Kaolin in paper filling and coating

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ABSTRACT

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Kaolin is the most extensively used particulate mineral in the filling and coating of paper. It improves paper appearance, which is characterized by gloss, smoothness, brightness and opacity, and of greatest significance, it improves printability. Paper is also filled with kaolin to extend fiber.

The characteristics of kaolin that have the greatest influence on the quality of paper are the purity, rheology and particle geometry of the processed mineral. Generally, the most deleterious impurities for brightness of kaolin are iron oxide and titanium oxide minerals. The rheology of kaolin–binder–water suspensions at high solid:liquid ratios (as much as 65%) must be approximately Newtonian for efficient blade coating at speeds as great as 1300 meter/min. Particle geometry, defined as particle size, particle size distribution, particle shape and aggregate structure, has a dominant influence over the rheological character of kaolin slurries, as well as on the properties imparted by the kaolin to filled and coated paper.

Increase in the aspect ratio of kaolin, as opposed to increase in surface area, exerts the dominant influence on the increase in low-shear viscosity. Although low-shear viscosities of undelaminated coating grades of kaolin show good correlation with surface area, the relationship breaks down for delaminated grades. Particle packing is believed to be the controlling parameter for viscosity at high rates of shear.

Opacity, gloss, printability and, to a lesser extent, brightness of paper imparted by coating and filling with kaolin, are largely functions of particle size and particle size distribution. The strength of coated and filled paper generally decrease with decrease in particle size. An increase in coating void volume generally has a deleterious effect on strength.

The principal commercial printing systems today are rotogravure and offset. Although other parameters are important, coating structures containing numerous voids generally give superior rotogravure printing, whereas smooth, relatively ink-impermeable surfaces are generally most favorable for offset printing.

INTRODUCTION

Kaolin is the most extensively used particulate mineral in paper manufacturing. Competing primarily with ground and precipitated calcium carbonate and much less with titanium dioxide and talc, kaolin usage is about 85% of the total (Hartman, 1986). Giving kaolin preference over other pigments is

the composite benefit derived from low cost, a high degree of whiteness and brightness, satisfactory rheology, relative chemical inertness, and a thin, platy, particle shape that permits excellent film formation.

Georgia, in the United States, and Cornwall and Devon, in the United Kingdom, are the major production centers of paper-quality kaolin. Kaolin currently being produced in the Amazon basin of Brazil is gaining in significance, and production of kaolin for use in paper coating has recently begun in Queensland, Australia. Many other deposits of lesser size and quality are found worldwide and are used to varying degrees in papermaking.

Although kaolin is the term traditionally used in the paper industry, the overwhelmingly dominant mineral present in most kaolin products is kaolinite. Some products contain small amounts of halloysite, and most contain trace quantities of quartz, mica, titania and feldspar. The products marketed by the major clay companies are essentially monomineralic kaolinite. In keeping with paper industry tradition, however, the term kaolin will be used throughout this paper.

The Chinese first coated paper in about 700 A.D., and used gypsum as the pigment and animal glue, gelatin, or starch as the binder. Not until 1870, when a patent was issued to H.D. Pochin and Co., United Kingdom, was kaolin used commercially in paper coating (Rice and Hudson, 1966). Kaolin was originally applied to the paper surface with brushes, and from 1870 to about 1930 essentially no technological improvements were made in this process. Roll coating was developed in 1930, and in the 1960s blade coating was introduced, which is currently the dominant coating method (Hagemeyer, 1984). Coating technology has been driven by increasingly stringent demands for high-speed coating and for printing fidelity. Thus, new kaolin products have been developed to accommodate the increasing requirements of both the paper coating and the printing industries.

First used in the filling of wallpaper in the middle 1800's, kaolin is now used in a wide range of groundwood and bleached kraft paper. Sophistication of kaolin pigments for use in paper filling has evolved less rapidly than for paper coating, but significant strides in filler pigments have been made in the last 10–15 years.

Kaolin as a filler is added at the beginning of the papermaking process, where it is admixed with pulp and water. The amount of filler ranges from little to none in newsprint to in excess of 30% in supercalendered paper (i.e., highly filled, uncoated paper) for use as color supplements in newspapers. In coating, the kaolin is mixed with water and binder and applied to a paper surface, usually by means of a high-speed blade coater. Coated paper may also contain in excess of 30% kaolin.

Kaolin is used in both filling and coating to improve paper "appearance", which is a combination of gloss, smoothness, brightness and opacity. Kaolin is also added to paper to extend the more expensive cellulose fiber, and, most

importantly, to improve printability. Kaolin as a paper coating is most effective in providing a smooth and optimally ink-receptive surface for the most stringent of requirements, four-color image printing, as is used in many popular magazines.

The paper industry imposes many types of requirements on kaolin products. As mined worldwide, kaolin has diverse characteristics, and must be carefully processed to meet rigid industry specifications of particle size, particle size distribution, particle shape, brightness, grit content, and rheology. Certain fundamental characteristics of kaolin, such as purity, particle geometry, and rheology and how they relate to performance in paper, must be well understood to satisfy current and growing industry needs.

This paper reviews current paper filling and coating knowledge with respect to kaolin and relates the contribution made by this mineral to the paper industry. Specific data are reported for coated papers of lightweight publication quality.

EXPERIMENTAL

Kaolin samples described in the tables are Georgia Kaolin Company products. Particle sizes of the kaolin samples described here were determined by the hydrometer-centrifugal sedimentation procedure after Norton and Speil (1938). Surface areas were determined by a three-point BET analysis using nitrogen, with a Quantichrome Quantisorb Jr. instrument. Average thicknesses and average diameters were determined by direct measurement of particles in shadowed, transmission electron micrographs. Samples were dispersed at a high clay:water ratio (0.63) in a Waring Blendor and diluted about 1000 times. A drop of this suspension was applied to a sample grid and allowed to air dry. After drying, grids were shadowed with platinum at an angle that produced a shadow length three times the particle thickness. The mean of the major and minor diameters was divided by the thickness to obtain the aspect ratio of each particle. Average aspect ratio of a sample was calculated from the aspect ratios of about 1000 particles.

Low- and high-shear viscosities were measured on Brookfield and Hercules viscometers, respectively, according to TAPPI test method T-648. The coating colors were applied with a hand blade at a coat weight of 7.5 g/m² to a groundwood-containing basestock with a basis weight of 36.7 g/m². The coated sheets were conditioned overnight at 22 ± 1 °C and 50 ± 2% relative humidity, followed by calendering (cotton-chrome) two nips at 38–2 °C and 2400 pli.

After reconditioning, the brightness, opacity and gloss of the coated sheets were measured according to TAPPI test methods T-452, T-425 and T-480, respectively. Smoothness was measured on a Parker Print Surf paper roughness tester at a pressure of 105,465 kg/m². The actual measurement of

smoothness or roughness was made under conditions that would be found in a commercial printing press and is expressed as the "root mean cube gap" between the surface of the paper and a reference surface.

Print gloss (reflectance at 75°) and picking strength measurements were made on sheets printed on a Prufbau Printability Tester, using a Kohl and Madden gloss blue ink and an IPI tack-rated black ink. The rotogravure testing was performed in the Diamond International Print Tester at a speed of 67 m/min and a pressure of 21,093 kg/m^2. A Bordon (6TRC18169E) test ink, having a viscosity of 30 ± 1 s as measured on a #2 Zahn cup was used. The rotogravure printability was reported as the number of missing dots out of a possible 2480 printed dots.

Using a pulp furnish consisting of 50% hardwood kraft and 50% pine, filled handsheets were prepared on a Williams sheetmold at a clay loading of 10%. After sheet conditioning, opacity was determined by the TAPPI test method indicated above.

Bursting strength is defined here as the hydrostatic pressure required to produce rupture of the paper when pressure was increased at a controlled constant rate through a rubber diaphragm to a circular area. Five determinations were made with a Mullen Burst Tester, and results were obtained in terms of kg/m^2. Mullen% was obtained by using the following equation:

$$\text{Mullen\%} = \frac{P}{W}$$

where P is the bursting strength (kg/m^2) mean value and W is the basis weight of paper in g/m^2.

KAOLIN PURITY AND PARTICLE GEOMETRY

The brightness of the kaolin is critical to the papermaker. Many paper products are manufactured to stringent brightness specifications, and the kaolin used exerts a major influence on this property. The two most significant impurities that affect kaolin brightness are TiO_2 and Fe_2O_3, and even partial extraction of these impurities can increase brightness by several percentage points.

Titania (TiO_2), occurring chiefly as anatase and secondarily as rutile, tends to be concentrated in the fine end of the particle size distribution of Georgia Cretaceous kaolin. This trend is reversed for Georgia Tertiary kaolins. Magnetic separation, selective flocculation, and flotation are processes that are currently used to remove titania from kaolin. Cornish kaolins have an extremely low TiO_2 content (Jepson, 1984).

The 0.2–2% Fe_2O_3 found in paper-quality kaolin seems to be largely structural (Jepson, 1984). Total iron is generally lowest for Georgia Cretaceous kaolins and highest for Tertiary kaolins. Cornish kaolin contain intermediate

amounts of Fe_2O_3. The extent to which structural iron influences brightness is not known. Iron oxyhyroxides occuring as encrustations on kaolin particles significantly affect brightness. These materials may be removed by a reduction with sodium hydrosulfite and acid dissolution.

Montmorillonite occurs locally in many kaolins and is concentrated in the smallest size fractions. Because of its deleterious effect on rheology and its resistance to extraction, selective mining is the typical method of control. Muscovite and quartz occur in the coarsest size fractions in Georgia kaolins. In addition, Cornish kaolins contain feldspars in coarse fractions. These coarse minerals can be harmful, causing paper-coating scratches. Relatively coarse particles of quartz and feldspar are highly abrasive and tend to dull paper-cutting knives. Dulled knives cause fiber and pigment dusting, which leads to serious problems in printing.

Particle geometry, size, shape and size distribution, as well as aggregate structure, play a major, if not dominant, role in the rheology of kaolin–water suspensions and in the optical and printing properties imparted by the kaolin to filled and coated paper. Kaolin filler and coating grades from Georgia generally range in particle size from about 60% $<2~\mu$m equivalent spherical diameter (esd) for coarse filler grades to about 98% $<2~\mu$m esd for the finest coating grade.

Table I shows a broad range of particle sizes used in paper manufacture. In addition to % $<2~\mu$m, % $<0.5~\mu$m is shown as an arbitrary size designation of the colloid fraction. In general, colloid content increases with decreasing particle size, but delaminated kaolins show some deviation from this pattern. Delaminated grades are, generally, made from coarse kaolin fractions from which many of the fines have been removed, and the colloid content is usually much lower than that of non-delaminated grades. The surface area generally corresponds to particle size, but is is anomalously high for calcined clay. This

TABLE I

Particle geometry of Georgia kaolin products

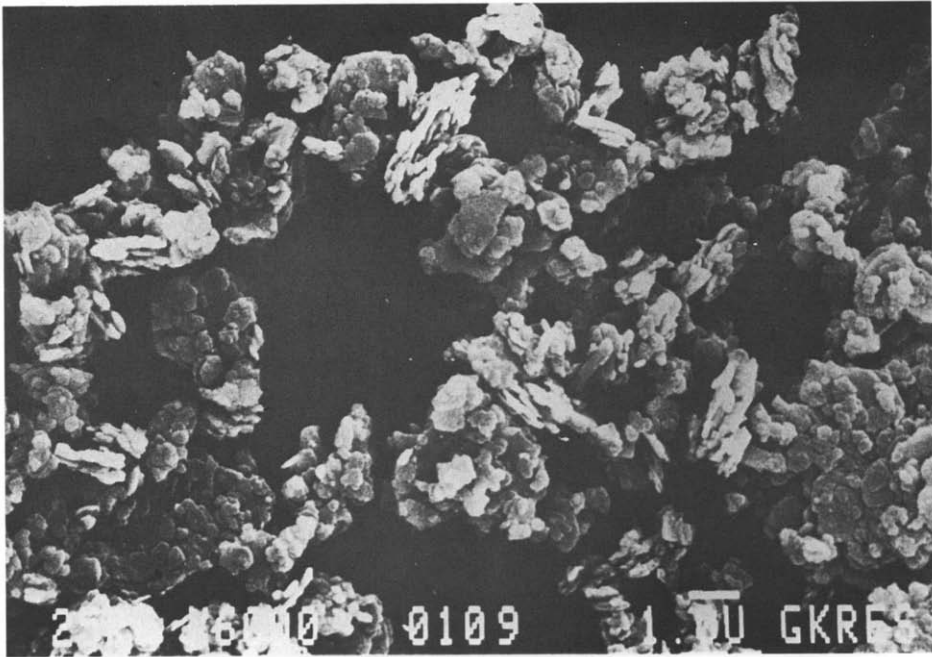| Kaolin product	Age	Size distribution		Surface area (m^2/g)	Average thickness (μm)	Average diameter (μm)	Aspect ratio
		$<2~\mu$m (%)	$<0.5~\mu$m (%)				
Fine No. 1	Tertiary	95	69	17.0	0.05	0.46	12.5
No. 1	Cretaceous	92	52	16.0	0.10	0.81	10.1
No. 2	Cretaceous	83	46	12.5	0.12	0.71	8.9
Delaminated	Cretaceous	79	38	12.5	0.15	1.61	14.7
Coarse delam.	Cretaceous	56	15	7.4	0.16	2.29	22.0
Calcined	Tertiary	83	11	14.0	0.39	1.18	4.82

Fig. 1. Scanning electron micrograph of fine-particle calcined kaolin from the Georgia Kaolin Company (calcined at $1050°C \pm 50$).

anomaly is apparently related to the internal surface area formed by porous aggregate structures.

Average thickness and average diameter generally decrease with decreasing particle size, but the aspect ratio tends to be minimal for the coarsest, undelaminated coating grade, No. 2, which corresponds to the size fraction containing the blockiest particles. Delaminated kaolins show an opposing trend; the aspect ratio becoming larger with increasing particle size.

Calcined kaolin (Fig. 1), also used in the filling and coating of paper, has a particle geometry significantly different from that of uncalcined kaolin. Its aspect ratio and colloid content are exceptionally low. These differences are due to the formation of aggregate structures arising from fusion at particle edges during calcination (Berube, 1978).

RHEOLOGY

Paper coating color materials consist of pigment, binder, water and minor amounts of other additives. Kaolin is the most common pigment, and binders may be natural, such as starch, protein, or synthetic, such as styrene butadiene latex, acrylic, or polyvinyl acetate. Binder levels, exclusive of size press

coatings, range from about 5% to about 25%. The rheology of the coating color must be such that the slurry is amenable to pumping and screening. The coating is generally applied with a blade at coating speeds of 600–1200 m/ min; shear values at the coating interface of as much as $2-10^6$/s can be developed (Kurath, 1969). For good runability of paper coating (i.e., minimal scratches and streaks in the coating and minimal paper breaks), the rheology of coating colors must be at least Newtonian and preferably thixotropic (Anderson, 1968). Because kaolin strongly influences the rheology of coating colors, an understanding of the specific properties of kaolin that influence rheology is paramount.

Suspensions of Georgia kaolins at high solid to liquid ratios exhibit Newtonian to dilatant rheological behavior that is influenced by numerous factors, including soluble salt content, mineralogical impurities (especially montmorillonite), dispersion of particles, particle geometry, colloid content, particle volume and particle packing. During the processing of Georgia kaolins soluble salts are generally removed to the point of minimizing their effect, and selective mining excludes montmorillonite. The dispersion is typically optimized by means of polyanionic dispersants. The principal parameters remaining are particle shape, particle size, particle size distribution and, consequently, particle volume concentration, and particle packing efficiency.

Table II shows relationships between kaolins having a range of geometries with low-shear viscosity. Numerous workers (Robinson, 1951; Mooney and Hermonat, 1955; Ormsby and Marcus, 1964; Bundy et al., 1966) have reported a relationship between surface area and low-shear viscosity, which they ascribed to an increase in effective particle volume due to adsorbed water. This relationship is true for undelaminated grades of kaolin.

For delaminated grades, the surface area appears to be inversely related to viscosity. Aspect ratio is the only shape factor which correlates with low-shear viscosity, and does so positively regardless of delamination.

TABLE II

Low-shear viscosity, η, of Georgia kaolin products

Kaolin product	Age	Low-shear viscosity, (centipoises)	Solids (%)	Surface area (m^2/g)	Aspect ratio	Relative[1] swept volume (cm^3)
Fine No. 1	Tertiary	560	71	17.0	12.5	4.28
No. 1	Cretaceous	440	71	16.0	10.1	3.48
No. 2	Cretaceous	400	71	12.5	8.9	2.62
Delaminated	Cretaceous	800	67	12.5	14.7	4.60
Coarse delam.	Cretaceous	3200	67	7.4	22.0	6.29

[1]Volume described by rotating particles.

The viscosity of colloidal suspensions of non-spherical particles generally exceeds that predicted by Einstein's equation for spherical particles:

$$\frac{\eta}{\eta_0} = (1 + \frac{1.25V}{1 - V/0.74})^2$$

where η is the viscosity of the suspension, η_0 is the viscosity of the suspending medium, and V is the volume fraction of spheres. This equation shows the unique importance of particle volume concentration for idealized systems.

In contrast to isometric particles, anisometric particles give rise to significantly greater viscosities (Coughanov and Norton, 1949). According to Kurath (1977) the viscosities of kaolin plates in suspension depend upon particle orientation with respect to the direction of fluid flow. Plates in sheared suspensions are in continuous rotation toward the flow direction, and, at low rates of shear, an opposing effect of rotational Brownian motion exists. The spherical volume described by rotating plates is thus the effective particle volume. As observed by Millman (1964), kaolin plates in rotational motion promote a change in effective or swept volume that increases disproportionately with an increase in particle diameter.

The lowest viscosity, shown by the No. 2 product, corresponds to the lowest aspect ratio (Table II). Aspect ratio can be thought of as a measure of blockiness, and the more blocky or the lower the aspect ratio the less volume occupied by rotating particles per unit of weight. A calculation for the volume occupied by rotating particles per unit weight is also shown in Table II. As with aspect ratio, swept volume of rotating particles correlates with low-shear viscosity. Neither average aspect ratio nor swept volume of rotating particles show a relationship to size distribution or packing. Perhaps the best measure of particle packing for suspensions under shear is high-shear viscosity, which does not correlate with low-shear viscosity. Thus, particle packing, at best, appears to be a less significant parameter for low-shear viscosity unless a critical solids level is exceeded. The Einstein equation for ideal suspensions of spherical particles seems to be applicable to low-shear viscosity of kaolin if swept volume is considered.

High-shear viscosity has a different correlation with particle geometry than does low-shear viscosity (Table III). Both average diameter and colloid content correlate with high-shear viscosity. A discrepancy exists, however, between No. 1 and No. 2 clays with respect to diameter. The large average diameter of No. 1 clay seems to be compensated for by a much higher colloid content, which may be the controlling parameter.

Beazley (1965) showed that the colloid fraction of a kaolin is not dilatant and that this fraction plays an important role in reducing dilatancy of coarser fractions. Although the data in Table III substantiate this finding, a size fractionation of fine No. 1 product to 100% < 2 μm produces a material that is

TABLE III

High-shear viscosity, η, of Georgia kaolin products

Kaolin product	Age	High-shear viscosity, (poises)	Solids (%)	<0.5 μm (%)	Average diameter (μm)
Fine No. 1	Tertiary	0.62	71	69	0.46
No. 1	Cretaceous	1.15	71	52	0.81
No. 2	Cretaceous	1.81	71	46	0.71
Delaminated	Cretaceous	15.6	67	38	1.61
Coarse delam.	Cretaceous	24.6	67	15	2.29

dilatant at a moderate rate of shear. The fine No. 1 (95% <2 μm) product is Newtonian through a shear rate of 4400 rpm. Fractionated to 100% <2 μm, this material has a dilatancy at 2080 rpm.

This seemingly anomalous dilatancy of ultrafine kaolin may be explained by an increase in effective particle volume due to adsorbed water and to electroviscous effects. The increase in effective volume caused by absorbed water increases disproportionately with decrease in particle size. Of the two electroviscous effects (Kurath, 1977), one results from the distortion of particle ionic atmosphere in a shear gradient. The other is due to the interaction of electric double layers, with the effect increasing as the square of particle concentration. The increase in surface area necessitates an increase in electroviscosity.

Ward and Whitmore (1950) showed that a broad range of particle size produces lower viscosities because of an overall higher degree of packing, in which smaller particles fit into interstices formed by larger particles. Inefficient packing in high solids systems leads to excessive encroachment within domains of rotation, abundant collisions and the development of dilatancy. Thus, the data in Table III indicate that small-diameter particles yield the lowest packing densities and viscosities under high-shear flow. Average diameter seems to be an indirect measure of particle packing. Excessive decrease in particle size leads to a redevelopment of dilatancy, presumably due to: (1) an increase in particle volume concentration and a consequent decrease in packing efficiency; and (2) an increase in electroviscous effects.

Calcined-clay viscosity, not shown in the Tables, is inordinately high compared to uncalcined clay. The data in Table I show that calcined clay has the lowest aspect ratio and indicate that its low-shear viscosity should be superior to that of all the other clays. Similarly, the high-shear viscosity of calcined clay, based upon average diameter and fines content, should be similar to that of the coarse delaminated clay. Indeed, quite the contrary is true, and the highest solids level that can be obtained with calcined clay is about 52% – substantially less than that of the uncalcined clays. Aside from the removal of

structural water and the reconstitution of the crystal structure, kaolin and calcined kaolin differ in two important ways: by their surface chemistry and aggregate structures.

Drzal et al. (1983) showed that calcined kaolins have a significantly lower surface energy than do non-calcined kaolins. This appears to stem from a diminution of the kaolin's edge charge. Measurements made in the Georgia Kaolin laboratory have shown that dispersed kaolins have about twice the zeta potential of dispersed calcined kaolins. At a smaller zeta potential (and, hence, a lower surface energy), particle–particle distances are much smaller, and flocculation via Van der Waals attraction is much more probable. The resultant floc structures produce higher viscosity.

Aggregate structures produced by fusion of particles during calcination impart major surface irregularities, e.g., abundant protrusions and reentrants (Fig. 1). These rough surfaces result in interlocking particle configurations, which should offer more resistance to shear. Void volume is necessarily high not only because of voids within the fused aggregates, but because of voids formed by the inefficient packing related to rough surfaces. Moreover, void volume is increased by low colloid content and the inefficient packing that results. Indeed, sediment packing volumes are exceptionally high as has been shown by Berube (1978).

RELATIONSHIP OF KAOLIN RHEOLOGY TO PAPER APPLICATIONS

Diagrammatic representations of particle packing in kaolin–water systems (Fig. 2) are useful to summarize the geometrical parameters that influence

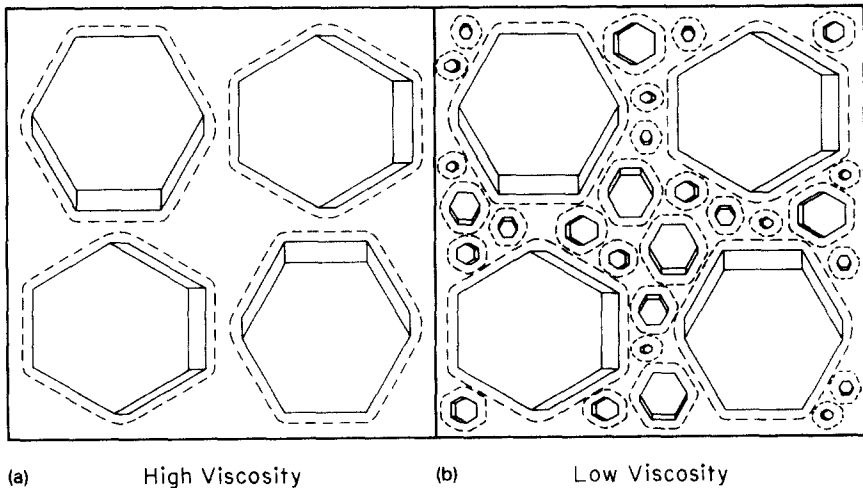(a)   High Viscosity   (b)   Low Viscosity

Fig. 2. Schematic representation of the packing of kaolin particles (after Bundy, 1967). Dashed lines represent sphere of adsorbed water. (a) Monodisperse system. (b) Polydisperse system.

rheology and to emphasize the effect packing has in papermaking. Figure 2a illustrates packing for a monodisperse system (a system containing single-size particles) representing an extreme, idealized condition. Such inefficient packing dictates that the solids level will be low and that viscosity will be high. Conversely, such systems will provide superior coating and filled-sheet optical properties. The printability of coated sheets will also be enhanced significantly.

The most desirable optical properties using kaolin in coating and filling can be achieved by developing structures, in which the kaolin particles are uniformly interspersed with voids that have diameters in the range 0.3–0.7 μm (Climpson and Taylor, 1976). The importance of voids is best shown by the Fresnel reflection coefficient, R:

$$R = \frac{(\eta_1 - \eta_0)^2}{(\eta_1 + \eta_0)^2}$$

where η_1 is the refractive index of the pigment and η_0 is the refractive index of the media. The equation emphasizes that the greater the difference in the refractive indexes of the components of a system the greater is the Fresnel reflection. Other than titania, air provides the largest difference in refractive index compared with that of kaolin, as well as the binder.

Monodisperse kaolins tend to form open structures in coatings and in filled paper. If the voids are near optimum in diameter, both the brightness and opacity of the paper are increased significantly. Similarly, such open systems extend titanium dioxide more efficiently. Titanium dioxide is synthesized as a fine particulate, white pigment and, because of its exceptionally high refractive index, is used in small quantities to enhance both brightness and opacity of the paper. Used with kaolins that produce open structures, the titania fits into the interstices, where the interface with (low refractive index) air produces maximum light scatter.

Figure 2b shows that much higher solid:liquid ratios can be achieved with polydisperse or wider size distributions. At high solid:liquid ratios, polydisperse systems produce significantly lower viscosities than monodisperse systems. The thickness of the adsorbed water is the same regardless of particle size; thus, smaller particle sizes have a disproportionately large effective particle volume. Large viscosities are expected and do exist for slurries containing abundant ultrafine particles.

Polydisperse kaolins, despite providing the best obtainable rheology, which is a desirable quality, give denser films and denser agglomerations in filled sheets. Such systems have undesirable light scattering and inferior optical properties. Indeed, the denser films, although giving rise to greater film strength in coatings, generally give rise to inferior printing properties. Typically, a paper coater must compromise on the choice of kaolins for a balance between acceptable rheology and acceptable optical and printing properties.

OPTICAL AND PRINTING PROPERTIES OF PAPER COATINGS

The overwhelming reason for coating paper is to improve printability. This statement, however, is not meant to diminish the importance of improvement in optical properties, brightness, opacity and gloss produced by coating. Electron micrographs of paper surfaces clearly show the improved quality derived from coating. Figure 3 shows an uncoated paper surface and the roughness and non-homogeneity produced by the interweaving of cellulose fibers. Figure 4 shows the same paper coated with kaolin and binder; note the smoother, homogeneous and more finely porous surface. Such a surface is essential for acceptable optical properties and for uniform ink reception.

Optical properties of coatings formulated for rotogravure printing are shown in Table IV. Similar trends in optical properties were obtained for offset coatings. Largely a function of pigment brightness, coating brightness is not included in the Table.

Coating gloss generally increases with a decrease in pigment particle size; however, delaminated clays show higher gloss than non-delaminated clay of an equivalent particle size. The reason that delaminated clays have higher gloss is believed to be related to coating holdout – the extent to which the

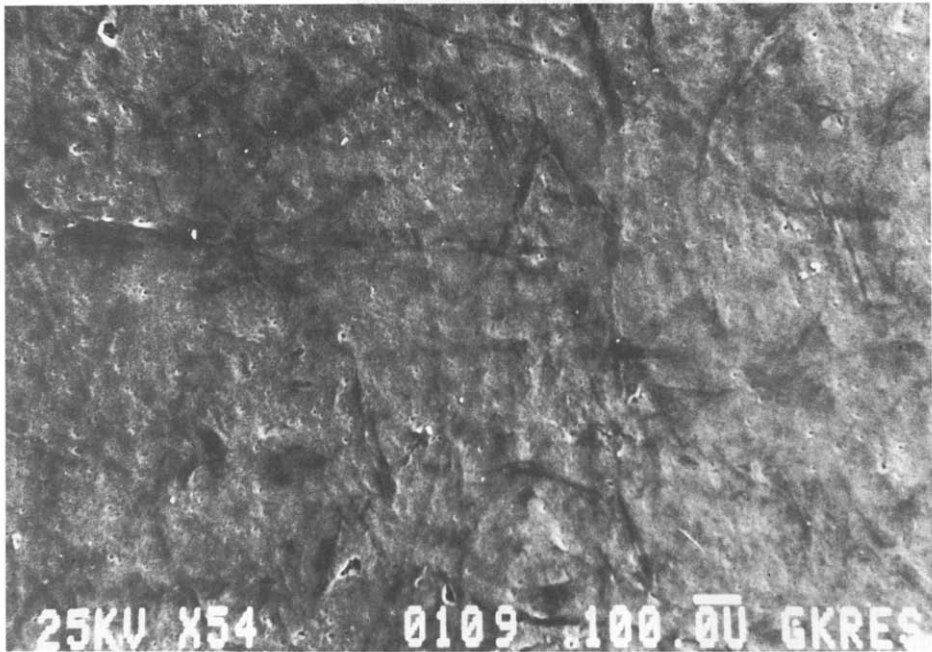Fig. 3. Scanning electron micrograph of uncoated paper (after Bundy and Harrison, 1986).

Fig. 4. Scanning electron micrograph of coated paper (after Bundy and Harrison, 1986).

TABLE IV

Optical properties of rotogravure coatings for Georgia kaolin products

Kaolin product	Age	Gloss (%)	Opacity (%)	<2 μm (%)	<0.5 (%)	High-shear viscosity (Poise)
Fine No. 1	Tertiary	58	81.7	95	69	0.62
No. 1	Cretaceous	53	82.5	92	62	1.15
No. 2	Cretaceous	51	82.4	82	46	1.81
Delaminated	Cretaceous	57	82.9	80	38	15.6
Coarse delam.	Cretaceous	50	82.6	56	15	24.6
90 Delaminated	Cretaceous					
10 Calcined	Tertiary	56	83.4	80	36	31.3

coating holds on the surface of the paper as opposed to penetrating between the fibers.

As described above, delaminated clays are produced from coarse kaolin fractions from which fine particle size material has been extracted. Because of the lower colloid content of the delaminated clay as compared to other coating grades having broader particle size distributions, the dewatering rate of coatings is increased giving rise to more rapid immobilization (Baumeis-

ter, 1980). By this mechanism, the coating is held on the surface and does not penetrate between the fibers into the paper. Because of the better coating holdout, void filling and leveling of the paper surface is improved. Such improved surfaces give enhanced specular reflectance or gloss.

Opacity contributed by kaolin in coatings generally improves with a decrease in the amount of colloids, which produces a more open structure to the coating. Coarse delaminated kaolin, however, has a slightly inferior opacity, probably caused by the formation of larger than optimum voids. Here, a somewhat higher colloid content may help optimize void diameter and thereby improve opacity.

Opacity, generally, correlates with high-shear viscosity. The more open structure implied by a large high-shear viscosity seems to carry over into the coatings. Again, coarse delaminated kaolin appears to form voids larger than optimum for light scatter.

The greatest opacity can apparently be obtained using kaolins having balanced particle size and colloid content, which contribute to an optimum coating structure. The introduction of a small percentage of calcined clay to delaminated clay results in a significant increase in opacity, apparently due to both internal and external void structures provided by the calcined clay.

In rotogravure printing the image is transferred from recessed cells on a metal cylinder to the paper. It is therefore imperative that for efficient ink transfer the coated sheet make intimate contact with the cylinder. Coating smoothness, therefore, is important to this process. Compared with other printing processes, exceptionally high pressures are applied in the rotogravure process. Printing occurs while the paper is compressed, and the extent to which ink comes into contact with the paper under this condition is the most realistic measure of rotogravure smoothness (Bradway, 1973). Conrad (1964) emphasized that capillary absorption is important to ink transfer. Thus, compressibility of the coating, to give the best smoothness and capillary absorption of ink seem to be the most important parameters for ink transfer. If the ink is not transferred or if transfer is incomplete, the result is called a "missing dot".

The greatest rotogravure printability is achieved with kaolins that impart maximum coating smoothness and an open structure for maximum compressibility. A clear relationship to smoothness was not demonstrated with the kaolins used in this study (Table V). Non-delaminated kaolins show an inverse trend with smoothness. Coarse, delaminated clay gives less smooth coatings, but substantially fewer missing dots. A mixture of calcined clay and delaminated clay yield a significant increase in smoothness, as well as a significant reduction in the number of missing dots. Calcined clay alone yields by far the best smoothness and the fewest in missing dots. With these inconsistencies in relationships of smoothness to missing dots, it is clear that parameters other than smoothness can exert an overriding influence.

TABLE V

Rotogravure printability data for Georgia kaolin products

Kaolin product	Age	Missing dots/6.45 cm²	High-shear viscosity (Poises)	Average thickness (μm)	<0.5 μm (%)	Smoothness μm
Fine No. 1	Tertiary	161	0.62	0.048	69	1.54
No. 1	Cretaceous	148	1.15	0.102	52	1.61
No. 2	Cretaceous	135	1.81	0.120	46	1.66
Delaminated	Cretaceous	91	15.6	0.154	38	1.55
Coarse delam.	Cretaceous	78	24.6	0.160	15	1.66
90 Delaminated 10 Calcined	Cretaceous Tertiary	76	31.3	0.178	35	1.49
Calcined	Tertiary	4	>31.3	0.390	11	0.82

Of the kaolin properties studied, the most significant correlations with the number of missing dots are high-shear viscosity and particle thickness (Table V). As high-shear viscosity increases, the number of missing dots decreases. The more open structure generally imparted to coatings by clays having large, high shear viscosity is consistent with the need for good compressibility. Brociner and Beazley (1980) concluded from studies of kaolins having a range of particle sizes and size distributions that a narrow size range independent of particle size is the most important property for imparting good rotogravure printability. They showed that narrow size distribution promotes improved compressibility and a consequent reduction in the number of missing dots. Certainly, the narrower the size distribution, the higher the high-shear viscosity. This reduction in the number of missing dots is supported by the data in Table V with respect to a reduction in colloid content, and reinforces the results of Sennet et al. (1982). For reduction in the number of missing dots, an addition of calcined clay seems to override the influence of colloid content.

Of the particle shape parameters, only thickness correlates with the number of missing dots, which decreases with an increase in particle thickness. The thickest particles, calcined kaolin, nearly eliminate the number of missing dots. Other blocky particles such as wet-ground calcium carbonate do not give a reduction in the number of missing dots. This discrepancy is probably related to poor coating holdout imparted by the broad particle size distribution of wet-ground calcium carbonate. Excessive abrasiveness precludes the commercial use of high levels of calcined kaolin in coating, and use as the sole pigment promotes extreme print mottle as shown in Fig. 5a, in sharp contrast to the use of the Fine No. 1 product (average thickness, 0.048 μm), which produces negligible mottle (Fig. 5b), but numerous missing dots.

Because blade application is the usual method of coating, troughs in the paper tend to be filled and crests tend to have an extremely thin or absent

Fig. 5. Rotogravure signatures show (a) print mottle with calcined clay and (b) missing dots with Fine No. 1 product.

coating. Selective filling of troughs seems to become most pronounced with increase in particle thickness (Hunger, 1977). This observation is true for lightweight coatings, but as coatweight increases kaolin particle geometry becomes less critical. Figure 6b shows a coating in which the sole pigment is calcined clay. Poor fiber coverage is apparent; hence, this paper should exhibit non-uniform ink absorption and print mottle. Crests in paper are produced by large, non-porous fibers. The calcined clay coating that fills troughs is uniformly porous and accepts ink more readily. Figure 6a shows the same paper coated with Fine No. 1 product. Note the relatively good fiber coverage. A major imperfection, however, is pinholes (lower middle) which are essentially absent in the coatings of calcined clay. The more rapid dewatering and better coating holdout produced by calcined clay minimize the number of pinholes.

The calcined clay and Fine No. 1 products represent the two extremes in coating character. Calcined clay fills troughs and effectively levels the surface without covering the crests, whereas the Fine No. 1 product imparts a thin coating in both troughs and crests leaving a more irregular swell and swale type of surface configuration. This interpretation of surface topography is reinforced by the major improvement in smoothness produced by calcined clay coatings compared with Fine No. 1 coatings (Table V).

If the calcined clay and Fine No. 1 coatings are examined in electro micrographs at much higher magnification, an additional major difference in coating structure becomes apparent. The calcined clay coating (Fig. 6b) shows a relatively large, uniform distribution of pores, and the Fine No. 1 coating (Fig. 6a) shows a relatively sealed surface. Obviously, the more open structure produced by the calcined clay gives the best ink transfer by means of capillary absorption. This surface porosity plus surface leveling readily ex-
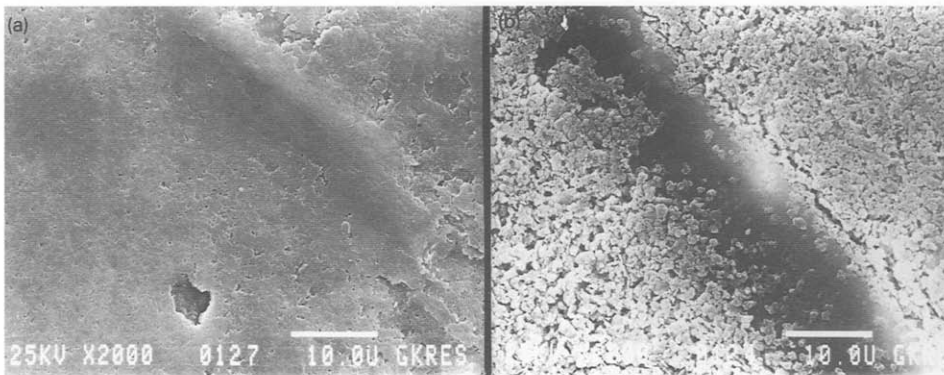

Fig. 6. Scanning electron micrographs of paper coatings using (a) Fine No. 1 and (b) calcined clay products.

plain the major reduction in the number of missing dots produced by the use of calcined clay.

The best compromise for good fiber coverage and the least number of missing dots is achieved by using delaminated clay. The thinner particles of delaminated clay give better fiber coverage than the calcined clay particles. The better coating holdout of delaminated clay gives less pinhole formation than with Fine No. 1. Blending delaminated clay with a small amount of calcined clay (Table V) allows the advantages of both systems to be realized, without developing print mottle.

In offset printing, the image is first transferred to a rubber blanket and then to the paper. Although coating smoothness is important, the rubber blanket tends to conform to the surface irregularities helping to ensure ink transfer. Offset inks are much more tacky than rotogravure inks; hence more binder must be used to give acceptable picking strength, which is the resistance of paper to plucking of particles or fibers by tacky inks. More interstices are filled with binder, and the porosity is significantly reduced.

Two of the most critical properties of paper for offset printing are print gloss and picking strength. Print gloss gives a more aesthetic appearance to four-color print images and tends to convey three-dimensional reality. As shown in Table VI, print gloss improves with a decrease in kaolin particle size. As with other coating characteristics, delaminated and non-delaminated kaolins behave differently. At equal particle size, esd, delaminated kaolins give significantly better print gloss than do non-delaminated kaolins. Smoothness is directly related to print gloss. Print gloss is a function of: (1) the extent to which the ink vehicle is held on the coating surface and (2) the resultant increase in smoothness by virtue of the filling of surface imperfections. Fine clay produces better print gloss because of its relatively good smoothness and low porosity, which produce good ink holdout. Delaminated clay is apparently superior to the Fine No. 1 product because of better coating

TABLE VI

Offset printability data for Georgia kaolin products

Kaolin product	Age	Print gloss (%)	Picking strength (rank[*1])	<2 μm (%)	Smoothness[*1] μm
Fine No. 1	Tertiary	64	4.5	95	1.54
No. 1	Cretaceous	63	3.5	92	1.61
No. 2	Cretaceous	62	2.0	83	1.66
Delaminated	Cretaceous	71	4.5	79	1.55
Coarse delam.	Cretaceous	63	2.0	56	1.66
90 Delaminated 10 Calcined	Cretaceous Tertiary	72	5.0	80	1.49

[*1]Lowest number best.

holdout, which improves smoothness and minimizes the formation of pinholes.

Because tacky inks can readily pull away specks of coating during the printing process, good picking strength is essential for four-color offset printing. Unlike print gloss, picking strength decreases with decrease in kaolin particle size. Here also, delaminated and non-delaminated kaolins behave differently. The more open structure of coatings produced with delaminated clay implies a less bonded surface and a consequent reduction in strength.

PAPER FILLING

Kaolin is used in the filling of paper to extend fiber for cost reduction and to improve opacity, smoothness and printability. Pigments disrupt paper strength by disrupting hydrogen bonding between cellulose fibers. As expected, this phenomenon is aggravated by a decrease in pigment particle size (Marton, 1974).

The rheology of kaolin–water systems is unimportant to paper filling. The kaolin–pulp mixture is handled at a low solid:liquid ratio (0.5–1.0%), and the kaolin is flocculated for retention within the fiber matrix using retention aids, such as aluminum sulfate and high molecular weight anionic and cationic polymers. The addition of these aids not only flocculates the kaolin, which facilitates physical retention, but may also bond aggregates to fibers by bridging.

Figure 7 shows agglomerates of kaolin in a filled paper concentrated at fiber intersections. Little kaolin is present along the length of fibers. Although both fibers and pigment enhance opacity, the weighted contribution by the pigment is substantially greater (Shaffer et al., 1982). The mechanism by which kaolin improves the opacity of paper is two-fold: (1) The kaolin disrupts bonding between fibers, which increases fiber area and light scatter (Bown, 1981); and (2) The aggregates of particles and voids within aggregates increases the light scattering interface.

Bown (1981) and Manasso and Schwartz (1986) showed that opacity contributed by kaolin to paper increases with decrease in particle size. Delaminated kaolins having the same particle size, esd, as non-delaminated kaolins produce superior opacity. Smoothness of paper, as well as retention of kaolin between fibers, increases with increasing particle size. Printability is improved by filling with kaolin, but considerably more work is needed to characterize the influence of particle morphology on this property.

The data in Table VII show that the opacity of filled paper contributed by kaolin increases with a decrease in particle size for non-delaminated products, confirming the work of the investigations listed above. Probably because of lower colloid content, delaminated kaolin produces a higher opacity than non-delaminated kaolin. Although the filler clay product gives the lowest opacity and at the same time has a lower colloid content, its particle size is
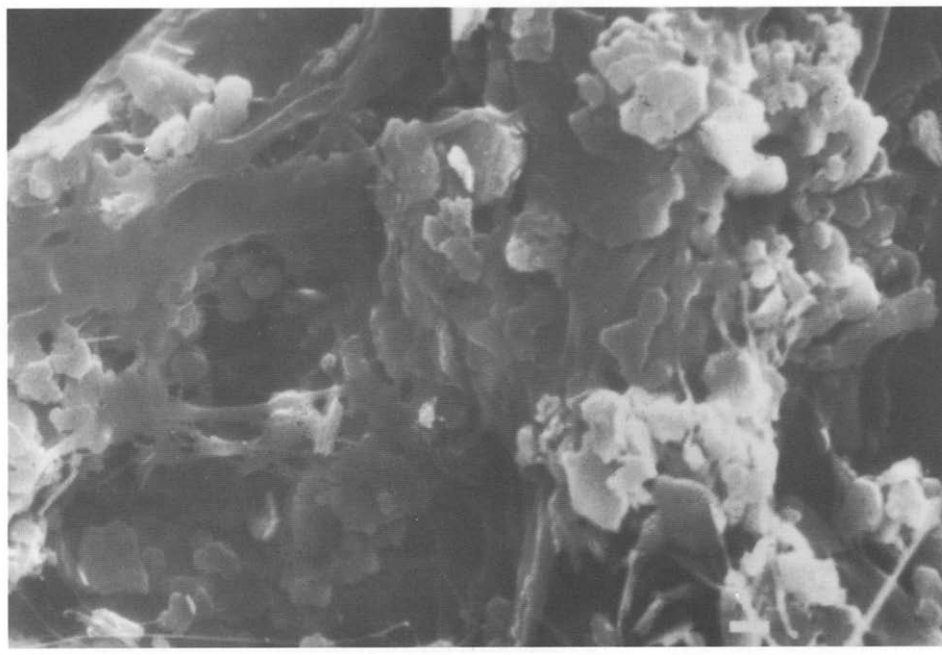
Fig. 7. Scanning electron micrograph of kaolin aggregates filling paper (scale = 1 μm).

TABLE VII

Properties of kaolin products as paper filles

Kaolin product	Age	Opacity (%)	Mullen burst strength (%)	<2 μm (%)	<0.5 μm (%)
Unfilled paper		65.8	63	–	–
No. 1	Cretaceous	75.9	19	92	52
No. 2	Cretaceous	75.1	20	83	46
Filler	Cretaceous	74.2	25	66	35
Delaminated	Cretaceous	76.0	19	79	38
Delaminated	Cretaceous	76.4	22	77	25
Calcined	Tertiary	80.4	17.5	83	11

too coarse to form voids on flocculation that are of optimum diameter for light scatter.

Calcined clay imparts inordinately high opacity compared with uncalcined clay, due to the following parameters: its high void content of fused aggregates, its open packing structure which is produced by its irregular shape and a paucity of colloidal particles, its tendency to form floc structures smaller

than those formed by uncalcined kaolin, and its disruption of fiber bonding. Its low surface energy compared with uncalcined kaolin reduces the extent to which the calcined clay will flocculate. The formation of small flocs is evident from the poor retention of calcined kaolin compared with uncalcined kaolin (J.A. Manasso, pers. commun., 1987). Because of these smaller floc structures, the light scattering interface and, hence, opacity, is enhanced.

The strength of filled sheets is indicated as Mullen burst strength in Table VII, which is a measure of bonding between fibers. Note that the introduction of kaolin substantially decreases Mullen burst strength. In general, strength increases with increase in particle size. In paper filling, as opposed to individual kaolin particles, agglomerates of particles produced by retention aids become the functional entity. Large agglomerates reduce the number of particles that interfere with hydrogen bonding between fibers, and therefore, have less of an adverse effect on paper strength. As shown by the data listed for the two delaminated kaolins, strength is inversely related to colloid content. Calcined clay produces relatively low paper strength, probably due, in part, to the formation of smaller aggregates, which produce increased debonding. Increased sheet bulk, resulting in a reduction in the bond area between fibers is considered to be a major reason for loss in paper strength (Gill, 1988). Certainly calcined clay does insure sheet bulk over most filler clays, and thus is probably a major factor in strength reduction. The relative influence on strength of the number of pigment particles versus sheet bulk deserves further study.

SUMMARY

Kaolin is the dominant particulate mineral used in both filling and coating of paper. It extends fiber, thereby reducing cost, and improves the appearance of paper, as reflected by gloss, smoothness, brightness and opacity. Kaolin has its greatest utility in the improvement of paper printability. Brightness is one of the most critical requirements of kaolin used in paper and is controlled largely by the elimination of impurity minerals, such as anatase and Fe_2O_3 occurring as "limonite".

To coat paper, high solid:liquid suspensions of pigment and binder are applied with a blade to the paper surface at high speeds. Because the rheology of the suspension is critical to this process and kaolin generally is the most abundant component of the coating suspension, an understanding of the parameters of kaolin that influence the flow characteristics of the suspension is essential. Low-shear viscosity of the suspension correlates with aspect ratio of the kaolin and is a direct function of effective particle volume. Effective particle volume is defined as the swept volume described by a rotating platelet. The effective particle volume of colloidal particles is also significantly influenced

by the amount of adsorbed water. High-shear viscosity is a function of particle packing, which is affected by colloid content of the kaolin and average diameter of the particles.

The optical properties of coatings are a function of particle size and particle size distribution. Low colloid content promotes the formation of coating structures that contain numerous voids, which enhance light scatter for improved brightness and opacity. In addition, low colloid content increases coating holdout, such that imperfections in paper surfaces are more effectively covered. This property and particle size are the major parameters influencing the gloss of coatings.

The most common commercial printing systems are rotogravure and offset, and one of the more important measurements of rotogravure quality is the number of missing dots. Three kaolin parameters correlate significantly with the number of missing dots: colloid content, average thickness, and high-shear viscosity. Because of reduced colloids, better coating holdout and greater void volume are obtained for coatings. Improved coating holdout of coatings lead to improved smoothness, and higher void volume produces superior compressibility, both phenomena facilitating better ink transfer – the ultimate mechanism for reducing the number of missing dots.

Average thickness of kaolin correlates positively with sheet leveling or smoothness, which permits more intimate contact of the coated paper with the printing cylinder. Large high-shear viscosity implies an open pigment structure, which persists as an open structure in the coating structure to give improved compressibility.

In offset printing, two of the most important parameters are print gloss and picking strength. Improved print gloss correlates inversely with particle size and directly with smoothness, and is favorably influenced by improved coating holdout. Picking strength generally decreases with decrease in particle size, but the reduction in bonded surface area arising from more open structures can have a deleterious effect on picking strength.

Filling paper with kaolin significantly influences opacity and strength. The opacity of paper can be enhanced via the introduction of pigment by the debonding of fibers with a resultant increase in the light scattering surface area. Increased light scattering interface, contributed by aggregates of particles and voids within aggregates, is the major mechanism by which filler pigments enhance paper opacity.

In contrast to opacity, strength decreases with decreasing aggregate size, probably due to interference with hydrogen bonding between fibers. The decrease in strength imposed by the incorporation of pigments within paper imposes a relatively low limit to acceptable filler loading. Kaolin technology in papermaking, although moderately well characterized, deserves considerably more research attention. Full characterization of mechanisms by which kaolins enhance quality and functionality of paper would not only enhance

knowledge of kaolin science, but would open corridors for innovative developments within the kaolin, paper and printing industries.

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