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Engineered clay products for the paper industry

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Abstract

The need for kaolin pigments by the paper industry with controlled optical and physical properties have significantly changed the type of filler and coating clays available to the paper industry. Processing equipment now used in the production of kaolin products is much more sophisticated and controllable than in the past. Better understanding of the mineralogy and the physical and chemical properties of kaolins, in addition to improved processing techniques, has allowed the kaolin processors to produce engineered or tailored grades that meet particular needs of the user. Particle size and shape, brightness, gloss, opacity, and viscosity can be altered and controlled to meet specific requirements of the paper coater. Examples of several types of engineered products available for use by the paper industry are discussed.
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1. Introduction

Kaolin clays are widely used as a pigment by the paper industry both as a filler and a coating. The world kaolin market, for high quality beneficiated kaolin, was estimated to be about 25 million tons (Wilson, 2003) of which about 10 million tons were used by the paper industry. The major sources of paper quality kaolin are located in three regions in the world. These are located in the states of Georgia and South Carolina in the United States, in the Cornwall area of Southwestern England, and in the lower Amazon region of Brazil (Murray and Keller, 1993). The Brazil and Georgia kaolins are sedimentary in origin and the Cornwall kaolin is primary.

The physical and chemical properties of kaolin determine its ultimate utilization. The three aforementioned sources have the quality that is needed by the paper manufacturers for use as coating and filler clays. Other kaolin deposits, in addition to those mentioned above, can be used by ceramic, paint, plastics, ink, catalyst, and many other industries (Murray and Keller, 1993). Some specific physical and chemical properties of kaolin are dependent on the geographic source and the method of processing. However, all

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kaolins that are used by the paper industry have the following characteristics:

- Good color (white or near white)
- Fine particle size
- Inert between pH 4 and 9
- Soft and non-abrasive
- Easily dispersable in water at high solids (65 to 72%)
- Platy particle shape
- Reasonably low viscosity at both low and high shear rates
- Non-toxic

Kaolin clays have been used as a filler in paper presumably hundreds of years ago in China and since the early 1800s in England. The first use as a coating pigment was about 1920. The advent of the on-the-machine coater in the 1930s precipitated the large increased use of coating grade kaolins. In the early years of the late 1930s up to about 1970, there were three or four standard coating clays marketed. The grade, particle size, and brightness of these coating clays are shown in Table 1. These coating clays were classified as regular coating clays.

In the early 1960s, two new processes were introduced into the kaolin industry that resulted in the availability of higher brightness products and a product with a high aspect ratio (diameter to thickness). Also very fine particle size kaolin deposits were discovered in East Georgia. These kaolins are tertiary in age and have a crude particle size of 85% <2 μm or finer in contrast with the middle Georgia Cretaceous age kaolins which have a crude particle size which ranges between 55 and 70% <2 μm (Murray, 1976). Table 2 shows the particle size and brightness of these coating kaolins.

These newer products were produced by delamination and flotation. Delamination (Fig. 1) is a process in which books or stacks of kaolinite are sheared to produce thin, large diameter plates (Lyons, 1959; Gunn and Morris, 1965). The high brightness coating kaolins were processed using flotation which removes a substantial portion of the titanium bearing minerals which are a major discolorant in the Georgia kaolins (Greene and Duke, 1962).

Table 1
Particle size and brightness of regular coating clays

Regular coating clay	Particle size	Brightness
No. 3	70–72%<2 μ	84.5–86
No. 2	80–82%<2 μ	85.5–87
No. 1	90–92%<2 μ	87–88

Table 2
Particle size and brightness of fine, delaminated and high brightness clays

Name	Particle size	Brightness
Fine No. 1	95% <2 μm	86.0–87.5
Delaminated		
Regular	80% <2 μm	88.0–90.0
Fine	95% <2 μm	87.0–88.0
High brightness		
No. 2	80% <2 μm	89–91
No. 1	92% <2 μm	89–91

Titanium dioxide is a relatively expensive prime pigment which has high brightness and opacity. It was discovered in the 1950s that by thermally treating kaolinite (calcining), the brightness and opacity were significantly increased. These increases were due to increased light scatter. Calcined kaolins can replace 50 to 60% of titanium dioxide with little or no decrease in brightness and opacity, thus significantly lowering the pigment cost of the paper filler and the coating. Calcined kaolins are now a standard product available to the paper industry.

New and improved processing has made it possible to produce special coating and filler grades of kaolin. These products are designated as engineered clays. Other terms used for these relatively new kaolin products are tailored clay, designer clay, clipped clay, chemically structured clay, thermally structured clay, and high bulking clay. These engineered clays are products whose particle size, shape, and distribution,

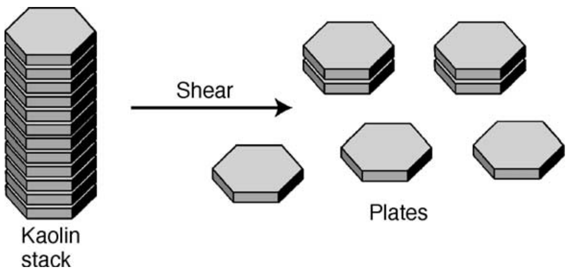

Fig. 1. Delamination of kaolin stacks.

and surface chemistry have been modified by mechanical, chemical, mechanochemical, or thermal means to enhance single or multiple performance attributes. Therefore, an engineered kaolin clay is a product which is processed to improve a particular physical or optical property or properties.

2. Mining and processing engineered kaolin products

Kaolin deposits are variable in quality and quantity, so in order to produce uniform and specific engineered kaolin products, the physical, chemical, and mineralogical characteristics of the crude kaolin ore must be evaluated. The most important physical properties to be measured are brightness, particle size and shape, and viscosity. Blending kaolins from different mines to achieve the desired properties is a common practice in the kaolin industry. All paper coating kaolins are wet processed (Kogel et al., 2002). Engineered kaolin products are altered to satisfy a particular need or needs of the paper manufacturer. The processes that can be used to alter the kaolin products are centrifugation, delamination, magnetic separation, flotation, selective flocculation, chemical leaching, pulverization, blending, calcination, and chemical structuring.

The physical and optical properties of kaolin that relate to their suitability for use as a pigment for coating paper are particle size and shape, the distribution of particle size and shape, brightness, color, opacity, viscosity, surface area, dispersability, and abrasion. These properties can be altered by selective processing. Pruett (2000) presented an excellent discussion of kaolin processing and process development at a workshop on Industrial Clay Mineralogy at the 37th Annual Meeting of the Clay Minerals Society. Following is a brief description of processes that affect the properties of the kaolin products.

2.1. Blunging

This process is normally the first step in processing sedimentary kaolins. The crude kaolin ore is mixed with water and a dispersant in a range of solids between 35% and 70% (Murray, 1980). The purpose of blunging is to mechanically disaggregate the kaolin particles so that the dispersed slurry is pumpable.

2.2. Refining

This step in the process is to separate the kaolinite particles from other minerals in the kaolin ore by particle size separation. Sand and silt size particles which are commonly quartz and muscovite are separated by gravity settling using the principle of Stokes law, in combination with screens. Hydrocyclones and continuous solid bowl decanter centrifuges are also used.

2.3. Classification

After refining, the fine particles that result from the refining process are classified or graded according to their particle size and shape by continuous bowl type decanter centrifuge. This type of centrifuge was developed in the 1930s (Murray, 1980) and it enabled the production of the No. 3, No. 2, and No. 1 coating clays (Table 1). The decanter centrifuge is the classification workhorse used by the kaolin industry. The disc nozzle centrifuge has a finer cut size that allows the production of very fine sized kaolin products and it is also used to de-fine or de-slime a kaolin coating clay, which removes the ultra-fine particles normally <0.5 um and less.

2.4. Brightness and color improvement

Brightness and color can be improved by several processes used by kaolin producers. Oxidative bleaching is necessary for certain gray kaolins that contain organic matter. Ozonation is commonly used to destroy by oxidation the organic matter because it is a cost effective process. Reduced acid leaching is a process used to remove soluble iron oxides from oxidized kaolin ores that are usually cream or pink in color. High intensity wet magnetic separation was first used in the kaolin industry in about 1970. This process removes titanium and iron minerals from the dispersed kaolin slurry and has become a standard process used to improve brightness (Mills, 1977). Flotation, a process commonly used to concentrate metallic minerals, was introduced to the kaolin industry in the early 1960s (Greene and Duke, 1962). Froth flotation removes iron bearing anatase and other titanium minerals from the kaolin slip, which in most instances, significantly improves the brightness. Selective flocculation is another process used to improve the brightness and whiteness of kaolin. The basis of this process is to flocculate certain minerals such as anatase and rutile and leave the kaolinite in suspension which permits gravitational setting of the flocs in a thickener. All the kaolin products that have a brightness of 90 or higher use one or more of these processes to improve brightness and whiteness. The particle size and brightness of the standard high brightness coating clays are shown in Table 2.

2.5. Delamination

After World War II, the production of coating grade kaolins increased yearly. This left a surplus of the coarse fractions rejected by the continuous decanter centrifuges. These rejects consisted of coarse kaolinite stacks and agglomerates much of which were pumped into waste impounds. Research and development work by the kaolin industry (Lyons, 1959; Gunn and Morris, 1965) and the U.S. Bureau of Mines (Feld and Clemmons, 1963) discovered that these coarse rejects could be delaminated by shear into large diameter platy particles (Fig. 1). Fig. 2a is an electron micrograph of a large kaolinite stack and Fig. 2b is a delaminated product that resulted from shearing the coarse kaolinite stacks to produce high aspect ratio plates. These high aspect ratio plates (diameter to thickness ratio) are very good products for certain paper coating applications, because they exhibit good sheet coverage and printability. Delamination is a standard process used by companies in the kaolin industry that supply paper coating products. The brightness and particle size of the delaminated products are shown in Table 2.

2.6. Calcination

Thermally treated kaolins are utilized as coating pigments and functional fillers by the paper industry. The heat treatment produces a product with increased brightness and improved opacity. Kaolinite dehydroxylates at a temperature of between 550 and 650 °C, which breaks down the crystal structure of kaolinite leaving an amorphous mixture of alumina and silica which is called metakaolin (Murray, 1991). Continued heating of the metakaolin to a temperature of about 1050 °C passed through temperature around 980 °C where the amorphous mixture of alumina and silica reorganizes to form small crystals of mullite and high temperature quartz. The relict plates aggregate at this higher temperature to form particles with an open structure that have relatively high light scattering coefficient. The standard calcined kaolin product used by the paper industry has a brightness ranging between 92 and 94.

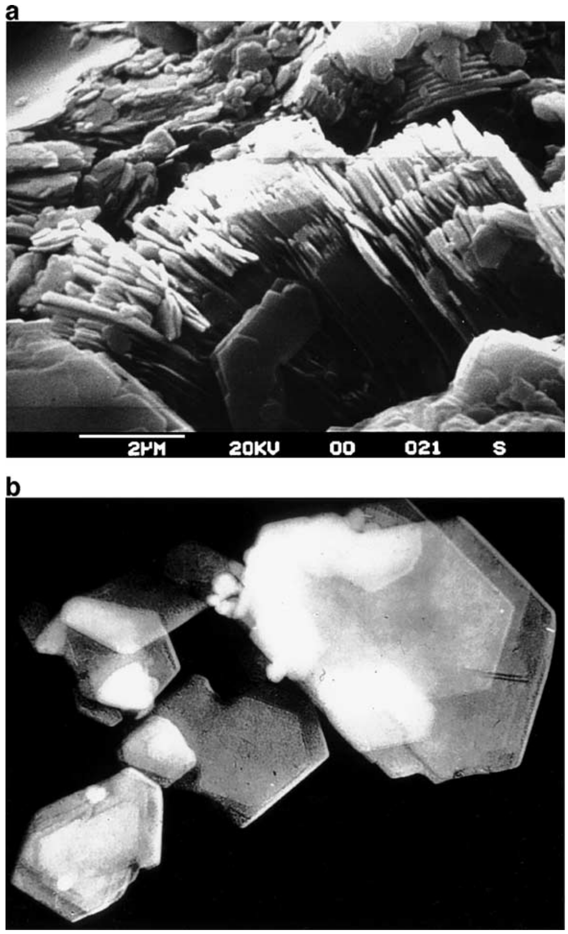

Fig. 2. (a) SEM of large kaolin stacks. (b) SEM of delaminated stack plates.

3. Engineered paper coating properties of kaolin products

Kaolinite has many properties that are advantageous for use as a paper coating pigment as shown in the introduction. Because kaolin is easily dispersable, the particle size and particle size distribution can be altered to effect sheet gloss, smoothness, adhesive demand, film strength, opacity, print gloss, ink receptivity, brightness and whiteness, viscosity, and runnability. The processes can be engineered to produce coating clays with single or multiple attributes that are needed by particular paper coating manufacturers. Traditionally in the past, kaolin coating clays were divided into three groups—standard hydrous kaolins, mechanically delaminated kaolins, and chemical or thermal structured kaolins. In the last ten or so years, engineered or tailored kaolin coating clays that have specific morphology, particle size, and particle size distribution have been developed to meet the demand for rigorous coated sheet properties and improved runnability.

Runnability is the ease of applying thin coatings at high speed and high solids content without streaks, scratches, skips, or paper breakage. Dilatancy generally correlates with poor runnability. Particle size and particle size distribution can be controlled to some extent to produce coating clays that are newtonian or nearly so in their flow characteristics at high rates of shear. Fig. 3 shows the relationship between thixotropic, newtonian, and dilatant flow with increasing rates of shear. A coating kaolin with good runnability can be achieved when an optimal percentage of fine particles are present which promotes more efficient particle packing (Fig. 4). Thus, a kaolin coating clay can be engineered to have good runnability.

Ultra fine particles in kaolin, however, do not effectively scatter light because the wave length of light is nearly the same as these very fine particles. Therefore, both opacity and brightness are affected as is binder demand because of the increased surface areas of the ultra fine particles. Brightness and opacity are functions of particle size and particle packing, adhesive content, and the amount of voids. Thus, by removing a significant portion of the ultrafine particles in the size range of 0.5um and smaller, the light scatter is enhanced which increases the brightness and opacity. Bundy (1993) pointed out that an openly packed coating structure produces more voids for light scattering interfaces. In paper coatings, the refractive index (R.I.) of the binder is about 1.5, which is close to the R.I. of kaolinite (1.56). Light scatter promoted by voids is 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. From the Fresnel

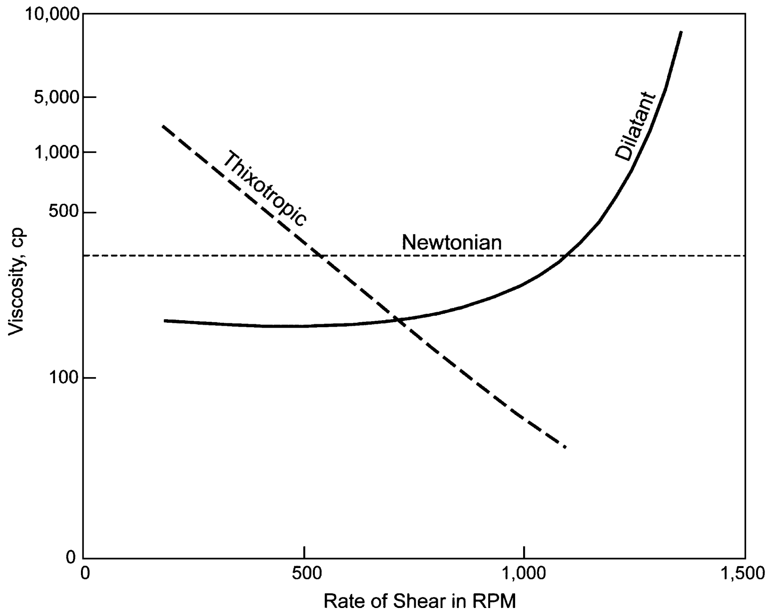

Fig. 3. Relationship between viscosity and rate of shear.

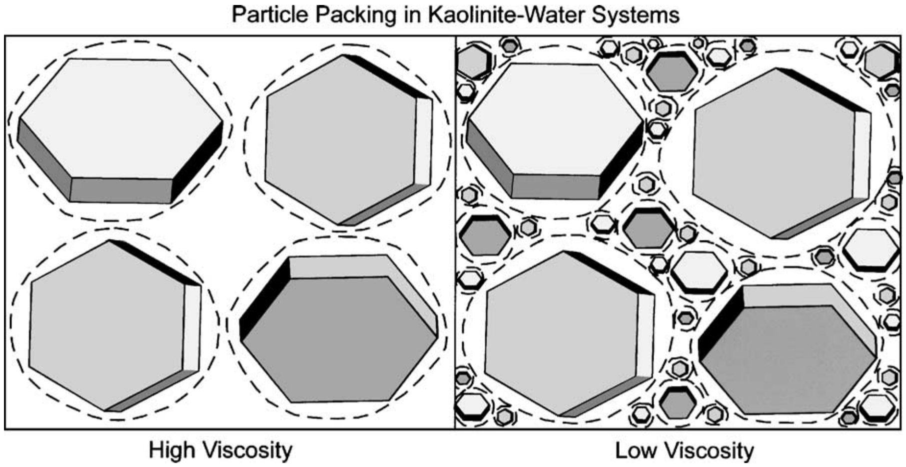

Fig. 4. Schematic representation of the relationship of viscosity to particle packing.

equation, the greater the difference in the refractive indices of the components, the greater the reflection coefficient. By incorporating air-filled voids (R.I.=1), the increase in reflection coefficient gives significant increases in brightness and opacity. Therefore, the incorporation of air interfaces into kaolin coating clays improves optical properties. Fig. 5 shows schematically the significant difference in the reflection coefficient *R* between starch and clay and clay and air. Air can be incorporated into kaolin coating clays by thermal (calcining), chemical, or particle packing means.

The open structure is also beneficial to printability. For ink transfer to be efficient in a rotogravure printing system, the coating must be smooth under pressure, compressible, and sufficiently porous for capillary ink absorption. Compressibility is enhanced by an open coating structure. In lightweight coatings (LWC), delaminated kaolins with a high aspect ratio and a low percentage of ultrafine particles are the most efficient coating pigments for lightweight paper coatings. The addition of a small percentage of fine particle calcined kaolin further enhances porosity so that blends of calcined kaolin with delaminated kaolin are a very effective pigment system for rotogravure printability.

In offset printing, the inks are more tacky than rotogravure inks, which necessitates higher levels of binder to prevent rupture of the coating during printing, which is designated as pick strength. Print gloss is favored by smoothness and ink holdout. The large diameter and thinness of delaminated kaolin favors the formation of smoother surfaces as well as providing good ink holdout. Table 3 compares the optical properties of regular coating with delaminated clays.

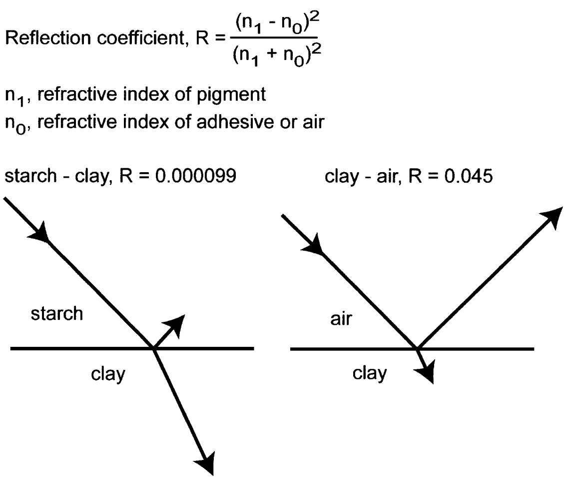

Fig. 5. Fresnel diagram.

Table 3
Optical properties of regular and delaminated clay in lightweight offset coatings

	No. 1	No. 2	Delaminated
Brightness	81.8	80.5	82.3
Opacity	81.8	81.4	82.2
Gloss	48.0	43.0	47.0
Print gloss	62.0	59.0	64.0

Table 4
Relationship between coating pore volume, opacity, and coating rheology

Kaolin	Total pore volume %	Opacity %	Viscosity (APS)[a]
No. 2	23	84.3	31
Delaminated	25	85.4	43
Chemically structured	35	86.2	61
85% delaminated, 15% calcined	15	86.2	71

[a] Hercules Hi-Shear Rheometer, 4400 RPM and "E" bob, 58″ coating solids.

Engineered coating kaolins can be produced with controlled particle morphology, particle size, and particle size distribution. As shown above, these particle parameters affect sheet gloss, print gloss, rheology, brightness, opacity, pick strength, ink holdout, and smoothness. By controlling the particle parameters certain physical and optical properties can be significantly enhanced. In addition, coater runnability can be improved by producing a coating kaolin that has a specially designed particle size distribution. The blending of calcined kaolin with hydrous kaolin promotes increased brightness and opacity. Fine particle size kaolins have increased gloss characteristics. Chemically structured kaolins that aggregate fine particles and create voids also have certain advantageous coating characteristics. Table 4 (after Ching, 1995) shows the relationship between coating pore volume, opacity, and coating rheology.

4. Some historical and recent developments of engineered clay products

One of the first engineered coating clays was a product patented by Rowland (1961). He found that by selecting from naturally occurring kaolin clay, a fraction consisting of clay particles of several size ranges with specific concentrations, a coating clay could be produced that had substantial improvements in gloss, brightness, and opacity. Rowland found that a coating clay having the following size distribution consistently showed improved brightness, gloss, and opacity. The size distribution in his patent was as follows: 99–100% by wt. <4 μm; 98–100% by wt. <1.7 μm; 85–97% by wt. <1.5 μm; 70–84% by wt. <1 μm; 25–37% by wt. <0.5 μm; and 10–15% by wt. <0.3 μm.

Another engineered coating clay product was described in a patent by Bundy et al. (1992). This kaolin coating clay product was a defined and delaminated clay. Bundy et al. found that this engineered coating clay showed improved opacity, print gloss, sheet gloss, and printability of a paper sheet coated with this clay. This defined and delaminated product is characterized by its narrower particle size distribution relative to commercial coating clays. The particle size distribution of this defined and delaminated product exhibits a particle size distribution such that at least about 70% by weight of the particles are larger than 0.3 μm and smaller than 2.0 μm in equivalent spherical diameter.

Another engineered paper coating kaolin pigment was described in a patent by Willis and Canavan (1992). By using kaolins from the Rio Capim basin in the state of Para in Brazil, they found that these mechanically delaminated kaolins possessed the opacity, smoothness, and printability advantages of conventional delaminated kaolin pigments, but have better viscosity and gloss than conventional delaminated kaolin pigments. The delaminated kaolin clay from the Rio Capim basin in Brazil had the following particle size distribution as determined by sedigraph. At least 95% finer than 10 μm; 37% or less than 0.5 μm; and 12% finer than 0.2 μm.

A relatively recent example of an engineered kaolin pigment composition for paper coating was described in a patent by Pruett et al. (2000). This engineered kaolin pigment contains stacks and platelets of unground coarse particles where greater than 96% by weight is less than 5 μm, of which some kaolinite books or stacks are concentrated in the coarser than 1 μm size fraction; 88% to 95% by weight is less than 2 μm; 65% to 85% by weight is less than 1 μm; and 15% to 25% by weight is less than 0.25 μm. This engineered product is processed so that a desired shape factor is attained which is equated to the aspect ratio or morphology of the pigment. This is the first engineered pigment in which the shape factor is measured and controlled so that the aspect ratio or morphology becomes an important factor that relates to the coating properties.

Another recent engineered coating clay pigment was described in a patent by Yuan et al. (2002). This clay pigment is comprised of a coarse delaminated kaolin with a shape factor greater than about 12. If this coarse delaminated kaolin is not fluid at 65% solids, then it is blended with a fine kaolin clay in amounts ranging from 0.1% to about 30% by weight of the blend. When this engineered clay product is used in a coating formulation, the sheet brightness, sheet gloss, sheet opacity, and print gloss are improved.

5. Summary

In recent years, the production of the so-called regular coating clays has significantly decreased in favor of many engineered kaolin coating clays. The reason for this change is that paper coaters use different base sheets and serve different special markets so each requires a coating kaolin with particular optical and/or rheological properties. Because of better and more sophisticated processing, better understanding of the fundamental properties of kaolins, and more effective quality control, kaolin producers are able to engineer a coating clay with the performance attributes needed by the paper coater. These engineered coating clays are produced by mechanical, chemical, mechanochemical, and thermal processes. Patents by clay scientists show that by engineering the particle size distribution and shape factor, superior kaolin coating pigments can be produced.

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