

Chapter 5

KAOLIN APPLICATIONS

Kaolin is one of the more important industrial clay minerals. Kaolin is comprised predominantly of the mineral kaolinite, a hydrated aluminum silicate. As noted in Chapter 2, other kaolin minerals are dickite, nacrite, and halloysite. Dickite and nacrite are rather rare and usually are found mixed with kaolinite in deposits of hydrothermal origin. Relatively pure halloysite deposits are rare and as was pointed out in Chapter 4, one of the only commercial halloysite deposits now operating is located on the North Island of New Zealand. The Dragon halloysite mine in Utah was operated for many years and then was abandoned. However, it is being reopened as additional reserves have been located, so it may become another source of commercial halloysite (Wilson, 2004).

Kaolinite, which is the dominant mineral in kaolin deposits, is a common clay mineral, but the relatively pure and commercially useable deposits are few in number. Kaolinite has physical and chemical properties which make it useful in a great number of applications.

In contrast to smectites and palygorskite and sepiolite, kaolinite is less reactive when incorporated into most industrial formulations which accounts for many of its more important applications. Such characteristics as low surface charge, relatively low surface area, white color, low ion exchange, and particle shape make it a prime pigment and extender in paper coating and paints and other specialty applications. An example of the difference in the clay mineral types is in their viscosity in water. Relatively pure kaolinite has a low viscosity at very high solids content up to 70% or slightly higher. Sodium montmorillonite, in contrast, has a very high viscosity at 5% solids because of its high surface charge, surface area, exchange capacity, and very fine particle size. Palygorskite and sepiolite have a high viscosity because of their elongate particle shape. Again, it is the fundamental structure and composition that controls the resultant physical and chemical properties which are important in determining their many industrial applications. The more important properties are listed in Table 11.

Table 11. Important properties of kaolin

1	White or near-white in color
2	Chemically inert over a wide pH range (4–9)
3	Fine in particle size
4	Soft and non-abrasive
5	Platy with the plate surface dimensions relatively large compared to the thickness
6	Hydrophilic and disperses readily in water
7	Because of its shape, it has good covering and hiding power when used as a pigment or extender in coatings
8	Plastic, refractory and fires to a white or near-white color
9	Low conductivity of both heat and electricity
10	A very low charge on the lattice
11	A low surface area as compared with other clay minerals
12	Some kaolins have a low viscosity and flow readily at 70% solids
13	Relatively low in cost

Table 12. Representative physical constants of kaolinite

Specific gravity	2.62
Index of refraction	1.57
Hardness (Mohs' scale)	1.5–2.0
Fusion temperature (°C)	1850
Einlehner abrasion number	4–10
Dry brightness at 457 nm (%)	75–93
Crystal system	Triclinic

All the properties listed in Table 11 contribute to the many applications of kaolin. Table 12 gives the representative physical constants of kaolinite. It is estimated that worldwide, some 40,000,000 tons annually are mined and processed. Table 13 shows typical chemical analyses of a Georgia soft and hard kaolin, an English primary kaolin, a Brazil soft and hard kaolin, and a theoretical kaolinite.

1. PAPER

One of the most important applications of kaolin is coating and filling paper. As a filler, the kaolin is mixed with the cellulose fibers in wood pulp and as a coating, the kaolin is mixed with water, adhesives, and various additives and coated onto the surface of the paper. The coating makes the paper sheet smoother, brighter, glossier, more opaque, and most importantly, improves the printability (Bundy, 1993). Paper that is not coated is made up of cellulose fibers interwoven in a random and open configuration. Uncoated paper does not meet the stringent

Table 13. Typical chemical analyses of some kaolins (wt.%)

Component	Cretaceous middle Georgia kaolin	Capim soft kaolin	Tertiary East Georgia kaolin	Jari hard kaolin	Theoretical kaolin
SiO ₂	45.30	46.56	44.00	44.45	46.3
Al ₂ O ₃	38.38	38.03	39.5	37.37	39.8
Fe ₂ O ₃	0.30	0.59	1.13	1.93	
TiO ₂	1.44	0.78	2.43	1.39	
MgO	0.25	0.01	0.03	0.02	
CaO	0.05	0.01	0.03	0.01	
Na ₂ O	0.27	0.03	0.08	0.01	
K ₂ O	0.04	0.02	0.06	0.12	
Ignition loss	13.97	13.8	13.9	14.45	13.9

requirements for high quality printing and particularly multicolor printing. The fine particle size and platy shape of kaolinite are ideal for imparting a smooth, dense surface that is uniformly porous. This gives the paper a more uniform ink receptivity.

The hydrophilic nature of kaolinite makes it easily dispersable in aqueous systems. Coating formulations consist of pigment, binder, water, and small amounts of other additives. This formulation, called a coating color, is metered onto the paper surface with a trailing blade coater or other types of coaters. The shear values at the coating blade interface are extremely high because the paper travels at speeds as high as 1500 m/min. The coating color rheology should be Newtonian or thixotropic (Fig. 57) so that the coating spreads readily on the paper. If the clay is dilatant then pinheads develop which cause streaks on the coated paper.

Optical properties of coatings are brightness, gloss, and opacity (hiding power). Brightness of the paper is largely a function of the brightness of the grade of kaolin used. Gloss increases with decrease in particle size. Opacity is controlled by light scatter, which is dependent on the difference in the refractive index of the kaolinite and of air-filled voids (Fig. 58). Particle size distribution and the amount of fines of the order of 0.25 μm have a large influence on the opacity.

Relatively fine particle size kaolin products of the order of 80% less than 2 μm or finer are the grades that are used in paper coatings. Delaminated kaolins are favored in lightweight coatings (LWC). The relatively large diameter of delaminated particles impart a shingle-like structure to coatings which gives good ink holdout and smoothness. The LWC have reduced the weight of the paper so that postal rates are lower for many

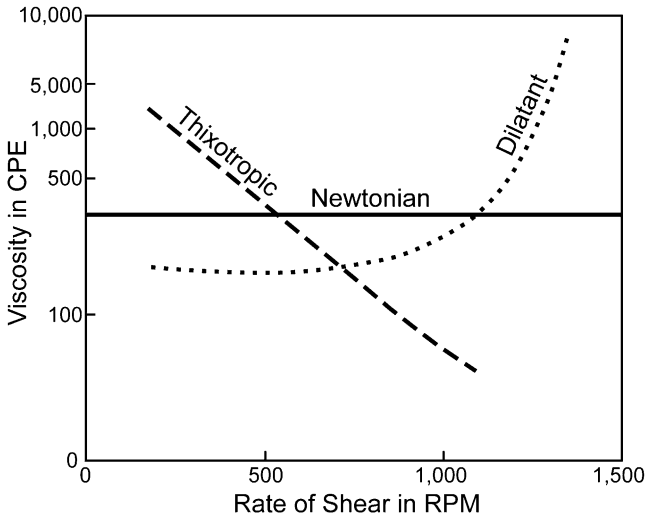


Fig. 57. Rheology—dilatant, Newtonian, and thixotropic.

$$\text{Reflection coefficient, } R = \frac{(n_1 - n_0)^2}{(n_1 + n_0)^2}$$

n_1 , refractive index of pigment

n_0 , refractive index of adhesive or air

starch - clay, $R = 0.000099$

clay - air, $R = 0.045$

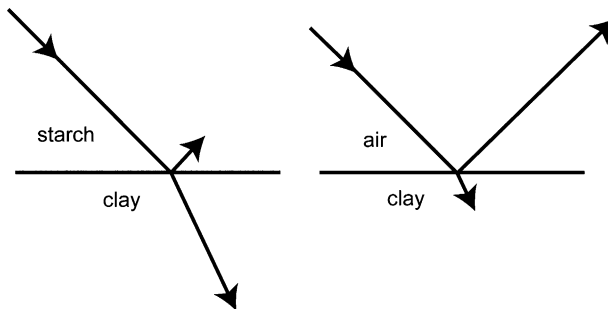


Fig. 58. Opacity.

magazines such as the weekly news magazines. Fig. 59 is an electron micrograph of a delaminated kaolin-coated paper and Table 14 shows many of the coating grades of kaolin and their particle size and brightness.

Another development in paper-coating clay is the production of engineered or tailored products (Murray and Kogel, 2005). These products are engineered to enhance specific properties such as opacity, gloss, brightness, ink holdout, whiteness, and print quality. This can be

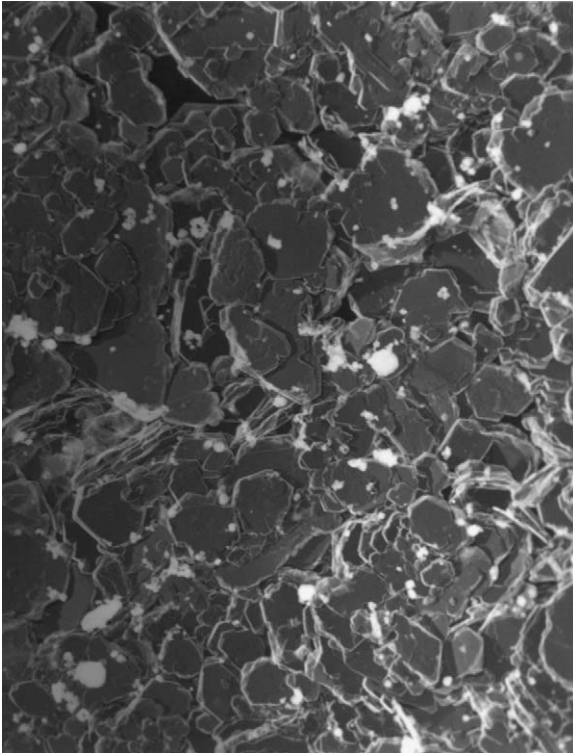


Fig. 59. SEM paper coated with delaminated kaolin.

Table 14. Particle size and brightness of some coating kaolin clays

	Particle size	GE brightness
<i>Regular coating clays</i>		
No. 3	72% < 2 μm	8.5–86.5
No. 2	80–82% < 2 μm	85.5–87
No. 1	90–92% < 2 μm	87–88.0
Fine No. 1	95% < 2 μm	86–87.5
<i>Delaminated coating clays</i>		
Regular	80% < 2 μm	88.0–90.0
Fine	95% < 2 μm	87.0–88.0
<i>High brightness coating clays</i>		
No. 2	80% < 2 μm	89.0–91.0
No. 1	92% < 2 μm	89.0–91.0
Fine No. 1	95% < 2 μm	89.0–91.0
Special engineered clays	80–95% < 2 μm	90.0–93.0
Calcined kaolins	88–95% < 2 μm	92.0–95.0

accomplished by processing the kaolin to a specific particle size distribution, brightness, increased aspect ratio, and control of the percentage of both the coarse and fine particle sizes. The closer that a particle size distribution is between 2 and 0.5 μm , the better the optical properties (Bundy, 1967).

Rheology (Murray, 1975) is a very important property to control for use in paper-coating formulations. Both low shear and high shear viscosity are important. Stringent viscosity specifications are set for coating clays. Factors which determine viscosity are particle size and shape, surface area and charge, mineralogical impurities, and chemical impurities (Lagaly, 1989; Bundy and Ishley, 1991). Morphology is an important factor in the viscosity of kaolin suspensions (Yuan and Murray, 1997). The presence of montmorillonite, mica, or halloysite is detrimental to good viscosity (Pickering and Murray, 1994).

A kaolin-based pigment having high surface area has been developed for ink jet matte-coating applications (Malla and Devisetti, 2005). Its unique morphology allows high solids dispersion with either anionic or cationic dispersants, yet has better viscosity than silica-based pigment slurries.

Kaolins used as fillers in paper are relatively coarse, ranging between 40% and 60% less than 2 μm . The brightness of the filler clays is normally less bright than coating clays, generally ranging between 80% and 85%. The coarse kaolin particles are mixed with the paper pulp or fed from headboxes onto the wet pulp, which is layered onto a wire mesh belt. The kaolin particles are trapped in the interstices of the cellulose fibers. The clay filler improves the brightness, opacity, smoothness, ink receptivity, and printability. A perfect filler, if available, would have these characteristics (Willems, 1958) (Table 15).

Kaolin, of course, is not a perfect filler, but meets several of the criteria listed in Table 15. It is used in white papers such as newsprint, printing grades, and uncoated book paper. Cost reduction is an important factor as the filler is much less expensive than the pulp it replaces. Table 16 shows filler grades of kaolin.

Rheology is relatively unimportant in paper filling except in the dispersion and pumping of the kaolin slurry. Up until about 1980, kaolin was the dominant filler in paper. The conversion of many paper mills from acid to neutral or alkaline papermaking has led to a much greater use of calcium carbonate, which is now the dominant filler. Both ground and precipitated calcium carbonate are used as filler. The development of onsite calcium carbonate precipitators at paper mills has further eroded the use of kaolin as a filler. However, there still is a fairly large tonnage of kaolin used annually as filler in paper.

Table 15. Properties of a perfect filler

1	Reflectance of 100% at all wavelengths of light
2	High index of refraction
3	Grit-free and a particle size close to 0.3 μm , approximately half the wavelength of light
4	Low specific gravity, soft, and non-abrasive
5	Ability to impart to paper a surface capable of taking any finish, from the lowest matte to the highest gloss
6	Complete retention in the paper web
7	Completely inert and insoluble
8	Reasonable in price

Table 16. Filler grades of kaolin

Type	Brightness
Airfloated kaolin	80–81
Whole clay filler	81–85
Water-washed filler	81–86
Delaminated filler	87–89
Calcined kaolin extender	91–95

Paper is filled to extend fiber for cost reduction and to improve several properties including opacity, brightness, smoothness, and printability. The loading levels of filler range from 2% to 8% in newsprint to as high as 30% in some papers. The two most important properties contributed by kaolin as a paper filler are opacity and brightness. Calcined kaolin gives much more opacity to paper than does hydrous kaolin.

A relatively new use of kaolin is as a fiber extender in the manufacture of gaskets for automobile and truck engines. Gaskets were previously formulated using 80–85% asbestos, but health problems associated with asbestos have led to the use of kaolin. The particle size distribution and platy shape of kaolin are important to the reinforcement and seal of gaskets (Bundy, 1993). Also important is the low abrasiveness of kaolin, which minimizes the die-wear as gaskets are precision die-stamped.

Calcined kaolins are used both as a filler and coating pigment, because of their high brightness and good opacity. Calcined kaolins are used as extenders for titanium dioxide, which is an expensive prime pigment used in both paper filling and coating. In many formulations, up to 60% calcined kaolin can replace titanium dioxide without serious loss of brightness or opacity. The cost of titanium dioxide is of the order of 6 times the cost of calcined kaolin products. Fig. 52 is an scanning electron micrograph (SEM) of the surface of a calcined kaolin particle which

exhibits hundreds of small mullite crystallites. The calcined kaolin products have brightness ranging from 91% to 96%. The opacity is increased because the kaolin particles are slightly fused together, which increases the light scatter due to air voids in the slightly fused calcined particles. Light scatter promoted by voids can be shown by the Fresnel reflection coefficient, R :

$$R = \frac{N_1 - N_0}{N_1 + N_0}$$

where N_1 is the refractive index of the pigment and N_0 is the refractive index of the media. The greater the difference in the refractive indices of the components of a system, the greater is the Fresnel reflection R . Air-filled voids have a much lower refractive index than the calcined kaolin. Calcined kaolin grades are normally very fine in particle size, generally 88–96% less than 2 μm . The calcined kaolin is used as an additive to hydrous kaolin in coating colors to increase brightness and opacity, usually in amounts of 20% or less based on the dry weight. Calcined kaolin is also used as a filler in paper.

2. PAINT

Paint is a significant market for kaolin, although it is considerably less than the market for paper coating and filling. About 600,000 tons annually are used worldwide as extender pigments in paint. The largest use is as a pigment extender in water-based interior latex paints. It is also used in oil-based exterior industrial primers. Calcined and delaminated kaolins are used extensively in interior water-based paints. These paints have moderate to high pigment volume concentrations ranging from 50% to 70%. For semi-gloss and high gloss water-based systems, fine particle size kaolins are used, but at less than 50% pigment volume concentration (Bundy, 1993). The particle size of these fine kaolins used in paint is about 98% less than 2 μm . Kaolin contributes to suspension, viscosity, and leveling of paints. The dominant pigment used in paint is titanium dioxide, so as much calcined kaolin as possible is used to extend the TiO_2 in order to reduce cost.

Delaminated kaolins, because of their high aspect ratio and relatively thin plates, give a smooth surface to paint films and a greater sheen. Scrubbability of a paint is improved with calcined kaolin, as is the toughness of the film. Washability, which is the ease with which a stain can be removed by washing, and enamel holdout (the ability of a

substance to prevent the entry of an enamel into its interior structure) are promoted by the use of delaminated kaolins in the paint. In flat paints, calcined kaolin gives better hiding power, film toughness, and scrubability, but gives poor stain resistance. By proper blending of extenders and pigments, paint formulations can be tailored to specific needs.

3. CERAMICS

Ceramics includes a wide range of products in which kaolins are utilized. These include dinnerware, sanitaryware, tile, electrical porcelain, pottery, and refractories. Kaolins and ball clays, which are kaolinitic clays, are both used as major ingredients in many ceramic products. The term ceramic refers to the manufacture of products from earthen materials by the application of high temperatures (Grim, 1962). Ceramics historically goes back to prehistoric times when early man used earthenware in cooking. He learned that he could form shapes with plastic clays and that heat would fix the shape and make them stable in water.

Through time, with the development of modern science, ceramic art has become an engineering profession. The ceramic properties of clay materials are variable depending on the clay mineral composition and such properties as particle size distribution, presence of organic material, and the non-clay mineral composition. The clay mineral composition is the most important factor determining ceramic properties. Kaolinite is the most important clay mineral used in ceramic applications because of its physical and chemical properties that are imparted to ceramic processing and finished products.

The more important properties that kaolin and ball clay impart to ceramics are plasticity, green strength, dry strength, fired strength and color, refractoriness, ease of casting in sanitaryware, low to zero absorption of water, and controlled shrinkage. Shrinkage is an important property because ceramic articles undergo shrinkage at two different points in the manufacturing sequence. During drying, the article will shrink in varying amounts depending on the composition and the percentage of water present. During firing, the ceramic article will further shrink. Therefore, it is important to know both the drying and firing shrinkage. Linear and volume shrinkage can both be measured, although linear shrinkage is more commonly reported (Jones and Bernard, 1972). In the unfired body, both the water of plasticity and shrinkage generally decrease as the particle size increases. In the fired body, the firing shrinkage and water absorption generally decrease, whereas the modulus of

rupture (MOR) and fired whiteness generally increase as the particle size increases (Adkins et al., 2000).

Plasticity is defined as the property of a material which permits it to be deformed under stress without rupturing and to retain the shape produced after the stress is removed (Grim, 1962). The measurement of plasticity has been difficult to determine quantitatively. In general, three ways have been used to measure plasticity. One is to determine the amount of water necessary to develop optimum plasticity or the range of water content in which plasticity of the material is demonstrated. Atterberg (1911) proposed that the lower value, called the plastic limit, and the higher limit, called the liquid limit, is the plasticity index. A second method is to determine the amount of penetration of a needle or some type of plunger into a plastic mass of clay under a given load or rate of loading (Whittemore, 1935). Another way is to determine the stress necessary to deform the clay and the maximum deformation the clay will undergo before rupture. Bloor (1957) presented a critical review of plasticity. A Brabender plastigraph can be used to measure the stress limits mentioned above. Recently, Carty et al. (2000) described a high pressure annulus shear cell or HPASC, as a new plasticity characterization technique.

Green strength is measured as the transverse breaking strength of a test bar suspended on two narrow supports in pounds per square inch or kilograms per square centimeter. Green strength has to be adequate for the piece to be handled without bending or breaking. Ball clays, which are finer in particle size than most kaolins, have a higher green strength (Holderidge, 1956).

Drying shrinkage is the reduction in size, measured either in length or volume, that takes place when the clay piece is dried to drive off the pore water and absorbed water. The drying shrinkage is expressed in percent reduction in size based on the size after drying. In the laboratory, the measurement is made on a test bar after drying for a minimum of 5 h at 105°C. The drying shrinkage is related to the water of plasticity. It increases as the water of plasticity increases and also increases as the particle size decreases. Ball clays have higher dry shrinkage than most kaolins. Table 17 shows that drying shrinkage of kaolinite increases dramatically with a decrease in particle size.

Dry strength is the transverse breaking strength of a test bar that has been dried to remove all the pores and adsorbed water. The dry strength of kaolins and ball clays is greater than their green strength. Dry strength is closely related to particle size which indeed is a major controlling factor. Table 18 shows that the finest fraction of kaolinite has a dry

Table 17. Linear drying shrinkage of kaolinites of varying particle size (Harman and Fraulini, 1940)

Particle size (μm)	Linear drying shrinkage (%)
10–20	1.45
5–10	1.89
2–4	2.19
1.0–0.5	2.35
0.5–0.25	2.69
0.25–0.10	3.70

Table 18. Dry strength of kaolinite in relation to particle size (Anonymous, 1955)

Size fraction	psi
Whole clay	243
Coarser than 1 μm	26
1–0.25 μm	88
Finer than 0.25 μm	750

strength about 30 times higher than the coarse fraction. The fine particle ball clays have a high dry strength.

The fired properties of kaolins and ball clays are most important in determining the ceramic application for a particular kaolin or ball clay product. It should be understood that the non-clay mineral components such as quartz, feldspar, and other mineral additives play an important role in determining the firing characteristics. If organic material is present as it is in ball clays, oxidation to destroy the organic material begins at a temperature of about 300°C and is completed at a temperature of about 500°C. At a temperature between 550 and 600°C (Fig. 60), kaolinite is dehydroxylated and the lattice structure of kaolinite becomes amorphous even though the particle shape is largely retained. This amorphous arrangement of the silica and alumina is retained until a temperature of about 980°C is reached. At that temperature, the amorphous mixture of silica and alumina in metakaolin combines to form a new phase. When this new phase forms, an exothermic reaction takes place. There is some dispute about the phase that is formed at this temperature, but most believe the exothermic reaction is caused by the nucleation of mullite (Johns, 1953). Further heating to a temperature of 1200°C results in larger crystallites of mullite, which Wahl (1958) calls secondary mullite. Kaolinite fuses at 1650–1775°C (Norton, 1968). The fired color of

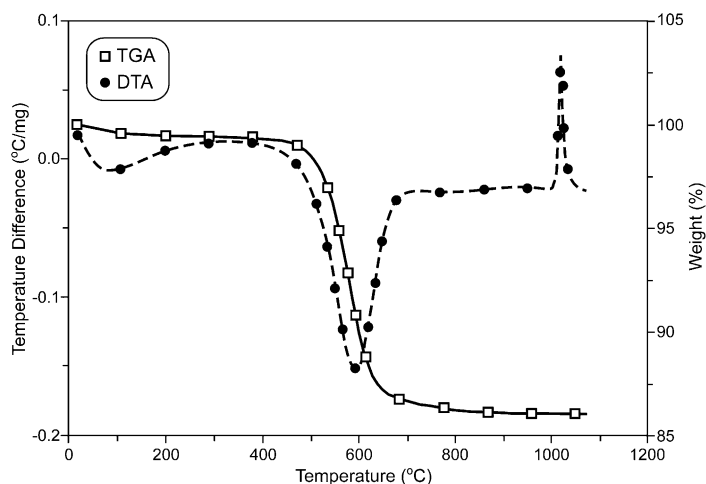


Fig. 60. Typical DTA–TGA curves of kaolinite showing the endothermic and exothermic reactions.

kaolinite is white or near-white. Ball clays fire to a light cream color. The MOR of fired kaolinite and ball clay is very high compared to the MOR of the dried counterparts. The MOR reported for the fired pieces is generally a blend of 50% fine silica and 50% kaolin or ball clay. The MOR ranges from 300 to 900 psi depending largely on the particle size of the kaolin or ball clay.

Casting rate is important in the manufacture of sanitaryware. Fine-grained bodies cast more slowly than coarse ones. The viscosity of a slip must be carefully controlled because if it is too viscous, the slip will not properly fill the mold or drain cleanly and relatively fast. Therefore, viscosity is measured on kaolins and ball clays that are used in the casting process.

Halloysite is used as an additive in the manufacture of high quality dinnerware. The addition of 5–10% by weight in the body provides high fired brightness and increased translucency, both of which are desirable properties of dinnerware.

The use of kaolins and ball clays in refractories began in the early 1800s in New Jersey. Refractory clays are used primarily to make firebricks and blocks of many shapes, insulating bricks, saggars, refractory mortars and mixes, monolithic and castable materials, ramming and air gun mixes, and other refractory products. The specifications for refractory clays are as many as the different uses. Resistance to heat is the most essential property and pyrometric cones are used to indicate the heat duty required. Table 19 shows the values of the pyrometric cones. The pyrometric cone measures the combined effects of temperature and time

Table 19. End points of small Orton pyrometric cones

Cone number	End point (°C)	Cone number	End point (°C)
07	1008	15	1430
06	1023	16	1491
05	1062	17	1512
04	1098	18	1522
03	1131	19	1541
02	1148	20	1564
01	1178	23	1605
1	1179	26	1621
2	1179	27	1640
3	1196	28	1646
4	1209	29	1659
5	1221	30	1665
6	1255	31	1683
7	1264	31½	1699
8	1300	32	1717
9	1317	32½	1724
10	1330	33	1743
11	1336	34	1746
12	1355	35	1763
13	1349	36	1804
14	1398		

(Norton, 1968). The cones consist of a series of standardized unfired ceramic compositions molded into the shape of triangular pyramids. The sample of kaolin, ball clay, or the refractory composition is molded into the standard cone shape and is heated along with standard cones so that the end point can be determined in terms of an equivalent cone number (Table 19). Refractory bricks are classed as low, medium, high, and super duty. The pyrometric cone equivalent (PCE) values of low duty are from 15 to 29, medium duty from 29 to 31½, high duty from 31½ to 33, and super duty above 33. Flint clays are very refractory but are non-plastic so are mixed with plastic kaolin and/or ball clays to provide the plasticity needed to form the piece and maintain its shape.

4. RUBBER

Kaolin is used in rubber because of its reinforcing and stiffening properties and it is relatively low cost in comparison with other pigments. In rubber goods which are black, the favored pigment is carbon black, but in non-black rubber goods, kaolin is used (Anonymous, 1955). As mentioned previously, there are hard clays which are fine in particle size

and soft clays which are relatively coarse in particle size. Hard clays are used in non-black rubber goods where wear resistance is important. Examples are shoe heels and soles, tires, conveyor belt covers, and bicycle tires. Hard clays give stiffness to uncured rubber compounds which is important in the manufacture of rubber hose, tubing, jar rings, and extruded stocks to prevent sagging or collapsing during manufacture. Hard clay is also used to eliminate mechanical molding troubles in hard rubber goods, household goods, toys, and novelties. Other applications for hard clay in rubber are gloves, adhesives, butyl inner tubes, reclaimed rubber, and neoprene compounds.

When high pigment loadings are used to reduce costs and when abrasion resistance is not particularly important, then soft clays are used. Examples are tire bead insulation, household goods, blown sponges, hard rubber toys, and novelties. Larger amounts of soft clay can be incorporated into the rubber and the extrusion rate is faster than when hard clay is used. Delaminated kaolin with a high aspect ratio is used as a filler in the white sidewall tire because it acts as a barrier to air leakage. Also, there are special surface modified kaolins that are used in order to get better dispersion in the rubber and for improved reinforcement. It is estimated that the total annual tonnage of kaolin used for rubber filler is about 600,000 tons.

5. PLASTICS

Kaolin is used as a filler in plastics because it aids in producing a smooth surface finish, reduces cracking and shrinkage during curing, obscures the fiber pattern when fiberglass is used as reinforcement, improves thermal stability, contributes to a high impact strength, improves resistance to chemical action and weathering, and helps control the flow properties. Filler loading in various plastic compositions varies from about 15% to as high as 60%.

The most important use of kaolin is in polyvinyl chloride (PVC) coatings on wire and cable. Calcined kaolin and silane surface modified kaolin are used to improve electrical resistance and to lower cost. Electrical resistance of PVC is improved by fillers that are hydrophobic. Calcining kaolin to about 1000°C reduces surface energy (Drzal et al., 1983), which develops some hydrophobicity which makes calcined kaolin a preferred filler in PVC. Surface treatment with silanes and other hydrophobic materials further increases the hydrophobicity of the surface.

Generally, the finer the particle size of the kaolin, the better the reinforcement of the physical properties in all polymers. Further improvement in strength can be obtained by virtue of coupling agents, which produce

chemical bonding between the kaolin filler and polymer. Fine particle kaolins can substantially increase the impact strength of plastics, for example, in polypropylene and PVC. Bundy (1993) discussed the interaction of silane with the hydroxyl group on the kaolinite surface. The benefit of the silane surface treatment is primarily to improve the dispersion of the kaolin filler. The particle shape of kaolinite as thin platelets benefits some polymers in that flexural modulus, dimensional stability, surface smoothness, and barrier properties (Carr, 1990) are improved.

6. INK

The major inorganic pigment used in ink is kaolin. This is a small but important use of kaolin. Ink formulations are similar to those of paper coating and paint with vehicles (binders) and pigments as the basic components. The most important uses of kaolin in inks are to improve ink holdout and to extend both colored and white pigments (Stoy, 1989). To preserve the gloss of ink films, the kaolin extender must not be so coarse in particle size that the particle protrudes above the film surface. A particle size of the extender kaolin pigment between 0.2 and 0.5 μm is the most effective. Additional requirements for extenders are low abrasion to minimize printing plate wear, easy dispersability, and low oil absorption. Fine particle size water-washed kaolins meet these requirements. For ink to give high print gloss, the ink vehicle must hold out on the paper surface. The platelet shape of kaolinite reduces film permeability, which aids in the holdout of the vehicle on the surface. Fine particle size delaminated kaolins do this most effectively.

Gravure printing represents the biggest ink market for kaolin. Gravure inks can accept relatively large amounts of kaolin, 5–15% on the weight of the resin. Kaolin extends the colorant, sharpens dot formation by imparting thixotropy, and improves holdout. Kaolin is used in low viscosity inks for flexographic printing. Some kaolin is used to extend colorants and to provide thixotropy in inks used for offset printing. Silk screen printing uses relatively thick ink films, that can tolerate the larger particles of calcined kaolin, which provides better light scatter to improve opacity and whiteness. Surface modification of kaolin to make it hydrophobic increases its usefulness in oil-based inks.

7. CATALYSTS

The most important mineral used in the manufacture of carriers for catalysts is kaolin. The largest use of kaolin is in catalyst substrates in the

catalytic cracking of petroleum. Because many catalysts are used at high temperatures and pressures, the refractory character of kaolin is appropriate for these applications. The purity of the kaolin is critical in this petroleum cracking operation so a processed kaolin with low iron, titanium and alkali, and alkaline earth compounds is preferred.

Kaolin is converted to a zeolite in the preparation of the cracking catalyst supports. This conversion of kaolin to zeolite increases the surface area of the catalyst that is exposed in the reaction. [Hettinger \(1991\)](#) stated that the low cost, high purity, and platelet shape promotes the formation of good pore structure, ease of acid leaching, and ease of conversion to zeolite make kaolin the preferred clay used for catalyst carriers. It is estimated that over 200,000 tons of kaolin are used annually to produce petroleum cracking catalysts ([Hettinger, 1991](#)).

Automotive exhaust emissions are controlled by catalytic converters located in the exhaust system. Oxidation catalysts in the converter convert the carbon monoxide and other gases and hydrocarbons produced from incomplete combustion into carbon dioxide and water. Catalytic materials in the converter are supported on a ceramic honeycomb monolith ([Fig. 61](#)). This honeycomb contains 46–62 square channels per square centimeter and each channel is coated with an activated alumina layer called a washcoat. Platinum, palladium, and rhodium metal catalysts are dispersed in the washcoat. The ceramic monolith is cordierite, which has a very low coefficient of expansion, so can withstand continued heating and cooling cycles ([Murray, 1994](#)). The raw materials used to make the cordierite monolith are calcined kaolin, calcined talc, alumina, and hydrous kaolin. Cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) is comprised of 13.7% MgO, 34.9% Al_2O_3 , and 51.4% SiO_2 . [Fig. 62](#) shows the tertiary diagram. The kaolin must be very plastic and have a high green and dry strength ([Murray, 1989](#)).

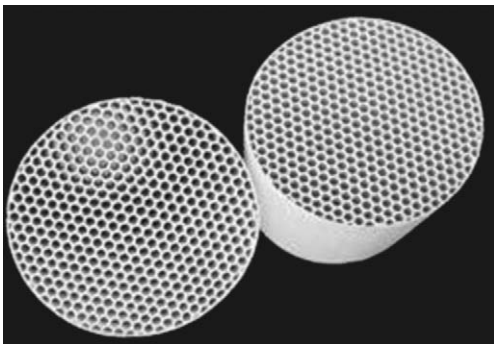


Fig. 61. Catalytic converter honeycomb.

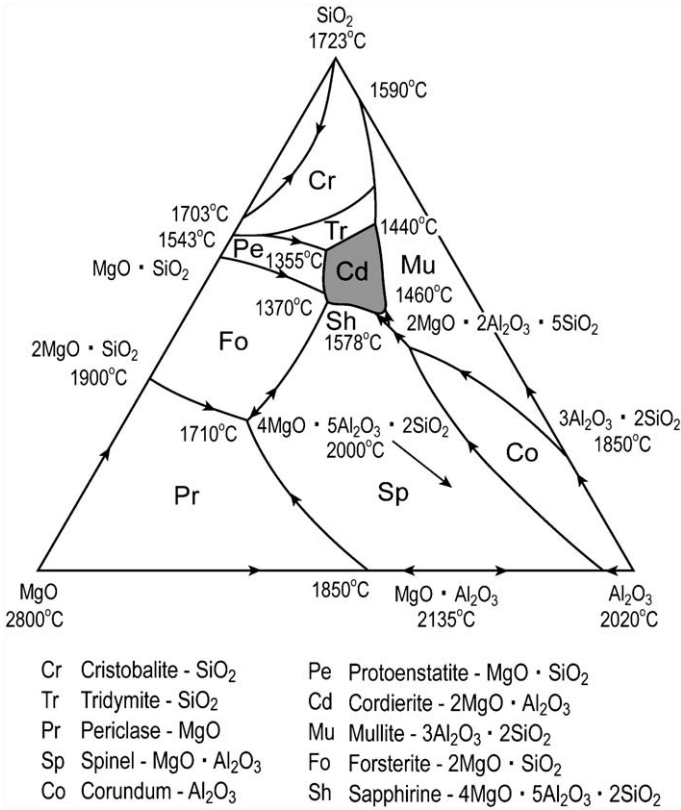


Fig. 62. Temperature and composition to form cordierite.

Kaolin and halloysite are used to make cracking catalysts, as a polymerization catalyst, peptide bond formation, and others (Van Olphen, 1977). Halloysite and metakaolin are used in the manufacture of molecular sieves used as petroleum cracking catalysts. The kaolin for this application must be low in iron and in alkalis and alkaline earth elements. The dry surface of kaolinite is very acidic (Solomon and Murray, 1972) and is used to promote the polymerization of styrene, heterolytic breakdown of organic peroxides, dehydration of alcohols, hydrolysis of esters, and isomerization of alkenes (Solomon et al., 1971).

8. FIBERGLASS

Kaolin is a major component used in the production of fiberglass. Fiberglass has a large number of applications, including insulation, reinforcement of plastics, textile yarn, electronic circuit board substrates, paper, cloth, and roofing shingles. The basic component materials used

to make fiberglass are silica, kaolin, and limestone, along with small amounts of boric acid, soda ash, and sodium sulfate. The kaolin must meet rather stringent chemical specifications (Watkins, 1986): Al_2O_3 $38.5 \pm 0.6\%$; SiO_2 $45.0 \pm 0.5\%$; TiO_2 $1.5 \pm 0.3\%$; Fe_2O_3 0.6% maximum. A sizeable tonnage of kaolin, which is dry processed, is used annually in this market and the estimated tonnage is about 800,000 tons.

9. PORTLAND CEMENT

Cement is made by mixing materials containing lime, silica, alumina, and iron oxide. This mixture is sintered and then pulverized at which time a retardant, gypsum is added. Kaolin is an ideal source of alumina and silica and also makes the cement whiter. Relatively recently, a metakaolin (partially calcined) product is used as a pozzolanic additive in certain cements where high strength is needed. The reactive amorphous alumina and silica in the metakaolin reacts with excess calcium to produce a calcium aluminum silicate which is elongate, thus increasing the strength of the concrete. The use of kaolin in cement is a very minor use at present, but the metakaolin pozzolan potential could be substantial. Recently, it has been shown that the addition of this metakaolin pozzolanic material increases the strength of oil well cements by as much as 40%.

10. MISCELLANEOUS USES

There are a multitude of uses of kaolin which are briefly described. The kaolin surface is acidic, but as shown by Solomon and Murray (1972), the acidic surface of kaolinite is largely neutralized in the presence of water, but dry surfaces show a large increase in acidity. At 1% surface moisture, the acidity is equivalent to 48% sulfuric acid and at approximately 0% moisture surface acidity is equivalent to 90% sulfuric acid. This surface acidity and activity must be considered in many of its uses which enhance some and is deleterious in others.

The properties which make kaolin useful in many of the miscellaneous uses are its fine particle size, white color, platy shape, chemical composition, absorbency, low abrasiveness, surface activity, hydrophilic surface which can be easily converted to be organophyllic or hydrophobic, low dielectric constant, low heat conductivity, ease of dispersion, and low viscosity at high solids concentration.

10.1. Alum

In the process to make alum the hydrous kaolin is heated to about 650–700°C, which forms metakaolin, an amorphous mixture of alumina and silica. The metakaolin is reacted with sulfuric acid to produce alum ($\text{Al}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$). To a much lesser extent, kaolin is reacted with phosphoric acid to produce aluminum phosphate.

10.2. Abrasive Wheel Bonding

Plastic and refractory kaolins are used to bond the abrasives used in an abrasive wheel. The kaolin and the abrasive are mixed, formed, dried, and fired. The drying and firing shrinkage must be low in order to prevent shrinkage cracks in the abrasive wheel or an abrasive bar.

10.3. Adhesives, Sealants, and Caulks

Adhesive, sealant, and caulk products are used in a large number of end uses and several industrial minerals are employed as fillers, extenders, and pigments. The mineral content in adhesive formulations ranges from 10% to 70%. Kaolin is incorporated into some formulations to improve adhesion, lower drying time, and to increase viscosity. Calcined kaolin, because the hydroxyls on the surface have been eliminated, gives low moisture pickup which provides excellent performance in moisture sensitive sealant applications. The platy shape and white color are important properties in some adhesives and sealants.

10.4. Cosmetics

Cosmetics serve a luxury market and the products have a high added value. Baby powder and body powder attractively packaged may sell for over a hundred times the cost of the kaolin or talc, which make up the powder with a scent additive. Because of the association of talc with fibrous asbestiform minerals, delaminated kaolins have replaced a large portion of the talc which was used formerly. Sterilized delaminated kaolin can make up 75% of a body powder formulation. The particle size of the kaolin is very fine and grit-free. It has good covering power, excellent grease resisting properties, and has good adhesion to the skin. The other major use of kaolin in cosmetics is in face packs and masks. Up to 5% of the formulation can be a fine, particle size kaolin. A recent use of kaolin

is in the formulation of a hair conditioner. The kaolin adds body to fine hair, which increases the apparent hair volume.

10.5. Crayons and Chalk

Fine particle size, grit-free kaolin is often used to stiffen crayons and make them more resistant to bending at higher temperatures. Also, the kaolin helps disperse the dye or other organic colorants that are used. The platy fine particle kaolin promotes a smooth thin surface coating on paper or other medium which are colored. Kaolin is also used in chalk because of its softness, plasticity, binding power, and volume.

10.6. Enamels

Porcelain enamels are glassy coatings fused onto metals to provide corrosion protection and decoration. Enamel producers formulate special glasses called frits, which are the major constituent in enamels. The frits are compounded to meet color, opacity, chemical resistance, and processing requirements of the user. The enamel is applied in a thin coat and fused permanently to the metal surface in a low temperature furnace. The frit is compounded to include a number of finely pulverized ingredients which are oxides of coloring agents, whiting, feldspar, kaolin, ball clay, borax, and finely ground glass with a low melting temperature. Kaolin and ball clay are used because of their suspending power at high solids in water and to enhance the dispersion of all the ingredients. The kaolin and/or ball clay used for this purpose must be fine grained and have a white or near-white color when the enamel is fused to the metal surface at low temperature.

10.7. Fertilizers

Kaolins are used as additives to chemical fertilizers as diluents to provide the optimum relative concentration of elements. Kaolins are also used as prilling materials to coat particles of ammonium nitrate, a major component in many fertilizers. The ammonium nitrate particles are deliquescent and become sticky. A thin coating of kaolin makes the ammonium nitrate prills free flowing.

10.8. Fluoride Absorption

Kaolinite has an affinity for fluoride which reacts and perhaps replaces hydroxyls in the structure. If drinking water contains high fluoride levels,

kaolinite is used to remove or lower the fluoride content by absorption. A potential new application is in scrubbers to reduce fluorine emissions in some ceramic and clay plants.

10.9. Food Additives

Kaolins are non-toxic and contain little or no deleterious metal ions. It is approved for internal use by the pure food and drug administration. Therefore, it is used in a limited number of foods as an additive. Examples are to stiffen frosting on cakes, added to coatings on chocolate to prevent melting, as a dusting agent in sugar to improve the adherence of the sugar on doughnuts (Rosner, 1958), and for emulsifying certain liquid foods.

10.10. Foundry

Plastic clays which are kaolinitic are widely used in bonding molding sands when a relatively high refractoriness is required, particularly when a molten metal is poured which has a high temperature. Ball clays with a high plasticity are commonly used. These fine particle kaolinitic clays have a lower bond strength than montmorillonite clays. In some very high temperature, molten metal foundries require that sand size granules of kaolin calcined at temperatures of about 1300°C to form mullite are used instead of silica sand.

10.11. Fruit and Vegetable Protection

A relatively new application of kaolin is in spray-coating apples, olives and tomatoes, and other fruits and vegetables to protect them from sun damage as they ripen. A thin coating protects the fruit and vegetable from sun damage by absorbing ultraviolet rays. Rain will wash off the coating, which requires that the fruit or vegetable be spray coated again. Insecticides can be added to the coating to protect the fruit or vegetable from insect damage (Martin, 2002).

10.12. Insecticide and Pesticide Carriers

Some kaolin products with a very fine particle size are used as carriers of insecticides and pesticides. In most applications, the moisture content must be less than 1%. The clay surface must be compatible chemically with the active ingredients to avoid deterioration or breakdown of the chemical with the resulting loss of potency. In some applications, the

kaolin is used as a diluent. As described above, kaolin is treated with selected pesticides and/or insecticides and is sprayed as a slurry onto fruit trees and other garden products. Many pesticides are in concentrated form, which can have a harmful effect on plants and must be diluted for effective and economical application.

10.13. Medicines and Pharmaceuticals

Kaolins are used as an absorptive for gastro-intestinal disorders, as a tablet or capsule diluent, as a suspending agent, in poultices and for dusting in surgical operations (Russel, 1988). As an absorptive, clays absorb toxins and harmful bacteria in addition to forming a soothing protective coating on inflamed mucous membrane in the digestive tract (Goodman and Gilman, 1955). Kaolins used in medicines and pharmaceuticals must be free of toxic metals, grit, and be sterilized to remove pathogenic micro-organisms. Kaolin is used as a suspending agent for pectins in the well-known product kaopectate. Kaolin is also commonly used as a diluent in capsules and tablets. In tablets, it aids in making the tablet strong and dense when the tablet is compressed.

10.14. Pencil Leads

Fine particle kaolin is used along with a minor amount of bentonite to bond graphite in pencil leads (Murray, 1961). The graphite and plastic kaolin are mixed and extruded to form the pencil lead. The lead is dried and fired to produce a strong pencil lead. The hardness of the lead, 2 H, 3 H, 5 H, etc. is controlled by the percentage of clay in the lead. A soft lead 2 H contains less clay than a harder 5 H lead.

10.15. Plaster

Kaolins are used in plaster as a white colorant, to disperse and improve the uniformity of the plaster, to increase the percent solids and reduce the water content, and to improve the workability and flowability. Fine particle size kaolin is preferred for this use.

10.16. Polishing Compounds

Ultra-fine calcined kaolin is used in many polishing compounds. The particle size is 100% finer than 3 μm and 90% finer than 2 μm . Calcined kaolin has a hardness of between 6 and 7 on the Mohs' hardness scale. This product is used in toothpaste, automobile polishes, polishes for

silver and gold, which are soft metals and require a mild polishing action which removes the oxidized surface. The calcined kaolin must be free of coarse, abrasive particles, which would cause scratching or gouging. Most automobile polishes contain this fine particle size calcined kaolin as the major polishing agent in the polish.

10.17. Roofing Granules

Granular calcined kaolin is spread on the surface of the asphalt paper used to cover roofs. The calcined kaolin is white so is a good reflector. It is hard, durable, and insoluble, which are properties needed for granules spread on a roof. The granules can be sized to make coarse, medium, or fine products.

10.18. Sizing

Kaolins, generally mixed with an adhesive, are used to coat nylon and other synthetic fibers and also for some cotton goods. Very fine particle size kaolins, less than 2 μm , provide a white color and make the filaments in a spinning yarn more homogenous and better able to withstand the strain and friction of weaving. Another related use of kaolin is in carpet backing. A relatively coarse kaolin is used for this purpose. The major reason for use in carpet backing is to reduce cost as the kaolin is much less costly than the rubberized backing.

10.19. Soaps and Detergents

Kaolins are used in soaps as a partial replacement for the fatty acid component because of their emulsifying action, their affinity for carbon particles, and their detergent affect. In all probability, the kaolin is inert and serves only to dilute the soap and to aid in the dispersion of the fatty acid component. In recent years, much of the phosphate used in detergents has been replaced by synthetic zeolites. Zeolites can easily be prepared from kaolin by reacting the kaolin with sodium, calcium, or magnesium hydroxide at a temperature of about 100°C. A pressure vessel will speed up the reaction. A low iron kaolin is preferred for this use.

10.20. Tanning Leather

Kaolins are used in the tanning of leather to lighten the color and to give the leather a softer and smoother feel. A fine particle size kaolin is necessary as the fine particles can readily penetrate the leather and fill the pores.

10.21. Welding Rod Coating

Kaolin, especially metakaolin, has a high dielectric constant and is used to coat welding rods. This coating keeps the electric current moving to the top of the welding rod so it will melt and provide a molten metal fusion.

10.22. Wire Coating

Metakaolin is used to fill the plastic- or rubber-coating material on wires that carry an electric current. The high dielectric constant of the metakaolin in the coating contains the electric field in the wire. This is a sizeable market for metakaolin.

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