CLAYS, USES

1. Introduction

Clays are fine particle size materials comprised of clay minerals, which are basically hydrated aluminum silicates with associated alkali and alkaline earth elements. The clay mineral groups are kaolin, smectite, palygorskite-sepiolite, illite, chlorite, and mixed-layered clays. The properties of these clays are very different because of differences in their structure and composition. All are extremely fine and contain non-clay minerals such as quartz, feldspar, mica, calcite, dolomite, opal CT, and minor heavy minerals including ilmenite, rutile, anatase, tourmaline, zircon, kyanite, and other detrital minerals. The mineral content can be determined using X-ray diffraction techniques. Each group of clay minerals has very different applications because of differences in their physical and chemical properties.

The structure and composition of kaolins, smectites, and palygorskite-sepiolite are very different even though each has silica tetrahedral and alumina octahedral sheets as their basic building blocks. The arrangement and composition of the octahedral and tetrahedral sheets account for most of the major and minor differences in the physical and chemical properties of those clay minerals and thus on their ultimate application. Also important are the type and amount of non-clay minerals that are present. A brief summary of some of the important characteristics and properties of kaolins, smectites, and palygorskite are summarized in Table 1.

The particle size, shape, and distribution are physical properties that are intimately related to the applications of the clay minerals. Other important

Table 1. **Some Important Properties of Clay Minerals that Relate to Their Application**

Kaolin	Smectite	Palygorskite
1:1 layer	2:1 layer	2:1 layer inverted
white or near white	tan, olive green, gray or white	light tan or gray
little substitution	octahedral and tetrahedral substitution	octahedral substitution
minimal layer charge	high layer charge	moderate layer charge
low base exchange capacity	high base exchange capacity	moderate base exchange capacity
pseudohexagonal flakes	thin flakes and laths	elongate particles
low surface area	very high surface area	high surface area
very low absorption capacity	high absorption capacity	high absorption capacity
low viscosity	very high viscosity	high viscosity

properties are surface chemistry, area, and charge. These along with color and brightness affect many properties including low and high shear viscosity; absorption capacity and selectivity; plasticity; green, dry, and fired strength; casting rate; permeability; bond strength; and optical coating properties for paper and paint. In most every application the clays and clay minerals perform a function and are not just inert components in the system. Improved processing techniques, which have evolved over the past 40 years, have had a profound effect on the traditional and new applications. Statistical information supplied by the U.S. Geological Survey (formerly the U.S. Bureau of Mines) classifies clays into six groups: kaolin, ball clay, fireclay, bentonite, Fuller's earth, and common clay and shales. Because kaolins, eg, spill over in the figures for ball clay and fireclay and Fuller's earth includes attapulgite (palygorskite) and calcium montomorillonite, it is difficult to get correct tonnage and monetary values for the clay mineral types.

The name palygorskite and attapulgite are synonymous. The International Nomenclature Committee (INC) favors palygorskite because it predates the name attapulgite; however, attapulgite is so well ingrained in commercial literature and usage that industry continues to use the name attapulgite. The term Fuller's earth is used for any fine-grained material that is absorbent and is a naturally active bleaching earth. The origin of the term goes back to when earthy material was used in cleansing and fulling wool, thereby removing lanolin and dirt and thus the name Fuller's earth (1). Both palygorskite (attapulgite) and calcium bentonite are classified in the Government statistics as Fuller's earth.

The discussion of uses will be grouped using the following headings; kaolins, smectites, palygorskite-sepiolite, and common clays.

2. Kaolins

As mentioned in the article on Clays, Survey (see CLAYS, SURVEY) kaolin is a group mineral name for kaolinite, dickite, nacrite, and halloysite. The most common mineral in the kaolin group is kaolinite. It's physical and chemical properties and applications are discussed in this section. The uses are governed by several factors including the geological conditions under which the kaolin formed, the mineralogical composition of the kaolin deposit, and the physical and chemical properties of the kaolinite. Kaolin deposits can be sedimentary, residual or hydrothermal (2) and in almost every instance the kaolin has different properties and thus must be fully tested and evaluated to determine its utilization. Sedimentary kaolins are called secondary deposits and residual or hydrothermal kaolins are called primary deposits.

The occurrences of kaolin are numerous but commercially useable deposits are few in number. The best known and most highly utilized deposits are the primary hydrothermal kaolins in the Cornwall area of southwestern England, the secondary kaolins in Georgia and South Carolina in the United States, and the Jari and Capim kaolin deposits in the lower Amazon region of Brazil (3). Other important kaolin deposits that are regionally utilized, are the primary kaolin deposits in the Czech Republic (4); the primary kaolin deposits in Caminau and Kemmlitz in eastern Germany (5) and the secondary kaolins in Bavaria near Hirschau Germany (6); in Spain a primary kaolin near Galicia and a secondary kaolinitic sand in the state of Guadalajara (7); and a large primary kaolin deposit near Proyanoski in Ukraine (8). Other kaolin deposits used locally are located in Argentina, Australia, Brazil, China, Chile, Egypt, Indonesia, India, Korea, Mexico, Portugal, Tanzania, South Africa, Suriname, and Venezuela (3).

Kaolins are fine in particle size and are hydrophilic. With a small amount of chemical dispersant kaolin will easily disperse in water. The particle shape of kaolinite is important for many applications. The thin pseudohexagonal plates orient on coated surfaces such as on paper or in paint because of their two-dimensional nature (Fig. 1). Kaolin is one of the most versatile industrial minerals (Table 2) because it

1. It is chemically inert over a wide pH range (4–9).
2. It is white or near white in color.

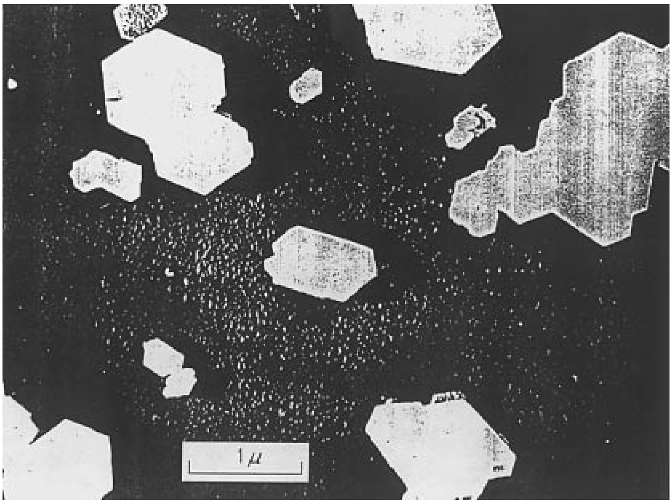

Fig. 1. Electron micrograph of platy kaolinite particles.

Table 2. **Uses of Kaolin**

paper coating
paper filling
extender in paint
ceramic raw material
filler in rubber
filler in plastics
extender in ink
petroleum
fiberglass
foundry bond
dessicants
cement
pencil leads
adhesives
tanning leather
pharmaceuticals
enamels
pastes and glues
insecticides
medicines
sizing
textiles
food additives
bleaching
fertilizers
plaster
filter aids
cosmetics
crayons
detergents
roofing granules
linoleum
polishing compounds

3. It has good covering or hiding power when used as a pigment or extender in coatings.
4. It is soft and nonabrasive.
5. It is fine in particle size.
6. It is plastic, refractory, and fires to a white or near white color.
7. It has low conductivity of both heat and electricity.
8. It is hydrophilic and disperses readily in water.
9. Some kaolins have a very low viscosity and flow readily at 70% solids.
10. It is relatively low in cost.

2.1. Ceramic Products. A large proportion of the annual production of ball clay and fireclay and a large amount of kaolin are used in the manufacture of ceramic products. Ball clays, which are fine particle size kaolinitic clays, are used as a raw material in whiteware, sanitaryware and tile. These clays are plastic, have high green, dry, and fired strength, are relatively low in shrinkage, fire white or near white, and have good casting qualities for sanitaryware. Fireclays are used in the manufacture of refractories because of their high melting point and low shrinkage. A special type of fireclay is the high alumina clays and flint clays found in Missouri (9), Kentucky (10), and Australia (11). Flint clays are very dense and brittle and are essentially pure, extremely fine-grained kaolinite. Another use for the high alumina clays and kaolins is to calcine them at high temperature (1300°C) to produce refractory grog. The grog is used in the refractory mix to reduce shrinkage and increase the melting point of the refractory brick for molten glass and metal processing. Kaolins are widely used as an important ingredient in whiteware, tile, insulators, and sanitaryware. Relatively pure kaolins melt or fuse at a temperature of 1850°C. Kaolin is an important constituent in the manufacture of catalytic converters for automobiles because of it's plasticity, controlled shrinkage, and fired strength. Ball clays and kaolins are used as suspending material to carry the frits and coloring pigments in porcelain enamels so that the coating is uniform.

For refractory applications the pyrometric cone equivalent (PCE) is measured. The pyrometric cone measures the combined effects of temperature and time (12). The cones consist of a series of standardized unfired ceramic compositions molded into the shape of triangular pyramids. The sample of kaolin or ball clay is molded into the standard cone shape and is heated along with several standard cones so that its end point of fusion can be determined in terms of equivalent cone number. Refractory PCE values are 32–35.

Casting rate in the production of sanitaryware is important and fine-grained bodies cast more slowly than coarse ones. Viscosity of a slip must be carefully controlled because if it is too viscous the slip will not properly fill the mold or drain quickly. Therefore, viscosity of kaolins and ball clays is measured and controlled on shipments used in the casting process.

2.2. Paper.

The paper industry is the largest consumer of wet processed kaolin (see CLAYS, SURVEY). Kaolin used in the paper industry has two main uses, as a filler where the kaolin is mixed with the pulp fibers and as a coating where the kaolin is mixed with water, adhesives, and various additives and coated onto the surface of the paper. The largest use of kaolin is for coating paper. As a filler kaolin improves the opacity of the paper sheet, imparts smoothness to the surface, and replaces some of the more expensive pulp fibers. In coatings on the paper sheet, the kaolin imparts opacity, brightness, a glossy finish, smoothness, and improved printing quality. For example, a coated sheet of paper in National Geographic Magazine contains ~35% by weight kaolinite.

Kaolins used by the paper industry are of three types based upon the type of processing: air-floated, water washed, and calcined (see CLAYS, SURVEY). Water washed kaolins are of higher value than air-floated because the more elaborate processing results in more uniform and higher quality products. Calcined kaolins are heated to ~1000°C, which converts the kaolinite to mullite and opal CT and results in significantly higher brightness and opacity (13). Titanium dioxide is a prime pigment that has very high brightness and opacity but is expensive. Calcined kaolin, which is much less costly, can replace a majority of the titanium dioxide with little or no loss in brightness or opacity. Calcined kaolins have brightnesses ranging between 92 and 95%.

The properties of kaolin that make it useful in the paper industry are brightness, viscosity, and particle size and shape. Air-floated kaolins are at the lower end of the brightness range for fillers used by the paper industry. The air-floated fillers are coarser and have a brightness range of 80–84%. The particle size is in the range of 50–70% finer than 2 m. They are low in cost but their uniformity and quality is not as high as the water washed filler clays. Improvement in paper sheet brightness and opacity results from the addition of kaolin filler clays. The best results are obtained using calcined clay followed by water washed kaolins and then air-floated kaolin (Fig. 2).

Coating grade kaolins are produced using a wet process (see CLAYS, SURVEY). The important qualities that are controlled for producing a finished product are brightness, particle size, and viscosity. Table 3 shows the typical kaolin grades produced in Georgia for the paper industry. The largest sources for coating grade kaolins are Georgia in the United States, Cornwall in southwestern England, and the lower Amazon region of Brazil (see CLAYS, SURVEY). Kaolins from each area have different characteristics that can be traced to the geologic origin of the crude kaolin. In the Southeastern United States, the kaolins of Cretaceous age that are mined in middle Georgia are relatively coarse and those of Tertiary age in east Georgia are very fine in particle size. In Brazil, the Jari kaolin is very fine and the Capim kaolin is much coarser. Both the Georgia

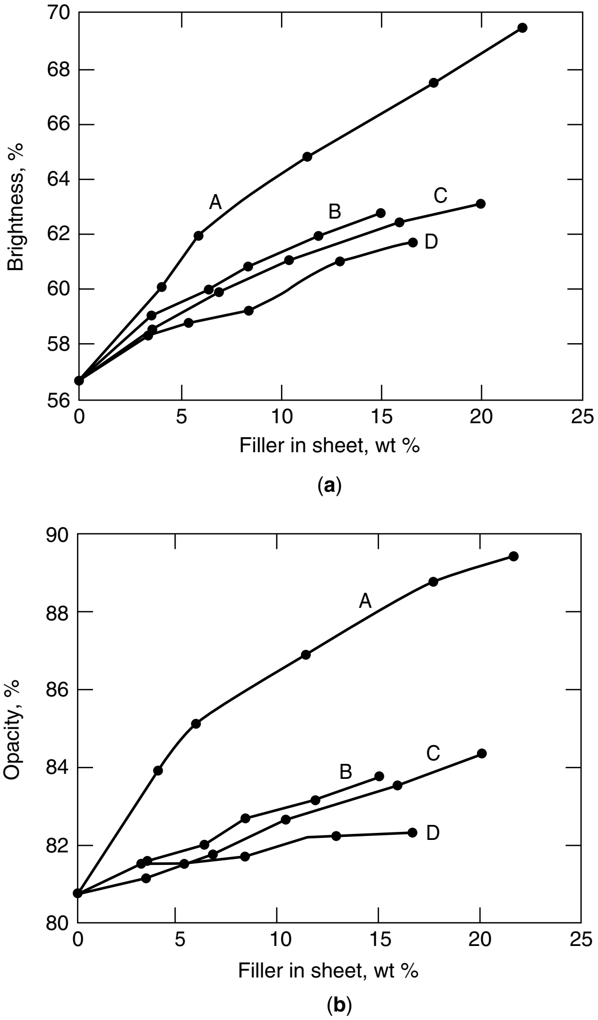

Fig. 2. (**a**) Brightness improvement obtained by use of kaolin as a filler in paper (**b**) Opacity improvement obtained as pulp fibers are replaced with various kaolins. A, calcined clay; B, high brightness No. 1 clay; C, coarse particle water washed filler clay; and D, air-floated kaolin.

and Brazil kaolins are sedimentary and the English kaolin is primary, which gives it somewhat different characteristics.

Viscosity of the kaolin coating grade clays is a very important characteristic. The viscosity is measured at 70% solids. Two types of viscosity are measured, the Brookfield low shear viscosity and the Hercules high shear viscosity, both of which are important to the paper coater. The low shear viscosity relates to the pumpability and flow from a tank car through the coating preparation facility, and the Hercules high shear viscosity relates to runnability on the coating machine (14).

Other properties of kaolin coating clays that are important to the paper coater are dispersion, opacity, gloss and smoothness, adhesive demand, film

Table 3. **Grades, Particle Size, and Brightness of Georgia Kaolins for Paper Coating**

Grade	Particle size	Brightness
No. 3	73% < 2 μm	85–86.5
No. 2	80–82% < 2 μm	85.5–87.0
No. 1	90–92% < 2 μm	87.0–88.0
fine No. 1	95% <2 μm	86.0–87.5
delaminated	80% <2 μm	88.0–90.0
high brightness No. 2	80% <2 μm	90–91
high brightness No. 1	92% <2 μm	90–91
high brightness fine No. 1	95% <2 μm	90–92

strength, and ink receptivity. In order to obtain the maximum efficiency of a coating clay, the individual clay particles must be completely dispersed. Kaolinite is easily dispersed because it is hydrophilic. Opacity is strongly influenced by particle packing that is dependent on particle size and shape and particle size distribution (14). Gloss and smoothness are related to particle size and shape. Superior gloss is obtained with kaolins of fine particle size. Coatings made with thin plates of kaolinite that orient parallel to the paper sheet have better smoothness. Adhesive demand is related to surface area. Finer particle size kaolins require slightly higher amounts of adhesive. The amount of adhesive in the coating affects the opacity, brightness, color, and smoothness and so the least amount of adhesive that will bond the coating to the base sheet is advantageous. Film strength or pick strength is related to preferential adhesive migration into the substrate and to the preferred orientation of the kaolinite particles (15). Maximum film strength is attained with well oriented dense films. If pick occurs within the coating layer it is generally caused by insufficient adhesive, excessive adhesive migration, or poorly dispersed kaolinite. Ink receptivity is related to film permeability as influenced by void volume. Small diameter particles, randomly oriented, give excellent ink receptivity. Uniform absorbency of the ink is particularly important or the printed surface may have a mottled appearance. The interrelationship of the kaolinite and adhesive is a major control over ink receptivity and holdout (16).

Particle size is a very important parameter to control in coating grade kaolins (Fig. 3). Table 4 shows how coated paper properties change with particle size. In general, finer particle kaolins give higher gloss, opacity, and brightness. For extremely fine kaolins, however, opacity and brightness may decrease as a result of the loss of light scattering power.

Testing. The Technical Association of the Pulp and Paper Industry (TAPPI) publishes test methods that are used by both kaolin suppliers and the paper industry. These include tests for viscosity, viscosity stability, brightness, pH, particle size distribution, moisture content, screen residue, and abrasion (17). These test procedures are continually upgraded and are monitored by a TAPPI committee. Other tests that relate to use properties are carried out by the kaolin suppliers.

Bentonite (Smectite). Because of its very fine particle size and high sorption capacity, smectite is sometimes used in the deinking process to recover cellulose fibers. The deinking process generally involves heating the paper in a

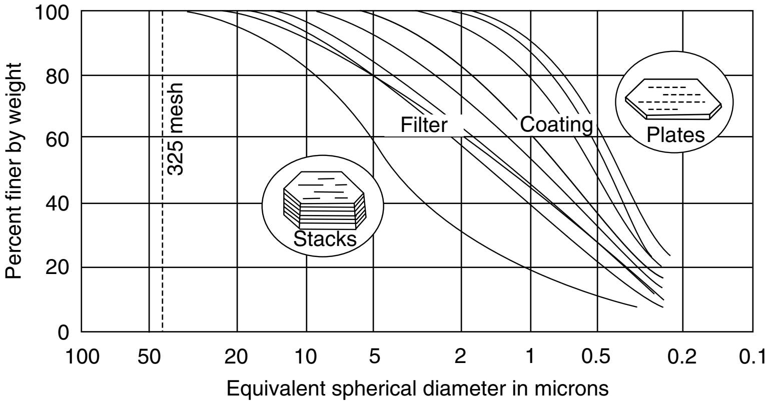

Fig. 3. Particle size distribution of coating and filler clays.

caustic soda solution to break down the ink in order to free the ink pigment. A detergent is then added to release the pigment from the paper fibers. Smectite is added, which serves to disperse the pigment particles and adsorb them. Washing then removes the smectite carrying with it the ink pigment. Sodium montmorillonite is the preferred smectite for this application. Smectite, usually sodium montmorillonite, is also used in papermaking to prevent agglomeration of pitches, tars, waxes, and resinous materials. The addition of 0.5% sodium montmorillonite, based on the dry weight of the paper stock, will prevent agglomerates so that the globules will not stick to screens, machine wires, press rolls, etc, and cause defects in the paper.

In some instances, small quantities of sodium montmorillonite have been used to increase the low shear viscosity in certain coating color formulations. One percent or less will significantly increase the low shear viscosity at 10 Rpm, particularly in high solids coating colors. Also, the addition may lower the high shear viscosity into the low dyne region. The addition of sodium montmorillonite will also retain water in the coating layer and slow down its migration into the paper substrate. The presence of small quantities of smectite, because of its high surface area and strong sorptive capacity, promotes ink receptivity and inhibits ink holdout (16). The amount of smectite used by the paper industry is very small.

Palygorskite (Attapulgite). Palygorskite is sometimes used in specialty copy papers particularly in non-carbon required (NCR) papers to make multiple

Table 4. **Effect of Particle Size on Coated Sheet Properties**

Particle size		Coated sheet properties		
% <2 μm	Median, μm	Gloss	Brightness %	Opacity %
35	3.80	25	71.6	84.2
54	1.80	31	72.2	84.6
78	0.75	33	72.6	84.6
85	0.68	39	72.7	84.7
96	0.46	45	72.6	84.7

copies without carbon paper. The receiving surface of the copy sheet is coated with paylgorskite. The lower or transfer surface is coated with adhesive containing minute encapsulated droplets of dyestuffs. Writing or typing breaks the dyestuff gobules so that they penetrate the palygorskite coated layer that catalyzes their conversion into a colored letter or mark. This use is decreasing because of the ever increasing use of computers and copy machines.

2.3. Paint. Clays are widely used in both water and oil-based paints. In this application, clays perform several important functions. They extend the much higher cost titanium dioxide opacifying pigment, control viscosity so as to prevent pigments from settling during storage, provide thixotropy so that the paint is easily applied yet does not sag or run after application, improve gloss, promote film strength, and aid in tint retention.

Kaolin. Kaolins used in paints are very similar to those used in paper but are processed differently so as to enhance the properties of the paint. The conductivity of the kaolin is measured so as to control the amount of soluble salts present. Soluble salts are detrimental to some of the ingredients that make up the paint formulation so the kaolin is well washed to remove the soluble salts. Both hydrous and calcined kaolins are used in paint formulations. Calcined kaolins are used to extend titanium dioxide with little or no loss of hiding power.

Surface treatments of the hydrophilic kaolin are sometimes used to enhance the oleophilic properties for use in oil-based paints. For certain paint applications the Hegman fineness of grind test specification is important. This test measures the degree of dispersion. Some paint customers specify that a pigment or extender must be finer than a particular Hegman number. Kaolin in water-based paints may constitute as much as 30% of the pigment.

Bentonite. Sodium montmorillonite is used as a viscosity control and suspending agent in water-based paints. Because of their fine particle size they do not contribute to opacity so are not used as an extender. The smectites used for paint are processed to remove oversize particles. Oganoclays that are organic treated sodium montmorillonite are widely used as suspending and antisag agents in oil-based paints. The most common surface treatment chemical is hydrogenated tallow quaternary amine. Whiter grades are preferred so as to contribute as little as possible to the color of the finished paint. The American Society for Testing and Materials (ASTM) provides procedures and specifications for paint raw materials (18).

Palygorskite (Attapulgite). Attapulgite is used as a viscosity control and suspending agent. Because of the elongate particle shape and surface properties of attapulgite it does not flocculate in the presence of electrolytes. The physical hindrance to settling because of its particle shape makes it a preferred thickening and suspending agent. Fine particle size attapulgite with no oversize coarse particles is required for this use.

2.4. Plastics and Rubber. Kaolin is the only clay used in plastics and rubber as extenders and functional fillers (19). Various grades are produced specifically for use by the plastics and rubber industries: Table 5 lists the more important kaolin grades used as components in plastics and rubber. More than half the tonnage used is air-floated kaolin, which is used extensively by the rubber industry.

Table 5. **Kaolin Grades for Polymer Applications**

Kaolin type	Brightness %	Median particle size, μm	Uses	Relative cost[a]
		Air floated		
regular	73–76	0.2–1.0	rubber	L
surface treated	73–76	0.2–1.0	rubber	M
		Water washed		
coarse particle	79–82	4.8	thermosets	M
intermediate	85–87	0.6	PVC[b]	M
fine	86–88	0.4	PVC[b]	M
		Calcined		
meta kaolin	84–86	1.4	PVC[b] insulation	H
high temperature	90–92	1.4	engineering plastics, PVC	H
surface treated	90–92	1.4	engineering plastics, PVC	Ht

[a] L = low; M = moderate; H = high; Ht = highest.
[b] Poly (vinyl chloride) = PVC.

As seen from Table 5, the kaolins used are air-floated, water-washed, and calcined. The calcined meta-kaolin is used almost exclusively in PVC wire insulation because it enhances the electrical resistivity of the wire coating.

Surface treated clays shown in Table 5 are an important group of clays used in polymers. These are made from calcined kaolin, air-floated kaolin, and water-washed kaolin. Several types of chemical compounds are used to convert the hydrophilic surface of the kaolinite into an oleophilic surface that is more compatible with polymers (19). Silane treatment of calcined and hydrous kaolins raises the cost significantly, but the improvement in polymer properties justifies the extra cost. The data in Table 6 shows the effect on physical properties of adding 40% of an aminosilane treated calcined kaolin to a nylon compound. The improvement in strength properties and the marked increase in heat deflection temperature are noteworthy.

Properties that make kaolin useful in the plastics and rubber industries are color, particle size and shape, and viscosity. Clays used in the polymers industry

Table 6. **Effect of Clay Filler on Nylon Properties**[a,b]

Property	Unfilled	Filled
tensile strength, MPa[b]	82	97
tensile elongation, %	60	8
tensile modulus, MPa[b]	2900	6200
flexural strength, MPa[b]	97	159
flexural modulus, MPa[b]	2900	6200
izod impact, J/m	0.020	0.017
deflection temp. at 1.82 MPa, C	77	204

[a] Data for 40% loading of aminosilane-treated calcined kaolin in nylon-6,6.
[b] To convert MPa to psi, mutiply by 145.

are required to be white or nearly so except for applications in black compounds. The refractive index of kaolin closely matches that of most polymer compounds so kaolins contribute little to opacity and color. Particle size and shape are important because large particles may give a rougher than desired surface whereas small particles are more effective in increasing polymer hardness. Particles having a high aspect ratio, ie, platy particles, usually give greater reinforcement than more equant particles. The incorporation of a kaolin filler into a polymer may strongly affect the viscosity of the compound, especially when fine particle size clays are added. In general, finer particle clays increase viscosity more than coarse particle clays. Depending on the polymer and its application, increased viscosity may be desirable or undesirable. For example, a polymer that is too fluid to handle by some processing equipment may be rendered sufficiently viscous to be utilized by the incorporation of a kaolin filler. Surface treated kaolins because of the more oleophilic surface, give lower viscosity compounds than do untreated kaolins. Also the surface treatments generally permit much higher loading in the polymer.

Testing. Various test methods are provided by ASTM (18). These include pigment tests such as chemical analyses, presence of oversize particles, oil absorption, particle size distribution, degree of dispersion, presence of soluble components, etc. Numerous tests are also given by ASTM to determine the properties of filled and unfilled polymers. These include such properties as impact resistance, stiffness, viscosity, tear resistance, hardness, color, and electrical resistivity.

2.5. Halloysite. Halloysite is a member of the kaolin group and has a layer of water between the unit layers (see CLAYS, SURVEY). This causes the shape to be elongate tubes, which greatly changes its applications. Halloysite is produced in New Zealand and is used primarily in whiteware ceramics as an additive where it adds dry and fired strength and makes the dinnerware more translucent. Halloysite is also used as a filler in paper and as a raw material to make synthetic zeolites.

As shown in Table 2, kaolin has a large number of uses. The uses for paper, ceramics, paint, plastics, and rubber have been discussed and the remaining miscellaneous uses will be discussed in the following sections.

2.6. Inks. Kaolins are a common ingredient in a large variety of printing inks. In addition to extending the more expensive polymers present, kaolin also contributes to improved color intensity, limits ink penetration into the paper, controls rheology, and improves adhesion. Kaolin for use in inks must usually be as white as possible and free from oversize particles. Surface treated kaolins are used in oil-based inks and also to improve color acceptance.

2.7. Cracking Catalysts. Kaolins are used as a raw material to make zeolites and aluminum silicates for use as catalysts in the refining of petroleum (20). Several thousand tons are used annually for this purpose. Halloysite has also been used in the manufacture of petroleum cracking catalysts.

2.8. Chemical Raw Materials. Several tens of thousands tons annually of air-floated kaolin are used as a chemical raw materials to make fiberglass. A low iron and titanium content is required for this application. Kaolin is used in some cement plants to whiten the color, to provide silica and alumina for the cement reactions, and increase cement strength. In the production of

Portland cement, the limestone and kaolin react when heated to ~1600°C to form a calcium alumino—silica clinker. The clinker is pulverized and when water and aggregate are added, concrete is formed (21). Kaolin is used as a raw material for producing zeolites, which are an ingredient in detergents.

2.9. Special Fillers.

Kaolin is used as a filler largely because of its fine particle size and white color in adhesives, pastes and glue, crayons, and linoleum (22).

2.10. Pencil Leads.

Kaolin is used as an additive to graphite in making pencil leads (23). The plasticity and fine particle size are useful in extruding the graphite-kaolin mixture, and when the lead is fired, the kaolin gives the lead strength or hardness. The hardness of the lead is controlled by the percentage of kaolin in the graphite. A2H pencil contains a small amount of kaolin and the hardness increases in 3H, 4H, and 5H pencils by adding additional amounts of kaolin.

2.11. Suspensions and Diluents.

Kaolins are used as suspending agents in pharmaceuticals, cosmetics, enamels, and medicines. A good example is kaopectate, which is a suspension of pectin in a kaolin slurry. Some pills use kaolin as a diluent and binder in pressing pills. Very fine particle size kaolins are best for these applications.

2.12. Fertilizers, Dessicants, and Insecticides.

Kaolin is used as a carrier for certain insecticides and fertilizers and is used as a dessicant to promote flow when mixed with highly deliquescent materials. Some kaolin dessicants are coated with organic compounds to make them better flow agents.

2.13. Foundry Binders.

Some plastic, fine particle kaolins are used as a binder for sand to make high temperature resistant molds for special metals.

2.14. Roofing Granules and Polishing Compounds.

Roofing granules are produced by calcining coarse granular particles of white kaolin. Fine particle calcined kaolin with a top particle size of 3 μm is used in polishing compounds for automobiles, silver, copper, brass, and other metals. The hardness of calcined kaolin is ~6.5 on the Moh's scale. Because of its hardness and very fine particle size, it is an excellent polishing agent.

3. Smectites

Smectite is the group name for a number of clay minerals including sodium montmorillonite, calcium montmorillonite, saponite, nontronite, and hectorite (see CLAYS, SURVEY). The rocks in which the smectite minerals are dominant are called bentonites. Industrial quality bentonites are predominantly comprised of either sodium montmorillonite or calcium montmorillonite and to a much lesser extent, hectorite. Industrial nomenclature for these materials is sodium bentonite, calcium bentonite, and lithium bentonite. These smectite minerals and bentonites have significantly different physical properties, which dictate to a large degree their industrial uses.

The most widely used sodium bentonite in the world is located in Wyoming, South Dakota, and Montana. Important calcium bentonites are located in Mississippi and Texas in the United States, England, Germany, Italy, and Greece in Europe, South Africa, India, China, and Argentina.

Table 7. **Industrial Uses of Smectites**

- drilling mud
- foundry binders
- iron ore pelletizing
- cat litter
- sealants
- animal feed binders
- paint
- agricultural carriers
- nanoclays
- industrial oil absorbants
- bleaching clays
- catalysts
- detergents
- ceramics
- cosmetics
- dessicants
- crayons
- medical formulations
- beer and wine clarification
- suspension aids
- deinking on paper
- tape joint compounds
- emulsion stabilizers
- slurry trench excavation
- adhesives
- pharmaceuticals
- organoclays

The uses of smectites are shown in Table 7. The largest uses by far are for drilling muds, foundry binders, iron ore pelletizing, cat litter, and sealants.

Smectites are very fine in particle size and the particles are extremely thin, which gives the material a high surface area. Smectites and particularly sodium montmorillonite have a high base exchange capacity on the order of 75–100 meq/100 g of clay. Sodium montmorillonite has a high swelling capacity of 10–15 times its dry volume. These characteristics give smectites a high degree of absorbency for many materials, and when mixed with water, the high charge and fine particle size give the fluid a very high viscosity. These properties of smectites control the many industrial uses shown in Table 7, which are described in detail in the following paragraphs. Bentonite production in the United States is 4,500,000 tons annually and the world production is ~10,000,000 tons.

3.1. Drilling Mud. Sodium montmorillonite is the major constituent of the Western bentonite, which is a high swelling clay. This high swelling property makes it a necessary ingredient in freshwater drilling muds throughout the world. Commonly, this Western or Wyoming bentonite yields 100 barrels of 15 CP drilling mud per ton (24). Only 5% by weight of this high swelling bentonite are required to produce the high viscosity, thixotropic fluid with low filter cake permeability that is necessary to meet the American Petroleum Institute (API) drilling fluid specifications. Hectorite also makes an excellent drilling mud but because it is used for more value added products, hectorite is not used for this purpose. Some calcium montmorillonites can be treated with a sodium salt such as soda ash to make a drilling mud, but neither the viscosity nor the water loss properties are as good as that of the Wyoming sodium bentonites.

3.2. Foundry Binders. The molding sands used in foundries are comprised of high silica sand and ~5–8% bentonite. The bentonite provides bonding strength and plasticity. A small amount of tempering water is added to the mixture to make it plastic. This mixture of sand, clay, and water can then be molded around a pattern shape and be cohesive enough to maintain the proper shape after the pattern is removed and molten metal is poured into the mold. The important foundry properties are green compression strength, dry compression strength, hot strength, flowability, permeability, and durability. These properties vary greatly with the amount of tempering water (24). Both sodium and calcium bentonites are used as bonding clays. Calcium bentonite has a higher green strength, lower dry strength, lower hot strength, and better flowability than sodium bentonite. Blends of sodium and calcium bentonite are commonly used to gain the optimum properties from each.

3.3. Iron Ore Pelletizing. Sodium bentonites are used to pelletize iron ores (25). Finely pulverized ore concentrates are pelletized into marble-sized balls ~2.5cm in diameter for ease of shipping and to produce a superior furnace feed. Sodium bentonite constitutes ~0.5 wt% of the ore. The superior dry strength of the sodium bentonite makes it the preferred clay for pelletizing.

3.4. Cat Litter. Both calcium and sodium bentonites are used in making cat litter. Because of its high absorbance quality, calcium bentonite is crushed and sized into a granular product for use as cat box filler. Calcium bentonites from Mississippi, Georgia, Illinois, and Missouri are the major sources for making the granular cat litter. Over the past several years, a new product called clumping cat litter has emerged as a preferred litter. This is made by blending high swelling sodium bentonite and calcium bentonite granules. When liquid feline waste hits this blend of granules, the sodium bentonite swells and forms a hard clump, which is easy to remove from the litter box. This has now become the highest tonnage use of sodium bentonite.

3.5. Sealants. Sodium bentonites are used extensively for water impedance because of their high swelling capacity. The bentonite is used to impede the movement of water through earthen structures such as dams, to seal irrigation ditches, to prevent seepage of water from ponds and impounds, and to prevent water from entering basements of homes. Sodium bentonite is also used in barrier walls and liners in landfills and toxic waste dumps (26).

3.6. Slurry Trench Excavations. High swelling sodium bentonite is used in the slurry trench or diaphragm wall method of excavation in construction in areas of unconsolidated rocks and soils (27). In this method, the trench being excavated is filled with bentonite slurry and the earth material being excavated is moved through it. A thin filter cake on the walls of the excavation prevents loss of fluid and the hydrostatic head of the slurry prevents caving and running of loose soil. This makes costly shoring unnecessary. This technique is used extensively in Europe and is becoming popular in the United States.

3.7. Absorbents. Calcium bentonites are excellent absorbent clays. Small granules of the bentonite are prepared and used for absorbing pesticides and insecticides for protecting farm crops. The absorbed pesticide is less toxic to humans and allows for targeted emplacement. Another use is absorbing oil and grease spills in factories and gas stations. The oil or grease is absorbed on the clay granules, which are swept up and discarded. The oil-soaked granules do not present a fire hazard and also provide an anti-slip surface to an oily floor.

3.8. Suspension Aids. Sodium bentonite is used as suspension aids in cosmetics, medical formulations, pharmaceuticals, and for use in the distribution of suspension fertilizers, which is becoming a popular method to spread fertilizer on farm crops.

3.9. Bleaching Clays. Calcium bentonites are treated with sulfuric and/or hydrochloric acid to remove ions from the surface and from the octahedral layer to increase the charge on the clay particle. These acid activated clays are widely used to decolorize mineral, vegetable, and animal oils. Almost all edible oils are bleached using acid activated clays (28).

3.10. Organoclays. Sodium montmorillonite and hectorite are processed so that the exchangeable sodium ions are replaced with alkylammonium cations to produce a hydrophobic surface (29). These organic clad sodium montmorillonites are used as thickeners in oil-base paints, greases, oil-base drilling muds, and to gel various organic liquids (30).

3.11. Animal Feed Binders. Both sodium and calcium bentonites are used to bind animal feed into pellets. The fine particle bentonite is very plastic and binds the feed into pellets, which are easy to package and handle. In addition, the montmorillonite acts as an absorbent for bacteria and certain enzymes, which when removed from the animal, promotes growth and health.

3.12. Wine and Beer Clarification. Both calcium and sodium bentonites are used to remove colloidal impurities such as haze-forming compounds in wine and beer. These colloidal impurities are positively charged and are attracted and coagulated by the negatively charged smectite clay.

3.13. Nanoclays. A recent development using sodium montmorillonite is the separation of the unit layers into almost unit cell thickness (1 nm or 10 Å) for use in polymer compositions called nanocomposites. These extremely thin, platy particles are exchanged using organic molecules, which will interact with the polymer to produce very strong and heat resistant composites. These nanoclays are currently being utilized in certain automotive components and in polymer food wrappings and packaging (31).

4. Desiccant

A calcium bentonite from Cheto, Arizona is processed for use as a desiccant. The bentonite is dried, crushed, and screened into small granules, which have the property of absorbing water. This particular bentonite can absorb moisture up to 80 % of its dry weight.

5. Palygorskite and Sepiolite

As mentioned in the chapter on (see CLAYS, SURVEY), palygorskite and attapulgite are names for the same mineral. Also, as previously discussed, attapulgite and calcium montmorillonites are classed as Fuller's earth. Therefore the term fuller's earth is quite often used to include palygorskite (attapulgite) and calcium montmorillonite. Palygorskite and sepiolite have a high surface area, a small octahedral layer charge, a fine particle size, and an elongate shape that gives palygorskite and sepiolite a high absorption capacity that makes these clays useful in many industrial applications. The elongate particles cause high viscosity when added to any liquid. The viscosity results from the elongate shape of the mineral and is not chemically induced so it is very stable as a suspending medium in many applications, eg, in salt water drilling fluids. The applications of these two minerals are many and diverse as shown in Table 8.

5.1. Oil Well Drilling Fluids. The drilling mud circulated through a well serves the primary function of removing rock cuttings from the hole. In addition, it lubricates the bit, prevents hole sloughing, and forms an impervious filter cake on the walls of the hole, thus preventing loss of fluid into porous formations. Of prime importance among the characteristics of a clay for drilling mud is the ability of the clay to build a suitable viscosity at a relatively low solids level, and

Table 8. **Industrial Uses of Palygorskite (attapulgite) and Sepiolite**

drilling fluids	agricultural carriers	ceramics
paint	industrial floor absorbents	asphalt
tape joint compounds	oil refining	adhesives
paper	cat box litter	pharmaceuticals
suspension fertilizers	animal feed binder	wax emulsion stabilizer
catalyst supports	medicinal suspension	polishes

to maintain the desired viscosity throughout the drilling of the well (32). Sodium bentonite is widely used for this purpose, but can only be used with fresh water. Brines and soluble salts encountered in many oil wells prevent the swelling of bentonite so it becomes ineffective in maintaining the desired viscosity when these salts are present. Attapulgite does not depend on swelling for viscosity and is stable in the presence of these contaminants so it is the preferred clay when brines and other salt contaminants are encountered. Also attapulgite drilling muds are more stable under the high temperatures encountered in deep drilling.

5.2. Liquid Suspension Fertilizers. Liquid fertilizers supply an increasing proportion of plant food consumed in the United States and in Europe and China. Liquid fertilizers require the complete solution of the components in order to be useful. The suspension fertilizers bypass the limitation of all components being in solution and 1 or 2% attapulgite stabilizes the suspension and prevents settling of the insoluble components. Attapulgite is the obvious choice for this application because of its highly stable colloidal properties in high concentrations of salts.

5.3. Adhesives. In the production of corrugated paper board, the starch adhesives lose viscosity under shear making it very difficult to apply a constant amount of adhesive during production (32). Attapulgite develops viscosity under shear so the incorporation of attapulgite is an effective method for counteracting the loss of viscosity of the starch. The addition of attapulgite to other types of adhesives stabilizes them so that uniformity is maintained by keeping the components uniformly distributed.

5.4. Colloidal and Suspension Applications. As mentioned in the section Oilwell Drilling Fluids, attapulgite-based suspensions are very stable in the presence of salts and electrolytes. Uses that utilize this property are paint, medicinal suspensions, pharmaceuticals, and polishes. In all these applications, the attapulgite prevents settling and separation of the components thus maintaining uniformity of viscosity and distribution of the components.

5.5. Absorbent Applications. The high surface area and high porosity of attapulgite leads to its use as a floor absorbent, agricultural chemical carrier, and cat box litter. Attapulgite is used in granular form for the removal of oil, grease, and water from garage and factory floors. The pores in attapulgite are large enough to permit rapid saturation and are small enough to hold the liquid firmly by capillary action. These same properties make it useful in absorbing liquid pesticides and herbicides onto free flowing granules, which may readily be applied in the field, and for extensive use as a granular product for use in cat boxes as an absorbent for cat wastes.

5.6. Tape Joint Compounds. Attapulgite pastes are used to fill in and smooth the joints in wall board. The attapulgite makes the paste a thixotropic gel that is easily applied and smoothed and also does not shrink when the paste dries.

5.7. Oil Refining. The mechanical and thermal stability and high surface area of granular attapulgite makes it useful as a percolation absorbent to remove high molecular weight compounds such as sulfonates, resins, and asphaltines in petroleum oils. The granular clay is heated to 400°C and then charged to the filter bed. The oil is percolated through the clay bed until the oil reaches a predetermined quality. The attapulgite can be washed with naptha and regenerated by heating to ~600°C and the clay reused. After 10 or so cycles, the clay is discarded.

5.8. Miscellaneous Additional Uses. The use of attapulgite as a coating on carbon-less copy papers has been previously described in the section Palygorskite (Attapulgite). Attapulgite and sepiolite are used as binders for animal feed as described in the section 8.11. Attapulgite is used to stabilize asphalt and wax emulsions and is also used as a plasticizing agent in various putties, mastics, and caulking compounds. Recently, a highly refined attapulgite has been used as a suspension medium for special ceramics to keep the various oxides uniformly distributed and to prevent settling.

6. Common Clays

Common clays and shales are important raw materials for structural ceramic clay products in most every country in the world. The products include bricks, roof tiles, sewer pipe, conduit tile, structural tile, flue linings, and others. The properties that are important are plasticity, shrinkage, dry and fired strength, fired color, and vitrification range. Shales are largely comprised of the clay minerals illite and chlorite along with quartz. Clays occurring under coals and lignites are generally mixtures of kaolinite and illite with some organic carbon. Some of these underclays are used for face brick and a low grade refractory brick. No figures for the production of these structural products are available, but a good estimate would be of the order of 100,000,000 tons. Some shales and slates are used as a raw material to produce lightweight aggregate. These shales must contain a material that will produce a gas at the vitrification temperature of the shale so that small gas vesicles will form and cause the shale to bloat (33).

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