Paint	34,495
Others	125,236
Total	9,891,135

basic types of clays used in paper: filler clays and coating clays. Sales of kaolin by US companies for paper filling totalled 1.95 million tons in 1988 or 20% of the total sales, out of which 1.6 million tons were used domestically. The production of coating clays in the United States is dominated by Georgia producers. In 1988, the kaolin destined for paper coating end users amounted to 40% of the total US kaolin production. It is expected that if economic conditions stay generally healthy, production of paper and use of kaolin by the paper industry should continue to increase.

The highest consumption of kaolin for non-paper end uses is in the ceramics and refractory industries and amounted to 1.3 million tons corresponding to 13% of total usage.

The use of kaolin in the plastics, adhesives and fiberglass industries is as a filler, to substitute for the resin which is an expensive material. Consumption of kaolin by the fiberglass, mineral wool and insulation industries in 1988 was 508,246 tons which represents 5% of the total consumption. The plastic and adhesive industries consume 65–67,000 tons of kaolin in the US. These figures are likely to increase further given the faster rate of price increase of resin compared to that of kaolin.

The rubber industry uses kaolin with inferior color to that of the average industrial kaolin. This material is mainly air floated, is primarily mined in South Carolina and corresponds to 3.2% of the total consumption. Air floated clays from South Carolina are usually used in the rubber industry which application requires a constant specific gravity, very fine grain size and low
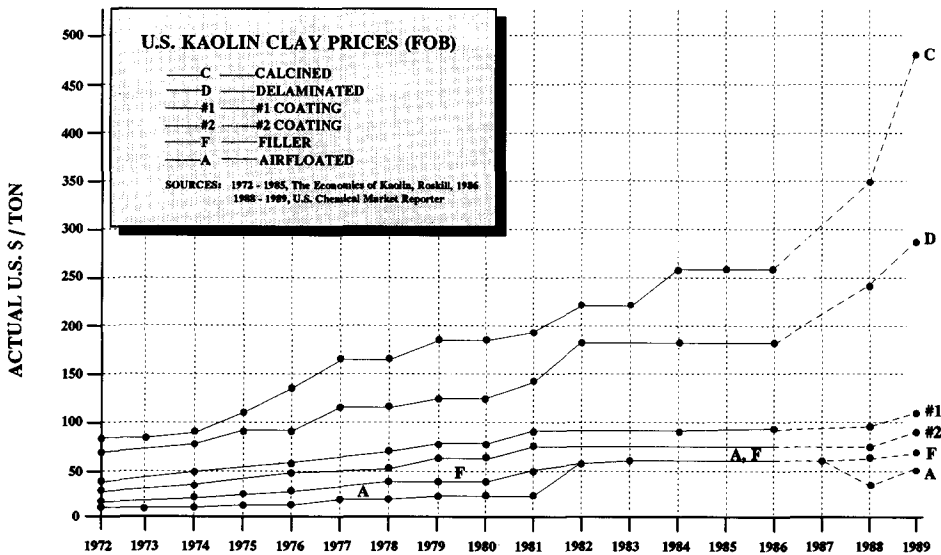

Fig. 5. Evolution of kaolin prices for different grades.

amounts of impurities for formulation with other ingredients of the rubber compounds.

The paint industry consumes 324,465 tons of kaolin in the USA and requires a high brightness and a particle size 70–80% smaller than 2 microns. The chemical industry consumes 233,625 tons of kaolin for the manufacture of aluminum sulfate, phosphate and trichloride. Production of catalysts account for 119,600 tons of kaolin and the pharmaceutical industry uses kaolin in minor quantities as inert filler.

The prices of various kaolin products for different grades are regularly reported by Chemical Marketing Reporter and a comparison of the different types of clays with variations in their price between 1972 to 1989 is given in Fig. 5. The unit price for various kaolin products and grades has seen a steady growth over the past 17 years. However, it is noticed that the prices of coating grades 1 and 2 and filler grades do not show a major change between 1981 and 1989 whereas, the calcined and delaminated clays show a steep rise in their prices in recent years.

MINING

Mining methods

Most of the clay in the world is mined by open-pit methods. Although a few underground mines exist, in most cases the cost of production and poor roof conditions prohibit underground mining of clay deposits. Mining and exploration for kaolin in the Georgia–South Carolina sedimentary belt use conventional open-pit methods and are reviewed by several authors (Guillet, 1984, 1986; Jepson, 1984; Murray and Kriens, 1984). In the United Kingdom, the mining is often done by hydraulic methods (Guillet and Kriens, 1984).

Open-pit mining

The economy of this mining method depends on the costs associated with overburden removal. The type of mining equipment used depends on the depth of the overburden. Mechanical shovels or backhoes may be used to load trucks to remove the overburden from the site (Guillet and Kriens, 1984). If the overburden exceeds sixty feet, scrapers and dozers may be used which are aided in most cases by large draglines. When the overburden is removed, the clay is excavated by small draglines and fed into blungers where it is suspended in water with the aid of a dispersing agent. The clay slurry is pumped to central degritting stations where coarse sand and mica are removed by gravity settling and hydrocyclones followed by screening. The product of this preliminary beneficiation is stored separately in large tanks until testing de-

termines the blending necessary for feed to the main processing plant. The clay slurry is pumped to the main processing plant through pipelines of 15–30 cm diameter over distances of 10–32 km or more.

Hydraulic mining

The Devon and Cornwall deposits in the United Kingdom are usually worked by the hydraulic mining preconcentration technique to avoid handling of excessive amounts of waste rock as reported by Patterson and Murray (1975). Mining is carried out using water jets at pressures of up to 250 psi and preferentially removing the soft kaolin from the matrix leaving behind the hard unkaolinized rock. Selective mining is important because of the variability in the deposits. As the rock face is washed, the slurry containing the kaolin in suspension flows to the lowest point in the pit. Initial treatment to remove the coarse particles from the slurry is carried out in spiral classifiers followed by the separation of finer sand and mica particles in hydrocyclones. The slurry is thickened in a large diameter thickener and finally fed to centrifuges for fine sizing.

PROCESS TECHNOLOGY

The geological history of a kaolin deposit can materially affect the processing technology required to beneficiate it. Hence, a thorough knowledge of the mineral composition is imperative. Process selection depends on the nature of the deposit and the intended applications of the products. There are two basic methods of processing kaolin, a dry method or a wet process (Guillet and Kriens, 1984). The dry method is called air flotation which separates the clay from contaminants. The wet method produces water washed clay where the clays are fractionated, beneficiated or otherwise modified from their original state. When used in the paper industry, air floated clays are used exclusively as filler pigments while water washed clays are used as both fillers and as coating pigments.

Major process developments have enabled the industry to grow and become much more efficient. These major developments and their significance of the growth of the kaolin industry have been summarized in earlier reviews (Murray, 1980; Pemberton, 1983; Yoon and Shi, 1986; Welch, 1989). The primary step in processing kaolin is to separate the abrasive minerals like quartz and undesirable minerals such as mica. This process is simpler in the case of secondary deposits which have undergone natural classification during transportation. By contrast, the separation of kaolin from primary deposits is more difficult due to the presence of a high proportion of abrasive minerals that have survived the alteration process.

Dry process

The dry processing of kaolin is relatively simple, has lower costs, lower yields and lower quality products than the wet process. The general flowsheet utilized in dry process is shown in Fig. 6. The essential feature of the dry process is to dry the crude clay so that it can be pulverized. The crude clay, as it enters the storage shed, is shredded or crushed to relatively small pieces. The crude at this stage contains 20–25% moisture which is removed in a rotary drier. After drying, the kaolin is pulverized in a roller mill and is fed into the grinding section of the mill where plows lift the clay into the area where the rollers grind it against the grinding ring. The disintegrated kaolin may then be air classified whereby the finely ground product is lifted through the top of the machine to the outlet duct. In the outlet duct, the particles encounter the whizzer which separates by size. The light weight particles travel up through the whizzer and are collected separately. The coarse particles which lack the speed to escape the whizzer are rejected through the ports on the side of the mill. This product may be subjected to further grinding to recover additional amounts of previously unliberated clay.

Wet process

The wet processing of kaolin is more complex than the dry process technique. The water wash process scheme for kaolin coating and filler production is shown in Fig. 7. The first step is simply to make the crude clay into a slurry. In order for the kaolinite to be separated from the mineral impurities such as quartz and mica and to be fractionated into fine, medium and coarse grades, the slurry must consist of individual mineral particles separated from each other and suspended in water. The kaolin particles exhibit opposite
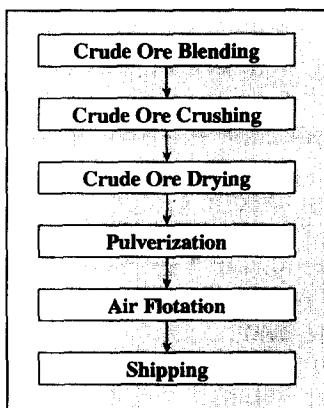

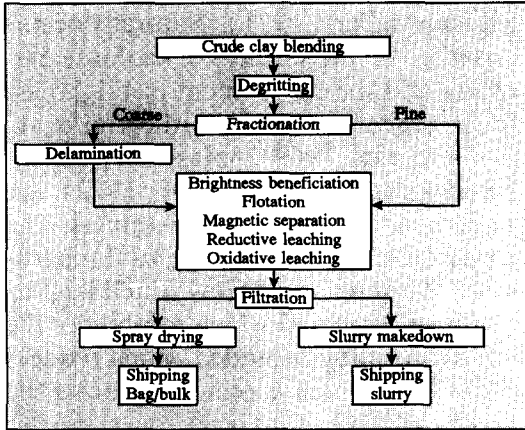Fig. 6. Schematic diagram showing the dry processing of kaolin.

Fig. 7. Schematic diagram for wet processing of kaolin.

charges on the edges and faces of the plates which attract each other and form flocs. A dispersing reagent such as sodium polyphosphate is added to separate the particles in the flocs (Von Wazar and Besmertruk, 1950). The clay water slurry is pumped from the blunger to settling boxes and screens to remove grit which is designated as the material coarser than 44 microns. After grit removal, the kaolin slurry is held in storage tanks at the plant site where it is analyzed and subsequently mixed with other batches to obtain the desired blend.

Fractionation

Kaolin slurries resulting from the primary processing at the mine are generally too coarse in size and it is therefore necessary to fractionate the slurry. A number of processes which accomplish the fractionation include settling tanks, hydroseparators, hydrocyclones or decanting centrifuges. Settling tanks and hydroseparators have been replaced by more efficient hydrocyclones or decanting centrifuges. Both of the latter processes depend on the increased sedimentation rate in a centrifugal field. The efficiency of separation of coarse and fine particles depends on the diameter of the cyclone, pressures and centrifugal acceleration. In the case of the decanting centrifuge, the separation depends on the bowl speed and the feed rate to the centrifuge.

Bleaching

Following fractionation, the kaolin may not have the brightness required for paper coating. Clays are often discolored by the presence of ancillary minerals such as mica, tourmaline and titaniferrous impurities, or by coatings of hydrated iron oxides. Various methods of chemical bleaching to improve the

brightness have been reported (Asdell and Mallary, 1971). Naturally occurring carbonaceous organic material adsorbed on the surfaces of kaolinite particles also contributes to light absorption and the impairment of brightness and color. Oxidative treatments involving the use of ozone (Allegrini et al., 1970), hydrogen peroxide (Bundy and Berberich, 1969), potassium permanganate (Duke, 1967) and sodium hypochlorite (Iannicelli et al., 1972), are used to remove the adsorbed layers of carbon to improve the brightness. The presence of hydrated iron oxides or oxyhydroxides that coat the kaolin particles may be either oxidized or reduced. The pink and yellow tinted kaolins are treated by lowering the pH to 3 with sulfuric acid which solubilizes the iron. A strong reducing agent, sodium hydrosulfite, is added which reduces the iron and keeps it in a soluble ferrous state which is removed during the dewatering/filtration step. It is also observed that kaolins occurring at greater depths under thicker overburden are gray in color and the iron is in a reduced state. These clays are treated initially by an oxidation process using ozone or sodium hypochlorite. Each type of kaolin may respond differently and if the bleaching results are not satisfactory alternative methods become necessary.

Magnetic separation

The process of magnetic separation is based on the differences among the magnetic susceptibilities of various mineral species. The colored impurities in the kaolin clay, e.g. anatase, rutile, hematite, mica and pyrite are freebly magnetic with susceptibilities typically as low as 10^{-6} cm^{-3}. When placed in a magnetic field they become magnetized in such a way as to either aid or oppose the applied field. The amount of magnetization induced on the particle depends on the mass and the magnetic susceptibility of the particle and the intensity of the applied magnetic field and this can be expressed as:

$$M = m\chi H$$

where M is the induced magnetization of the particle, m is the mass of the particle, χ is the specific magnetic susceptibility (per unit mass) and H is the magnetic field intensity (Norrgran and Ohrlich, 1988). High-intensity magnetic separation has met with considerable success in the beneficiation of industrial minerals (Frantz, 1936; Jones, 1955; Iannicelli et al., 1969). The relative attractability of various ferro and paramagnetic minerals is given in Table 4.

Magnetic separation has proven particularly successful with grades of kaolin that otherwise do not respond to conventional bleaching techniques. The development was a very significant process breakthrough in that it dramatically increased the reserves of kaolin in Georgia (Iannicelli, 1976). A major breakthrough in HGMS technology has recently been made with the first industrial application of superconducting HGMS. Using superconducting technology, extremely high magnetic fields may be achieved with virtually zero

TABLE 4

Relative attractability of various ferro and paramagnetic minerals (Norrgran and Orlich, 1988)

Mineral	Magnetic intensity (Gauss)	Attractability
Iron	500	Strong
Magnetite	1000	Strong
Pyrrhotite	1000	Strong
Franklinite	5000	Strong
Ilmenite	5000	Moderate
Chromite	5000	Moderate
Siderite	10,000	Moderate
Hematite	10,000	Moderate
Serpentine	10,000	Moderate
Olivine	10,000	Weak
Biotite	10,000	Weak
Bastinite	10,000	Weak
Garnet	10,000	Weak
Pyrolusite	15,000	Weak
Monazite	15,000	Weak
Goethite	15,000	Weak
Pyroxene	15,000	Feeble
Amphibole	18,000 and over	Feeble

power consumed by the magnet. Superconducting HGMS units are capable of generating magnetic fields up to 50 kG compared to a maximum of 20 kG for conventional water-cooled units and require only a fraction of the power.

Froth flotation

Froth flotation has been applied to process kaolins both from primary and secondary deposits. The application of flotation to the processing of primary kaolins was reported by Clark (1971). In the flotation process, the kaolinite and mica particles are separated and the resulting concentrates are suitable starting material for several commercial grades. The selective separation of kaolinite and feldspar by flotation is generally carried out in aqueous pulps with controlled pH values. Flotation using cationic or anionic surfactants as collectors under natural pH conditions with water soluble salts with trivalent metal ions as activators and depressors has been investigated in detail (Wolfgang et al., 1988). However, the specific gravity of the two minerals

(app. 2.58 g/cm^3) is nearly the same and the effectiveness of separation depends on the particle sizes of kaolinite and feldspar in the ultrafine particle range and the induced differences in surface properties. Flotation tests with kaolin-quartz and feldspar-quartz mixtures are also described in a paper by Trondel et al. (Trondel, 1986). Aqueous pulps containing hydrofluoric acid and hydrochloric acid are used with long chain aliphatic amines as collectors for separating kaolinite and feldspar from quartz. Direct flotation for separating kaolinite and feldspar in the ultrafine range below 30 microns was reported in a patent mentioned earlier (Von Tybinski et al., 1988).

Processing studies on improving the quality of kaolins obtained from Minnesota clays indicate that the crude material contains significant quantities of "free" silica which carries through in the final processed products (Prasad et al., 1991). The free silica content in this context refers to silica that is not associated with the kaolin mineral. The presence of free silica increases the abrasiveness of kaolin slurries and shortens the life of coating equipment besides affecting the quality of coated paper. The removal of "free" silica from kaolin by the application of direct cationic flotation was attempted on Minnesota clays at an acid pH of 2.5. The results indicate that essentially complete removal of "free" silica from a flotation feed of minus 65 mesh size containing 49% free silica was obtained using amine acetate as a collector (Prasad et al., 1991).

Application of flotation for secondary deposits is centered mainly on removing the titaniferous impurities which affect the brightness of the final product. The presence of titanium impurities are usually in the form of ultrafine particles less than 2 microns in diameter which are present in small amounts and are difficult to remove with direct flotation. The concept of carrier flotation, also known as ultraflotation or piggy-back flotation, was introduced by Green et al. (1961, 1962). The anatase impurity is removed from kaolin clay by flotation using coarse calcite particles as an auxiliary mineral for the separation of very fine minerals or slimes (Green and Duke, 1962). In this technique, the crude clay after degritting through 325 mesh screen and dispersion with sodium silicate (3.5 lb/T) was conditioned with ammonium sulfate (6 lb/T) and carrier particles (−325 mesh calcite). The carrier mineral particles pick up the micron sized anatase particles and are separated from the kaolin in the flotation process. The carrier particles are reactivated by a suitable collector such as tall oil. The mechanism of carrier flotation of clay was studied by Wang and Somasundaran (1980). Using the zeta potential measurement data on anatase, kaolinite and calcite at pH 10.1 and various sodium oleate concentrations, they concluded that coagulation is induced by hydrophobic interaction between the collector-coated minerals. The study also concluded that the major mechanism involved in carrier flotation is enhanced aggregation between fine anatase and coarse carrier particles under intense agitation.

Ozone treatment in the flotation process before floating colored impurities from the clay has been reported (Allegrini et al., 1970). The chemical analysis of the floated products show that beneficiated kaolin containing 0.42% TiO_2 without ozone treatment was reduced to 0.31% TiO_2 when ozone treatment was carried out before flotation. The brightness of the beneficiated clay was improved from 86.8% to 90.6%. Several researchers in the clay companies from southeastern states in the US have studied flotation for removing the titanium mineral impurities from kaolin with the following results:

– An improved method of froth flotation has been accomplished by forming an acidic aqueous slurry using conventional dispersing agents. Kaolin is separated from TiO_2 using a conventional collector or talloil at acidic pH. It is postulated that titanium mineral impurities are agglomerated or aggregated during the conditioning at the acidic pH and agglomeration facilitates subsequent removal of impurities. The process is not effective when the clay feed is too fine and is therefore limited to coarser applications (Smith, 1973).

– The use of low resin acid tall oil which acts as a collector and also as a controlled frothing agent has been suggested to remove the colored imurities from kaolin clay (Mallary, 1974).

– Mica, which is detrimental due to abrasiveness, may be separated by froth flotation in an alkaline pulp using a complex phosphate ester of a nonionic surfactant of the ethylene oxide-adduct type with aluminum salt as an activator for the mica (Yang, 1974). Another method of removing micaceous impurities, especially muscovite, is by stagewise froth flotation in an alkaline medium in the presence of a collector such as the phosphate ester of a nonionic surfactant of the ethylene oxide-adduct type (Yang, 1974).

– The use of complex phosphate esters or salts of a nonionic surface active compound are reported to be effective collectors for removing titanium impurities from kaolin clays in froth flotation to achieve an improved brightness of the clay (Nott, 1978).

– The combined use of aliphatic complex phosphate esters or salts of a nonionic surface active compound along with aliphatic fatty acid as a collector during flotation to remove titanium based impurities from kaolin clays has been reported (Bilimoria and May, 1984).

– The use of hydroxamate collectors in the flotation process by which kaolin clay can be cleaned of its colored impurities have also been investigated (Yoon and Hilderbrand, 1986). The process uses a collector, a compound or a mixture of compounds having a general formula:

$$R - \underset{\underset{O}{\|}}{C} - \underset{\underset{OM}{|}}{\overset{\overset{H}{|}}{N}}$$
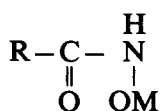
in which R is an alkyl, aryl or alkylaryl group having 4–28 and preferably 6–24 carbon atoms and M represents an alkali metal, an alkali earth metal or hydrogen. It is proposed that the collector adsorbs specifically on the colored mineral surfaces without requiring the use of activators.

Selective flocculation and coagulation

East Georgia clays do not respond to the flotation methods described above for the removal of titaniferous impurities due to the extremely fine particle size of kaolinite present in the crude (over 90% passing 2 μm). Several researchers have developed selective flocculation and coagulation processes (Attia, 1982).

The application of selective coagulation is described by Maynard et al. (1968). When a clay slip is overdispersed with excess of sodium hexametaphosphate and the suspension is left undisturbed, some of the titaniferrous impurities coagulate and settle out preferentially. This method was applied commercially for some time before being replaced by selective flocculation. Another example of selective coagulation was developed by Nott and Price (1978) in which a freshly prepared magnetite is added to the deflocculated kaolin slurry. The magnetite particles and titaniferous impurities mutually coagulate and are removed by magnetic separation. Selective coagulation of titaniferous impurities is also observed if alkali earth metal oxides or salts such as those of Ca, Ba, Mg and Sr are added into the kaolin slip at pH 8–11 (Sennet and Oliver, 1969).

The application of selective flocculation was reported by Maynard (1974) in which kaolinite is flocculated with a high molecular weight and strongly anionic polymer while leaving the titanium and iron contaminants in the suspension. Although the application of selective coagulation and flocculation processes have been proved to be highly successful for the separation of titaniferous impurities from East Georgia clays, they do have some limitations; these include the use of low pulp density, low kaolin recoveries due to the entrapment of the clay in the settled flocks and the deleterious effect of the polymer on the final product.

Special processes

Delamination

Kaolin is a material of naturally fine particle size. Individual kaolinite particles are often finer than two microns. Kaolinite is a flake shaped mineral with high aspect ratio (ratio of mean diameter to thickness) of approximately ten. Often the kaolinite plates are stacked together by cohesive forces. Many of the so-called coarse flakes are in effect stacks of fine particles which because of their greater mass are perceived as coarse particles. Several processes
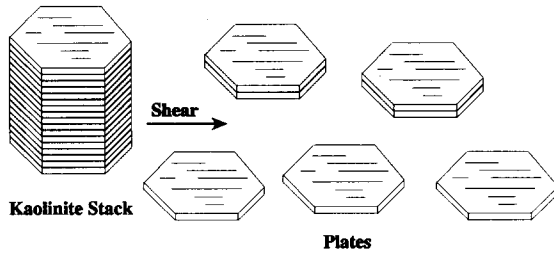
Fig. 8. Diagrammatic representation of delamination of a kaolinite stack (Murray, 1984).

TABLE 5

Properties of calcined kaolins (Murray, 1984)

Brightness GE	90–92
Opacity	85–87
Size: $+44 \mu$m	0.1 max
Less than 2 μm	90
Moisture	0.5% max
Specific gravity	2.4–2.5
Bulk density	15-19 lb/ft^3
Solids for fluid slurry	55%
Valley abrasion index	20

have been developed to delaminate these stacks to increase the yield of products meeting paper coating grade specifications. Delamination is a process where a large kaolinite stack is separated into several thin large diameter plates (Fig. 8). The process involves the high shear agitation of a kaolin slurry with pellets or beads at optimum pulp density. To achieve effective delamination, it is necessary to remove the bulk of less than two micron particles contained in the feed slurry and the coarse fraction is delaminated in the attrition mills with fine glass beads or plastic pellets as media. The brightness and whiteness of the delaminated kaolin are improved along with certain coating properties.

Calcination

Calcination is a process to produce special grade kaolin products. Two different grades of calcined kaolins are produced depending on the treatment temperature. Calcination at temperatures in the range 650–700°C removes the structural hydroxyl groups and the escaping water vapor produces a bulky product with enhanced resiliency and opacity which are desirable attributes for paper coating applications. Alternatively, improvement of brightness of 92–95% can be obtained by thermally heating kaolins at 1000–1050°C, even though the abrasiveness is increased (Guillet and Kriens, 1984). The properties of calcined kaolins are given in Table 5.

Surface treatment

Kaolin surfaces are chemically modified to produce hydrophobic and or-ganophillic characteristics. Generally, an ionic or a polar nonionic surfactant is used as a surface treating agent. Many manufacturers develop their own methods and the demand for specialty clays continue to grow rapidly throughout the world.

PHYSICAL AND CHEMICAL PROPERTIES

The physical properties of kaolins are very important with respect to their suitability for different applications and several authors have reviewed these relationships (Murray, 1979; Roskill, 1988; Bristow, 1989). Typical chemical analyses of kaolins from Georgia and England are presented in Table 6. The major variation of the chemical composition of Georgia kaolins (secondary deposits) is in the iron and titanium values while for English clays (primary deposits) the major differences are in the kaolin content and free silica values. The following are some of the important properties which should be determined in order to evaluate kaolin for different applications.

Particle size determination

The shape and size distribution of kaolin are important factors in controlling many other properties like brightness, viscosity, opacity, gloss, ceramic strength and shrinkage. These also affect the paper filling and paper coating properties such as the mechanical, optical and printing characteristics of a finished sheet of paper. The particle size is expressed as e.s.d. (equivalent spherical diameter) and is determined by sedimentation methods from a de-flocculated suspension of clay in water.

Cumulative particle size distribution curves for kaolins of different origin

TABLE 6

Typical chemical analysis (Murray, 1986)

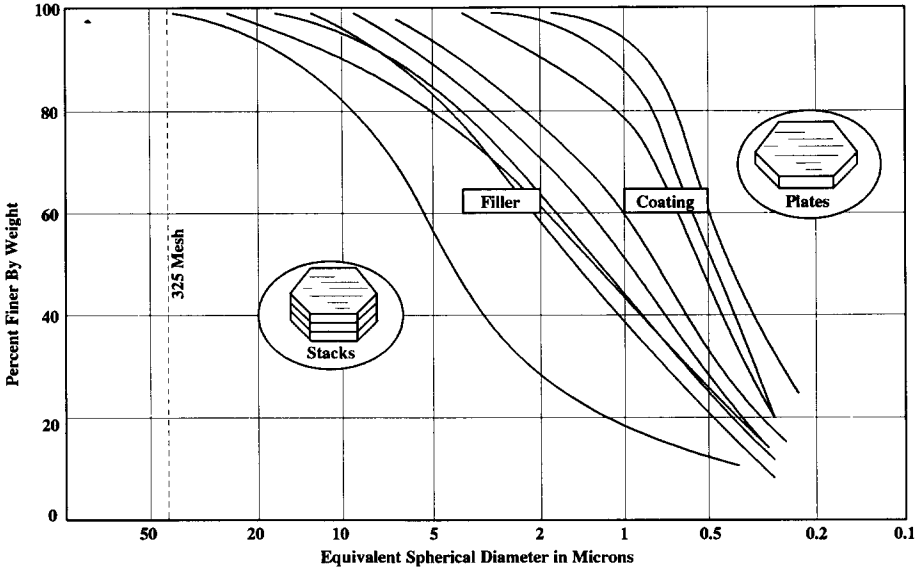| Component (%)	Middle Georgia (Cretaceous)	East Georgia (Tertiary)	English kaolin
SiO_2	45.30	44.00	46.77
Al_2O_3	38.38	39.50	37.79
Fe_2O_3	0.30	1.13	0.56
TiO_2	1.44	2.43	0.02
MgO	0.05	0.03	0.24
CaO	0.25	0.03	0.13
Na_2O	0.27	0.08	0.05
K_2O	0.04	0.06	1.49
L.O.I.	13.97	13.90	12.79

Fig. 9. Particle size distribution of coating and filler clays (Patterson and Murray, 1975).

are shown in Fig. 9. The 2 μm point is used as the commercial control point. The coarser kaolins are usually used as filler clays and the finer materials are normally used as coating products. The shape of the particle is closely related to its size, the filler clays usually contain an abundance of stacks and the coating clays a preponderance of thin plates (Olivier and Sennett, 1973).

Brightness and whiteness

The optical properties of kaolins are important in most commercial applications. They are usually interpreted in terms of absorption coefficient (k) and a scattering coefficient (s) by using the K–M theory (Kerker, 1969; Starr and Young, 1978). The absorption coefficient of a kaolin can be modified by chemical treatment or by beneficiation to remove colored impurities. The standard brightness values of kaolins are determined by measuring the diffuse reflectance of light of a particular wavelength generally 457 nm and is compared to a subsidiary standard which has been calibrated in a laboratory approved by the International Standards Organization (Windle and Gate, 1968). The presence of ancillary minerals such as micas, tourmaline and titaniferous impurities contribute substantially to the light absorption as do hydrated iron oxide coatings on the kaolinite particles (Robbins, 1972; Karicknoff and Bailey, 1973; Faye et al., 1974).

Rheology

The flow properties of kaolin slurries are very important both at low and high shear rates. The relation between bulk kaolin properties and coating slurry rheology is very complex (Beazley, 1972; Murray, 1973). The most important variables seem to be specific surface area, particle shape and particle packing. Ideally, a clay should have Newtonian flow properties, that is, it should have the same viscosity at different rates of shear. Unfortunately all clays are dilatant, which means that the viscosity of the slurries increases as the shear rate increases. Measurements of the viscosity of clay-water slurries are made at precise solids concentrations, normally 67% for delaminated clays and either 70 or 71% solids for ultrafine size clays.

The surface area of the clay controls the low shear viscosity at a given solids level. The coarse clays generally have lower Brookfield viscosities than fine clays. High shear rheology is more dependent on the particle shape. Most regular coating clays are controlled in the range of 300 cp or less at 20 rpm. At high shear rates as measured on a Hercules Viscometer, coating clays might range from 18 dynes cm $\times 10^5$ at 700 rpm bob speed to 3 or 4 dynes cm $\times 10^5$ at 1100 rpm bob speed (Welch and Dahlquist, 1984). In order for a coating clay slurry to be easily pumped, it should have a low viscosity at high shear rate. The delaminated clays, because of their shape and aspect ratio give higher high shear viscosity. The presence of contaminants and soluble salts has an adverse effect on rheology. Expanding minerals such as smectite which swell when they encounter water are favorable for drilling mud but unsuitable for aqueous slurries for paper coating. Processes have been developed to remove these minerals from crude clay by continuous centrifuging (Bronciner, 1971) or to modify them chemically. Alternatively, they can be converted to the nonswelling form by the addition of positively charged aluminum-hydroxy species to a suspension of kaolin and then raising the pH to about 7. Under these conditions the smectite layers become attached to each other and to the

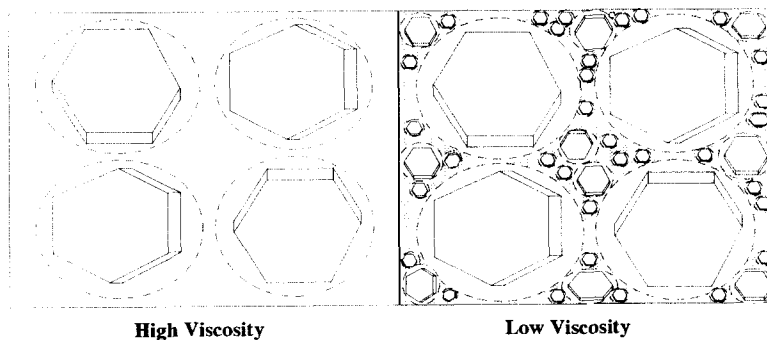**High Viscosity**   **Low Viscosity**

Fig. 10. Relationship between particle packing and viscosity.

kaolinite platelets (Adams, et al., 1977; Kunkle and Kohlman, 1978). Particle packing of kaolinite-water systems and its relationship with viscosity is shown in Fig. 10.

pH

The pH of coating clays range from 6.5 to 7.5. A high pH generally indicates the presence of soluble salts which can cause severe problems in many applications.

Screen residue

Screen residue indicates the presence of coarse particles that are retained on a 325 mesh screen. Quartz, mica and feldspar along with agglomerates of tightly bonded clay and the most common minerals are retained on the screen. This is an important property to be determined in both dry and wet processing of clay.

Sheet properties

Sheets of paper can be coated with kaolin and a binder following standard procedures outlined by the Technical Association of the Pulp and Paper Industry. In order to evaluate the application of a particular clay for coating purposes, the coated sheet must be conditioned, calendared, dried and many properties determined. The following properties are important (Murray, 1979)

Opacity: This is influenced by particle packing and is largely dependent on size and shape of the particle distribution. The presence of ultrafine particles in the range of 0.1 μm and less reduces the opacity (Bundy et al., 1965) and the optimum opacity or covering power of coating clay is developed by the presence of particle in the size range 0.3–1.5 μm (Maloney, 1939).

Gloss and smoothness: The presence of fine particles improves the gloss on the coated paper. Gloss is commonly related to high pore volume which reinforces the specular reflectance. Gloss is affected by the presence of ultrafine particles. Smoothness is not dependent on optical phenomena. However, fine, thin and small diameter particles are necessary for the ultimate development of smoothness.

Film strength: This is related to preferential adhesive migration into the substrate and to the preferred orientation of the kaolin particles. A well dispersed coating clay of fine particle size with low relative sediment volume will give the highest film strength.

Ink receptivity: This coating property differs for different grades of clays. Small diameter particles randomly oriented give excellent ink receptivity. The

presence of small quantities of smectite promotes ink receptivity but inhibits ink holdout due to its high surface area and strong sorptive capacity. In general, as the clay particle size decreases ink holdout increases.

Adhesive demand

Adhesives, such as starch or latex, bind the clay particles together and to the sheet of paper. Adhesive requirement is directly related to the surface area of the clay and must be carefully controlled since it also influences opacity, brightness, color and smoothness.

APPLICATIONS AND SPECIFICATIONS

Kaolin is an extremely useful mineral raw material. Its properties of white color, softness, small particle size and chemical inertness make it suitable for a number of different industrial applications. The desired properties of kaolin vary greatly in these applications. What might be a good clay for paper coating might not be an acceptable clay for use as filler in rubber. In this section the various kaolin uses are discussed with respect to grade specifications and the present market outlook.

Paper

The paper industry is by far the largest single user of kaolin. The paper industry accounted for 5,902,367, or 59.7%, of the 9,891,135 tons of kaolin sold or used by U.S. producers in 1988. Kaolin is used in paper to add a bright, glossy sheen as in magazines, to improve the ink receptiveness and smoothness of fibrous papers, and as a substitute for pulp. There are two basic types of clays used in paper; filler clays and coating clays.

Paper filling: Kaolin's principal function as a filler is to act as a substitute for the expensive pulpweb, thereby reducing costs. The actual loading level depends on the type of pulp used and the final product requirement. Kaolin also enjoys a principal advantage over its rival calcium carbonate by way of its chemical inertness to other paper making materials. In addition to reducing costs, kaolin filler enhances opacity, brightness and printability.

Paper coating: Paper, even if filled, is often unsuitable for modern printing unless properly coated. A filled paper may be considered as a sheet of interlaced pulp fibers, the interstices between which are partly filled by mineral particles. If such a paper is subjected to halftone printing, some of the tiny ink-coated dots on the printing blocks may fail to make contact with the paper

and an inferior print quality will result. Kaolin when used as a coating pigment, an application which requires some of the highest demands in terms of quality, endows the paper with a topographically smooth, bright surface, possessing good ink receptive properties and also good opacity. In addition, kaolin possesses rheological properties suitable for modern high-speed paper coating machines. A smooth surface is at prerequisite in producing high gloss paper with good printability.

Typical specifications for kaolin filler and coating grades are shown in Table 7. The suitability of kaolin as a filler or coating pigment relates principally to the physical properties with particle size, brightness and low abrasiveness being important for filler grade products and the addition of favorable rheological properties being required for good coating grade material.

Ceramics and refractories

One of the highest volume non-paper end-uses for kaolin is in the ceramics and refractory industries. Clay is an essential raw material in ceramic products, comprising 25–100% of the ceramic body. Kaolin, however, is only one of a number of clays used in this industry. Kaolin makes up an average of 25% of earthenware, 60% of porcelain, 20–30% of vitreous-china sanitary ware, and 20% of electrical porcelain and wall tiles. Refractory uses include linings

TABLE 7

Specifications of kaolins, coating and filler grades

Properties	Coating	Filler
mineralogical composition (%)		
Kaolinite	93–99	95–90
Mica	7–10	5–10
Others	Trace	3-Trace
Chemical composition (%)		
SiO_2	45–47	46–48
Al_2O_3	37–38	37–38
Fe_2O_3	0.5–1.0	0.5–1.0
TiO_2	0.5–1.3	0.04–1.5
LOI	13.9–14.3	12.3–13.7
Physical properties		
Particle size		
Less than 10 μm	100	85–97
Less than 2 μm	89–92	60–80
Brightness (%)	90–92	82–85
Viscosity (cps)	74	–

of open-hearth and blast furnaces in the steel industry, and in cement and ceramic films.

The uses of kaolin in the ceramics and refractory industries can be separated into two groups based on the importance of a white firing color to the end-use. White-firing colors are most important in the production of porcelains and wall and floor tiles, which are rather low volume industries in the US. White color is much less important in the production of refractories. Important properties for the use of kaolin in ceramics and refractories are green strength, dry strength, drying and firing shrinkage, refractory grade and fires color. Green strength and dry strength refer to the wet and dry strength of the clay in question. Kaolin has high green and dry strengths but is not very plastic when wet, which creates some problems when molding. Shrinkage is important to the ceramics manufacturer who usually wants a clay with low shrinkage. The general compositions and properties of kaolins used in ceramics are shown in Table 8.

Plastics, adhesives and fiberglass

The use of kaolin in the plastics, adhesives, and fiberglass industries is as a filler, to substitute for some of the resin, which is one of the most expensive materials in the manufacture of these products. The use of kaolin in these products can be separated into uses in which kaolin is important only in lowering raw material costs, and those in which the use of kaolin also gives secondary benefits based on its physical properties. The perfect filler for these industries would have a number of characteristics including low cost, good

TABLE 8

Compositions and properties of kaolins used in ceramics

Property	%
Chemical composition	
SiO_2	48–49
Al_2O_3	36.1–37
Fe_2O_3	0.6–1.0
TiO_2	0.02–0.10
L.O.I.	11.2–12.5
Particle size (μm)	
Less than 2 μm	40–70
Less than 10 μm	80–96
Less than 53 μm	100
Modulus of rupture at 110°C (kgf/cm^2)	10–31
Brightness	75–90

availability, low oil absorption, small and uniform particle size, good dispersion, low density, good chemical resistance, light color, and low free-moisture levels. Kaolin, while not having all of these properties, does have perhaps the best selection of properties of any filler available.

The use of kaolin in fiberglass is further facilitated by an unusual chemical characteristic. Kaolin remains chemically stable when heated to about 1000°F (537°C) at which point it begins to dehydroxylate losing its water. This process is usually not damaging to the product involved. At 1700°F (927°C) the dehydroxylation is complete, and the fiberglass melts and reacts with the kaolin to form a much higher melting glass. The sequential release of water and the fiberglass-kaolin fusion allow the product to retain its shape, making this combination of kaolin and fiberglass one of the ultimate materials for fire resistance.

Rubber

The use of kaolin in the rubber industry is very similar to the use in the fiberglass, plastics, and adhesives industries. The primary beneficial quality of kaolin for rubber is its low cost, since it is much cheaper than either natural rubber or man made elastomers. Kaolin stiffens the compound and reinforces it when cured. It is also used as a low-cost pigment. Kaolin is normally used in non-black rubber goods such as toys and floor mats, although there are exceptions, such as in dark-colored automotive products and parts subjected to low mechanical stress. Kaolin used in the rubber industry must have low amounts of coarse materials, very fine grain size, low amounts of impurities, a pH value of 4.5–5.5 and a constant specific gravity so that it can be formulated with the other ingredients of the rubber compound.

Paints

Kaolin is complementary as well as competitive with other pigments in the production of paints. Kaolin is used in the manufacture of paint as an extender white pigment. It increases the whiteness of a paint, but on its own will not add to the covering (hiding) power of a paint as will higher quality pigments such as titanium dioxide. When used with other pigments kaolin will increase their covering power because of its flat shape in which particles arrange themselves in an overlapping pattern. Kaolin is also valued for its hydrophilic characteristics, which make it a premier extender in latex paint. Because of its high oil absorption characteristics, however, kaolin reduces the gloss in gloss paints and thus its use is limited to no more than 10% by weight in this application.

Other uses

The chemical industry consumes significant quantities of kaolin. Production of aluminum compounds such as aluminum sulfate, phosphate and trichloride account for major applications for kaolin. Aluminum sulfate accounts for about half of the chemical production using kaolin.

Another rather significant volume and high value end-use of kaolin is in making synthetic zeolites, or "sieve minerals". Zeolites are mainly used in the petroleum industry as cracking catalysts that increase the area of a catalyst exposed to a reaction which in turn increases its effectiveness. Zeolites can also be used as molecular sieves which allow filtration at very fine sizes. High quality calcined clay is used in the production of catalysts.

A relatively small end-use for kaolin is in the agricultural sector. Kaolins are used by the agricultural industry in the manufacture of fertilizers, pesticides, and animal feed. Kaolin is used in feed and fertilizers mainly as a filler to bring the product to the correct consistency, in pesticides as dilutants to dilute the toxic portion of the pesticide, and as dispersants to make the pesticide easy to apply. Kaolin is especially suitable for this last end-use because of tis flat particle shape which improves adhesion of the pesticide to the sprayed plants.

Finally, a minor kaolin use, in terms of volume, is in the pharmaceutical industry. The highest purity kaolin is used here mainly as an inert filler, but it can also be an active ingredient, such as in upset stomach remedies and cosmetic muds.

MARKET OUTLOOK

Increased levels of advertising have led to a greater demand for the production of lightweight coated papers in the printing and writing sector and this is expected to keep the kaolin market steady at least in the short and medium terms. The European paper industry annually consumes 4.5 million tons of both filler and coating grade kaolin and in the US the consumption of coating grade amounts of 2.5 million tons. The consumption of coating grade kaolin in Europe has shown a substantial growth for the past 15 years due to the need for high quality paper. In contrast, the growth of kaolin filler remained static. The replacement of TiO_2 pigment in the paper and paint industries by calcined clays have increased the demand for calcined kaolin processing capacity in the USA. For the past few years the kaolin filler market in the paper industry has been threatened by the increasing use of precipitated calcium carbonate (PCC) as a filler by paper manufacturers (Griffiths, 1988; Hagemeyer, 1989).

The paper industry is currently undergoing a change in processing techniques which could significantly alter kaolin consumption. One of the most

important processes in the production of paper is "sizing", by which the fibers are made non-absorbent. Until about 30 years ago calcium carbonates could not be used as a paper filler due to the acid environment produced by the resin/alum sizing systems used (the function of which is to make the paper more water resistant). Calcium carbonate fillers can be protected from these acid conditions by coating with starch and a polymer but the resultant product is expensive. Rosin, which is a gum, is soluble in an alkaline environment, but insoluble in water and acid systems. Kaolin, being inert, is an ideal material in such an acid environment. Recently, however, synthetic sizing materials alternative to rosin have been introduced which can be used in neutral or alkaline environments. These new chemicals are claimed to produce stronger paper at a lower cost. The adoption of these alkaline papermaking techniques also makes possible the substitution of unprotected calcium carbonate fillers for kaolin. It is claimed that alkaline sizing increases sheet strength thereby allowing the use of harder, cheaper pulp, while at the same time being less energy-intensive than acid sizing. The overall substitution of kaolin by PCC has grown steadily in the last 15 years and now comprises about 30% of the coating grades and 20% for the filler grades in the European paper industry. In contrast, calcium carbonate has about 10% of the filling and coating market in the USA. The use of alkaline processes is steadily increasing in U.S. paper industries and is resulting in increased demand for calcium carbonate fillers. The onsite production of PCC at paper plants (satellite PCC plant) for the production of PCC slurry for a papermill utilizing the waste carbon dioxide from the papermill and a local source of lime has enabled the construction of several PCC plants near papermills in the USA. The prediction of growth in these operations results in bullish forecasts for calcium carbonate usage in paper in the coming years.

Kaolin is used in the paint industry as a substitute for more expensive TiO_2 which by virtue of its superior weathering qualities and opacity tends to be used for exterior applications. In the USA the market share of kaolin in the paint industry is roughly the same as that of talc and the replacement of expensive TiO_2 by calcined kaolin has forced some of the major kaolin producers in the USA to increase their production levels. It is estimated that the demand for calcined kaolin for use as a TiO_2 extender in the paint industry will continue into the mid 1990's. However PCC and other extenders may slow the growth of calcined kaolin.

The market share of kaolin as a filler in plastics and for PVC coatings on cables is substantially smaller than in the paint industry accounting for 10–15% for the U.S. market and even less, 5%, for Europe. Even so, this still translates into a substantial tonnage and further applications are continuously being sought especially in value added materials.

SUMMARY AND CONCLUSIONS

Kaolin processing and its applications as described in the present review have been classified under two broad deposit categories, primary and secondary. This distinction is on the basis of geological formation of these deposits. Primary deposits are formed by the alteration of crystalline rocks such as granite while secondary deposits are formed by the erosion of primary deposits. The world production of kaolin is dominated by the United States and United Kingdom and has shown a gradual increase from 22.7 million tons in 1984 to 28.3 million tons in 1988 and the consumption also followed the same trend.

During the past decade, significant developments have taken place in the processing of both primary and secondary deposits to produce high quality kaolins. The removal of iron and titanium bearing minerals for the improvement of brightness of the clay by the improved process methods such as HGMS, flotation, selective flocculation and coagulation were reviewed. Special process methods for obtaining a high value added kaolin with process techniques such as "delamination" and "calcination" have been discussed.

In order to meet the diverse and growing applications of kaolin to various industries such as paper, ceramics, plastics, rubber and paint both as filler and extender, product specifications have also diversified. The evolution of product specifications to meet market needs have been summarized.

The market outlook for kaolin during the 1990's was discussed and it is probable that research on special processing techniques on low quality clays to improve physical properties such as size, brightness, viscosity and abrasion, will increase in an attempt to upgrade these materials to coating clay grades and increase their areas of applications. It is reasonable to believe that small operations will be developed to produce filler clays which could be either upgraded in quality to achieve coating grade or for use in ceramic industries. This activity would be expected to help the development of various primary deposits of lower quality all over the world.

ACKNOWLEDGEMENTS

REFERENCES

Adams, R.W., Bidwell, J.I. and Jepson, W.B., 1977. British Patent 1,481,118.
Allegrini, A.P., Jacobs, D.A. and Mercade, V.V., 1980. U.S. Patent 3,503,499.

Asdell, B.K. and Mallary, M.B., 1971. U.S. Patent 3,587,922.

Attia, Y.A., 1982. Fine particle separation by selective flocculation. Sep. Sci. Technol., 17(3): 485–493.

Bates, T.F., 1964. Geology and mineralogy of the sedimentary kaolins of the south eastern United States – a review. Clays and Clay Minerals, Proc. 12th Nat. Conf. Pergamon, New York, pp. 177–194.

Beazley, K.M., 1972. Viscosity: concentration relationships in deflocculated kaolin suspensions. J. Coll. Interface Sci., 41: 105–115.

Bilimoria, B.M. and May, A.A., 1984. U.S. Patent 4,518,491.

Bristow, C.M., 1969. Kaolin deposits of the United Kingdom of Great Britain and Northern Ireland, Proc. Symp. I, Kaolin Deposits of the World – A Europe, 23rd Int. Geol. Congr., 1968, Vol. 15. Academia, Prague, pp. 275–288.

Bristow, C.M., 1977. A review of the evidence for the origin of kaolin deposits in S.W. England. In: Proc. 8th Int. Symp. and Meeting on Alunite. pp. 1–19.

Bristow, C.M., 1989. World kaolins – gneiss, exploitation and applications, Indus. Clays, Indus. Min. Special Rev., pp. 8–17.

Bronciner, R.E., 1971. British Patent 1,221,929.

Bundy, W.M. and Berberich, J.P., 1969. U.S. Patent 3,477,809.

Bundy, W.M., Johns W.D. and Murray, H.H., 1965. Interrelationships of physical and chemical properties of kaolinites. Tappi, 48(12): 688.

Clark, N.O., 1971. British Patent 1,224,877.

de Souza Santos, P. and de Souza Santos, H., 1972. Kaolin clays of Brazil. In: Miner. and Prop. Int. Clay Conf. (AIPEA), Madrid.

Duke, J.B., 1967. U.S. Patent, 3,353,668.

Faye, G.H., Manning, P.G., Gosselin, J.R and Rembly, R.J., 1974. The optical absorption spectra of Tourmaline–Importance of chargetransfer processes. Can. Mineral., 12: 370–380.

Frantz, S.G., 1936. U.S. Patent 2,074,085.

Gaskin, A.J., 1969. Kaolin deposits of Australia. In: Proc. of Symp. I, Kaolin Deposits of the World – B: Overseas Countries, 23rd Int. Geol. Congr., 1968, Vol. 16. Academia, Prague, pp. 25–32.

Green, E.W., Duke, J.B. and Hunter, J.L., 1961. Froth flotation method, U.S. Patent 2,990,958.

Green, E.W. and Duke, J.B., 1962. Selective froth flotation of ultrafine minerals or slimes. Trans. Soc. Mining Eng./AIME, 223: 389–395.

J.B. Griffiths (Editor), 1988. Raw Materials for Pigments, Filers and Extenders. IM Consumer Survey, pp. 39–47, 58–69.

Guillet, G.R. and Kriens, J., 1984. Ontario and the mineral filler industry. Paper No. 5, Report on Industrial Mineral Section, Ministry of Natural Resources, Ontario, Canada.

Hagemeyer, R.W., 1989. Precipitated calcium carbonate – fillers for paint, paper and elastomers. SME Annual Meeting, Las Vegas, Feb. 27–March 1, 1989, Preprint No. 89–22.

Hill, B.F., 1988. The Weipa kaolin project. Austral. Bull. Proc., 293: 51–56.

Iannicelli, J., Millman, N. and Stone, W.J.D., 1969. U.S. Patent 3,471,011.

Iannicelli, J., Kunkle, A.C. and Maynard, R.N., 1972. U.S. Patent 3,661,515.

Iannicelli, J., 1976. New developments in magnetic separation. IEEE Trans. Magn., 12: 436–443.

Jepson, W.B., 1984. Kaolins: their properties and uses. Philos. Trans. R. Soc. London, A311: 411–432.

Jones, G.H., 1955. British Patent 768,451, 676,124.

Karicknoff, S.W. and Bailey, G.W., 1973. Clays. Clay Miner., 21: 59–70.

Kerker, M., 1969. Scattering of Light. Academic Press, New York, (1969).

Kerler, T.L., 1963. Environment and origin of the cretaceous kaolin deposits of Georgia and South Carolina. Georgia Miner. Newslett., Georgia Geol. Survey, 16 (1–2): 3–11.

Kunkle, A.C. and Kollman, C.E., 1978. U.S. Patent 4,105,466.

Kuzvart, M., 1969. Kaolin deposits of Czechoslovakia, In: Proc. Symp. I, Kaolin Deposits of the World – A Europe, 23rd Int. Geol. Congr., 1968, Vol. 15. Academia, Prague, pp. 141–178.

Mallary, M.B., 1974. U.S. Patent 3,827,556.

Maloney, W.T., 1939. U.S. Patent 2,158,987.

Maynard, R.N., Skipper, B.R. and Millman, N., 1968. U.S. Patent 3,371,988.

Maynard, R.N., 1974. U.S. Patent 3,857,781.

Minnesota Department of Natural Resources, Division of Minerals, 1989. Market and economic considerations for kaolin clay. pp. 1–42.

Murray, H.H., 1973. Proc. Porcelain Enamel Inst., 35: 97.

Murray, H.H., 1979. Diagnostic tests for evaluation of kaolin physical properties. In: Proc. 10th Kaolin Symp., Budapest, IGCP, Project No. 23, pp. 67–76.

Murray, H.H., 1980. Major kaolin processing developments. Int. J. Miner. Proc., 7: 263–274.

Murray, H.H., 1984. Clay. Tappi Monograph Series, 38: 69–109.

Murray, H.H., 1986. Clays. In: Ullmann's Encyclopedia of Industrial CHemistry, Vol. A7, 5th ed. pp. 109–136.

Norrgran, D.A. and Orlich, J.N., 1988. Fundamentals of high intensity magnetic separation as applied to industrial minerals. Miner. Metall. Process., Feb. 1988: 1–11.

Nott, A.J., 1978. U.S. Patent 4,098,688.

Nott, A.J. and Price, W.M., 1978. U.S. Patent 4,087,004 and 4,125,460.

Olivier, J.P. and Sennett, P., 1973. Particle size and shape in the Georgia kaolins – II. Clays Clay Miner., 21: 403–412.

Patterson, S.M. and Murray, H.H., 1975. In: Industrial Minerals and Rocks, 4th ed. American Institute for Mining & Metallurgical and Petroleum Engineers, Inc., pp. 519–585.

Pemberton, M.J., 1983. The Processing of China clays. Indust. Chem.Bull., Dec. 1983, pp. 21–28.

Petrov, V.P., 1968. Kaolin deposits of the USSR. In: Proc. Symp. I, Kaolin Deposits of the World – A: Europe, 23rd Int. Geol. Congr., 1968, Vol. 15. Academia, Prague, pp. 289–319.

Prasad, M.S., Sheetharama, V.N. and Reid, K.J., 1991. Process development for value-added products from primary kaolin resources of Minnesota. SME Annual Meeting, February 25–28, 1991, Denver.

Robbins, D.W. and Streus, R.G.J., 1972. Charge transfer in ferromagnesian silicates: The polarized electronic spectra of tri-octahedral micas. Mineral. Mag., 38: 551–563.

Roskill, 1988. Economics of Kaolin. 5th ed., Roskill Information Services, London, pp. 1–216.

Sarkis, G.A., 1988. Clays. In: Minerals Yearbook. Vol. I, USBM, pp. 251–288.

Sennett, P. and Oliver, J.P., 1969. U.S. patent 3,446,348.

Smith, S.J., 1973. U.S. Patent 3,744,630.

Starr, R.E. and Young, R.H., 1978. Papercoating formulations. A study of limitations in the determination and use of the Kubelka–Munk constants. Tappi, 61: 78–80.

Störr, M., 1975. Kaolin deposits of GDR in the northern Region of the Bohemian massif. In: Guidebook, 5th Int. Kaolin Symp. Ernst-Horitz-Arndt Univ., Griefswald, p. 243.

Trondel, H.M., 1986. Flotation von kaolin. Erzmetall, 37: 149–152.

Von Rybinski, W. and Tesman, H. and Dobias, B., 1988. U.S. Patent 4,744,892.

Von Wazer, J.R. and Besmertruk, E., 1950. Action of phosphates on kaolin suspensions. J. Phys. Coll. Chem., 54: 89–106.

Wang, Y.H.C. and Somasundaran, P., 1980. A study of carrier flotation of clay. In: Fine Particles Processing, Vol. II, Chapter 57. SME of AIME, Denver, Co., pp. 1112–1128.

Welch, L. and Dahlquist, R., 1984. Kaolin clay in the paper industry. Intern. Rep., J.M. Huber Corporation, pp. 1–36.

Welch, L.J., 1989. Kaolin clay: examination of coating characteristics by grade end uses. Pulp & Paper, May 1989, pp. 103–107.

Wells, A.F., 1984. Structure of Kaolins. Structural Inorganic Chemistry. Clarendon Press, Oxford, 1028 pp.

Windle, W. and Gate, L.F., 1968. Brightness measurement. Tappi, 51: 545–551.

Yang, D.C., 1974a. U.S. Patent 3,804,243.

Yang, D.C., 1974b. U.S. Patent 3,873,488.

Yoon, R.H. and Hilderbrand, T.M., 1986. U.S. Patent 4,629,556.

Yoon, R.H. and Shi, J., 1986. Processing of kaolin clay. In: P. Somasundaran (Editor), Advances in Mineral Processing. SME of AIME, Denver, Co., pp. 366–379.