NATURE AND UTILITY OF HEXAMETHYLENEDIAMINE-PRODUCED KAOLIN FLOC STRUCTURE

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Abstract—Kaolin floc structures of commercial utility are produced by adsorption of hexamethylenediamine. These flocs are largely face-to-face structures with small diameter platelets of colloidal kaolinite aggregated on larger platelets of kaolinite and muscovite. Because of its higher charge density, muscovite is more effective than kaolinite in scavenging colloidal particles.

Although earlier workers have been at odds as to where amines adsorb on kaolinite, the present work indicates that both edge and basal surfaces are involved. Evidence for this contention is two-fold: (1) Face-to-face and edge-to-face flocculation of hexamethylenediamine kaolins has been observed. (2) Polyesters have been observed adsorbed on basal and edge surfaces of ethylenediamine-treated kaolins.

The mechanism by which kaolinite particles are bonded together into floc structures is unclear. Bridging by hexamethylenediammonium ions is a probable mechanism up to satisfaction of the cation-exchange capacity; further amine addition continues to promote flocculation. From this observation it is inferred that, in addition to bridging, hydrogen bonding and, perhaps, van der Waals forces are instrumental in floc formation. Although rheologically inferior to the untreated equivalent, these chemically induced flocs of kaolinite provide loosely packed, randomly oriented structures in paper coatings. Improved brightness, opacity, and printability of paper coatings arise from this structure.

Key Words—Flocculation, Hexamethylenediamine, Kaolin, Muscovite, Paper, Rheology.

INTRODUCTION

The modification of clay surfaces by organic materials is important from both fundamental and commercial points of view. In contrast with smectite, only a few investigations of this type have dealt with the kaolin-group minerals, and little is known about the mechanisms of adsorption and the resultant aggregate structures that are formed. Grim *et al.* (1947) noted that the adsorption of organic cations by kaolin clays beyond their cation-exchange capacity (CEC) takes place by van der Waals bonding. The adsorption of ethylenediamine on hydrogen-exchanged kaolinite, studied by Conley and Lloyd (1971), is believed to be confined to edge faces. On the other hand, Solomon *et al.* (1971) contended that alkylamines adsorb on the basal surfaces of aluminum-exchanged kaolins. Intercalation of kaolinite with hydrazine has been demonstrated by Weiss (1963).

Amine adsorption on kaolins has been used in industry to produce greater dispersion in polymer systems and to neutralize catalytic surface activity of the clay. For example, Wilcox (1961) improved the hydrophobicity and wetting properties of kaolinite in organic media by the adsorption of long-chain fatty amines. Bundy (1963, 1965) used ethylenediamine-adsorbed kaolins, subsequently treated with an emulsified polyester or a long-chain fatty acid, to develop desired organophilic surfaces. Benesi *et al.* (1959) used amines to neutralize the surface acidity of kaolinite carriers, thereby inhibiting the catalytic decomposition of insecticides.

The surface treatment of kaolin with polyamines to improve its paper coating properties was described by Bundy (1978) and Bundy *et al.* (1983). Many functions of kaolin in paper coatings are improved by greater dispersion of the clay; however, the porosity of paper coatings can be optimized for improved optical and printing properties by the incorporation of specially designed floc structures. The adsorption of certain polyamines on kaolinite promotes the formation of such flocs. The present paper describes the nature of amine-induced kaolin flocs and their functionality in paper coatings.

EXPERIMENTAL PROCEDURE

Floc preparation

Floc structures for use in paper coatings are prepared commercially from kaolin clay, hexamethylenediamine, muscovite, and citric acid. Citric acid is used to disperse titania and other colloidal components, and mica is added to increase flocculation if excessive amounts of colloidal material are present in the kaolin. In the present study, kaolin flocs were prepared in the following manner: Cretaceous kaolin (200 g) from Washington County, Georgia, having an average particle size of 80 to 93% ≤ 2 μm was dispersed with 0.2% sodium polymetaphosphate in 800 g of water. Dry muscovite (0.2 wt. %) was added to the kaolin dispersion along with hexamethylenediamine (0.08 to 0.15 wt. %). Citric acid was added in amounts equal to that of hexamethylenediamine.
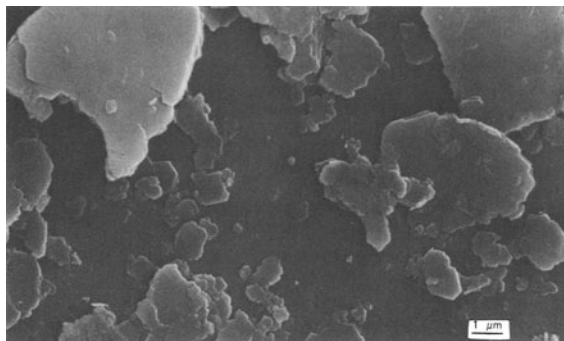
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Figure 1.   Scanning electron micrograph of kaolin floccula-
tion produced by hexamethylenediamine.

Methods

Zeta potentials of clay-water suspensions were de-
termined with a Lazer Zee Meter, Model 501, Pen
Kem, Inc. Particle geometry was determined by direct
measurement of particles in shadowed transmission
electron micrographs. Samples were dispersed at high
clay-to-water ratio (0.63) in a Waring Blendor and di-
luted 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. The average aspect ratio of a sample
was calculated from the aspect ratios of about 1000
particles.

Particle sizes were determined by the hydrometer-
centrifugal sedimentation procedure described by Nor-
ton and Speil (1938). Scanning electron micrographs
(SEM) were obtained with a JEOL JSM35-C scanning
electron microscope.

Cross sections of paper coatings were prepared by
dipping coated specimens in water for a few seconds
and mounting them in a surface-section cutting block.
The block was immersed in a beaker of liquid nitrogen
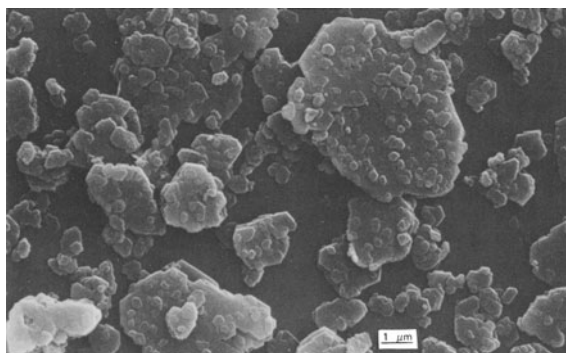until the intensity of boiling subsided. The portion of

Table 1.   Particle geometry of hexamethylenediamine-treat-
ed kaolin.

Particle size (e.s.d.) (μm)	Amine-treated (% less than)	Untreated (% less than)
5	99	99
3	97	97.5
2	90.5	92.0
1	65.5	70.5
0.5	31.5	41.0
0.3	12.5	22.0
0.17	5.5	9.5
Average aspect ratio	7.0	10.4
Average thickness (μm)	0.23	0.11
Average diameter (μm)	1.33	0.93

the sample extending above the block was snapped off
with tweezers, mounted on a sample stub with silver
paint, and coated with Au-Pd for scanning electron
microscopy.

PHYSICAL AND CHEMICAL NATURE OF FLOC STRUCTURE

Particle geometry

Kaolinite flocs produced by adsorption of hexameth-
ylenediamine are shown in Figure 1. Large diameter
plates are cluttered with small diameter platelets in a
face-to-face configuration. The structures are relatively
stable and can be disrupted only by high shearing in
suspensions having high solid to liquid ratios, generally
greater than 0.65. Untreated kaolinite, prepared in a
similar manner, shows few small diameter platelets
adhering to the basal surfaces of larger plates (Figure
2).

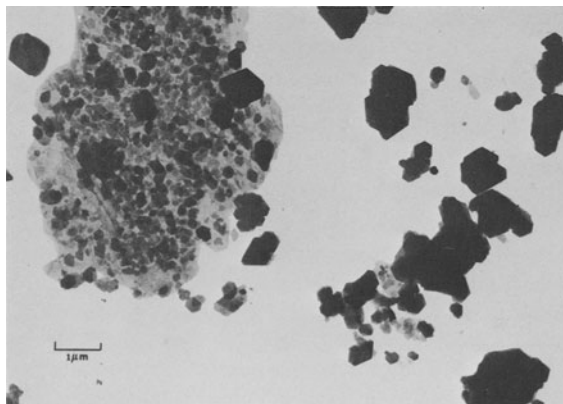The particle geometry data listed in Table 1 indicate

Figure 2.   Scanning electron micrograph of kaolin.

Figure 3.   Transmission electron micrograph of amine-treat-
ed kaolin showing kaolin flocculation on muscovite surface
at upper left.

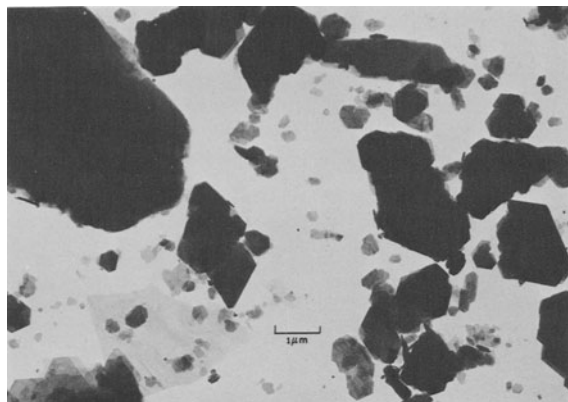Figure 4.   Transmission electron micrograph of mixture of kaolin and muscovite. Muscovite = transparent, irregular shaped particles.

Figure 6.   Transmission electron micrograph of ethylenediamine-treated kaolin showing adsorbed polyester micelles (black particles <0.01 μm).

that amine-treated kaolin contains significantly fewer particles in the ≤1-μm size range compared with untreated material, with the maximum difference (about 10%) being in the 0.3–0.5-μm size range. The aspect ratio of amine-treated kaolins is also less than that of the untreated material. The average thickness is about twice, but the average diameter only about 40% larger than the untreated kaolin, due to the face-to-face configuration described above and to overlapping flocs. Particle size measurements also show that the coarsest amine-treated particles are twice as abundant as their untreated counterparts.

Rheology

Changes in particle geometry and surface chemistry due to the amine treatment also produce major changes in the rheology of the kaolin. Clay-water suspensions of the untreated kaolin at 70% solids content closely approach Newtonian flow; however, suspensions of the amine-treated material cannot be prepared at a solids content much greater than 63%, and even at this lower solids content, the suspensions are highly dilatant. Such
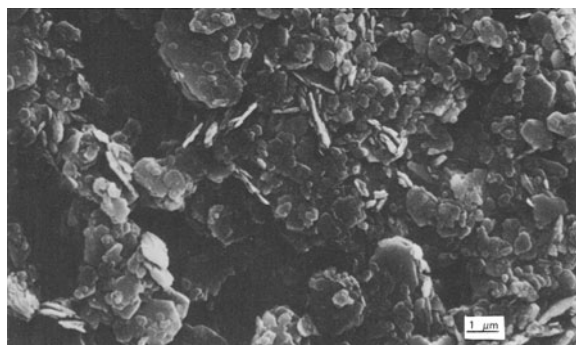

Figure 5.   Scanning electron micrograph of amine-treated kaolin, prepared by attrition grinding.
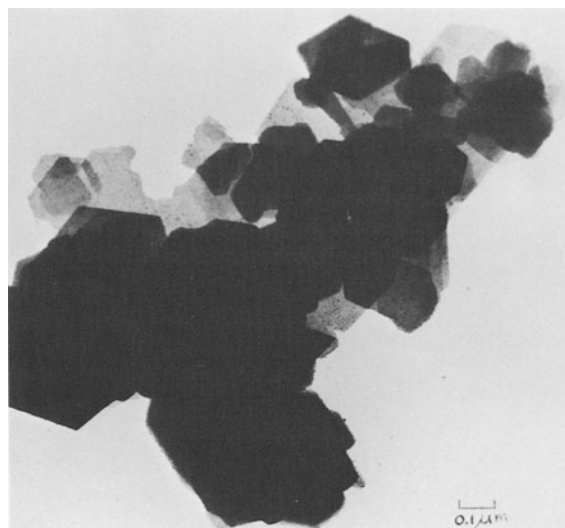
differences in rheology are thought to be due chiefly to the effective increase in particle volume produced by imbricate structures of the amine-treated kaolin. As the diameter of the flocculated particles increases, the volume occupied by a rotating particle, of course, increases by the cube of the diameter. As the effective diameter and volume increase, greater interaction between particles gives rise to a higher viscosity.

Zeta potentials of the untreated kaolin (−49 mV) are substantially higher than those of the amine-treated material (−38 mV). The decrease in zeta potential reflects the reduction in repulsive forces between particles, and the resultant increase in particle-particle interaction yields an increase in viscosity.

Amine-treated muscovite is a better flocculant of colloidal-size kaolinite particles than is kaolinite itself. As shown in Figures 3 and 4, the accumulation of colloidal kaolinite on the basal surfaces of amine-treated mica substantially exceeds that observed with large platelets of amine-treated kaolin—not surprising considering the higher charge density on mica (Greene-Kelly, 1962).

Although adsorption of hexamethylenediamine appears to occur on both basal and edge surfaces, the dominant floc configuration observed in electron micrographs is face-to-face. The preparation of samples for electron microscopy was at high solids content (63%) and created significant shearing action which may have more readily disrupted whatever edge-to-face structures that formed initially.

Conley and Lloyd (1971) suggested that amines adsorbed on edge sites of hydrogen-exchanged kaolins. Because of the correlation of amount of amine adsorbed and edge area, they considered the basal sur-
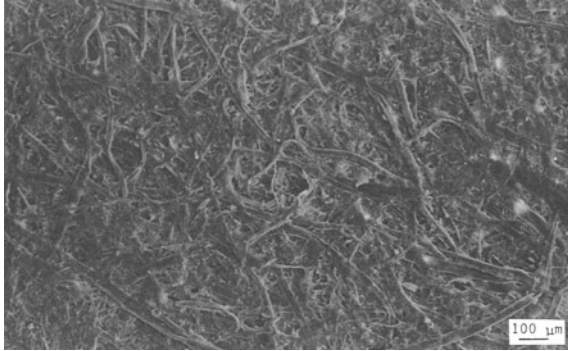
Figure 7.   Scanning electron micrograph of uncoated paper.

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

n_1, refractive index of pigment
n_0, refractive index of adhesive or air

starch - clay, R = 0.000099   clay - air, R = 0.045

Figure 9.   Schematic diagram showing influence of clay, starch, and air on Fresnel reflection.

faces to be largely unaltered. In contrast, Solomon *et al.* (1971) indicated that alkylamines adsorbed on aluminum-exchanged kaolins adjacent to cation-exchange sites located largely on basal surfaces.

That amine adsorption occurred on both surfaces is illustrated in Figure 5. The kaolin was subjected to attrition grinding with hexamethylenediamine. Grinding not only delaminated kaolin stacks, but fractured many platelets. The exposure of nascent surfaces clearly produced stronger bonding between particles and contributed to the persistence of edge-to-face structures despite the high shear dispersion techniques used in the TEM preparation. Further evidence for adsorption on both surfaces is provided in Figure 6, an electron micrograph of ethylenediamine-dispersed kaolin subsequently treated with an emulsified polyester (Bundy, 1963). Micelles of polyester, perhaps more concentrated at edges, seemingly have adsorbed on both edge and basal surfaces.

Cloos and Laura (1972) showed that the ethylenediammonium ion ($EDAH_2^{2+}$) is the dominant species below pH 7 on polyamine-treated smectites. Above pH 7, the monoprotonated species ($EDAH^+$) dominates, with the molecular species (EDA) increasing in concentration. Be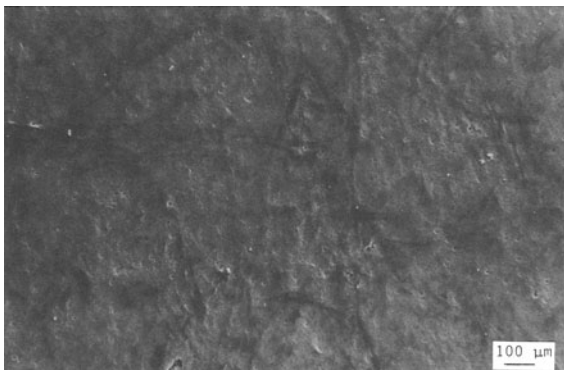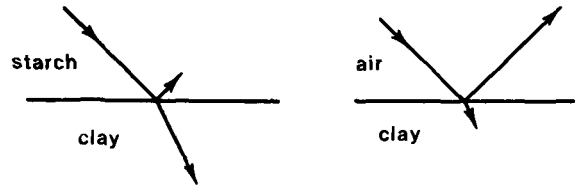low pH 7, the diprotonated form is adsorbed in amounts up to the exchange capacity of the clay. Above this value, both $EDAH^+$ and EDA are adsorbed by hydrogen bonding between NH_2 and NH_3^+ groups. Dimers as well as trimers are formed by virtue of adsorption beyond the exchange capacity.

Extrapolating the observations of Cloos and Laura (1972), similar phenomena probably take place in the adsorption of hexamethylenediamine on kaolin. Adsorption of diprotonated hexamethylenediamine in amounts up to the cation-exchange capacity apparently is accompanied by bridging to produce face-to-face and edge-to-face flocs. Beyond this value, flocculation continues, presumably by hydrogen and van der Waals bonding.

APPLICATION TO PAPER COATING

Kaolin in conjunction with binders (e.g., starch and styrene butadiene latex) is applied to paper surfaces to improve brightness, opacity, gloss, and, most importantly, printing properties. Figures 7 and 8 are electron micrographs of uncoated and kaolin-coated paper surfaces, respectively. The coated paper shows significantly greater smoothness and homogeneity, properties

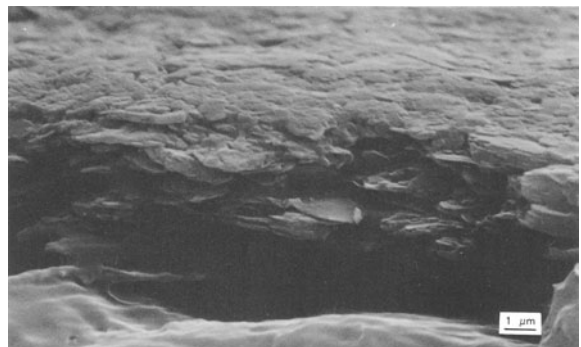Figure 8.   Scanning electron micrograph of paper coated with kaolin.

Figure 10.   Scanning electron micrograph of cross section of kaolin coating on paper.
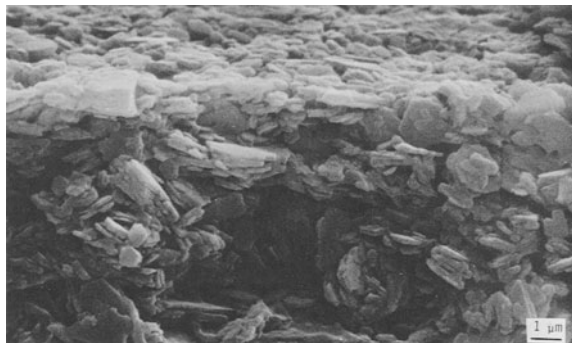
Figure 11. Scanning electron micrograph of cross section of amine-treated kaolin coating on paper.

that are essential for uniform ink absorption and for fidelity of four-color printing.

The combination of high refractive index titania pigments, anatase and rutile, with low refractive index materials in paper coatings results in high light scatter. To increase light scattering properties of low refractive index pigments, structures containing high porosity must be produced. The need to incorporate air interfaces into such materials to improve optical properties is indicated by the Fresnel equation and shown diagrammatically in Figure 9. From the Fresnel equation, the greater the difference in the refractive indices of the components of a system, the greater the reflection coefficient. In paper coating systems, the refractive index of the binder (about 1.5) is close to that of kaolinite, about 1.56. Incorporating air-filled voids (R.I. $\simeq$ 1) that interface with kaolinite results in a substantial increase in the difference between the refractive indices of the system components. As illustrated in Figure 9, a reflection coefficient several orders of magnitude higher can be obtained in an idealized clay-air system versus an idealized clay-starch system. This increase in reflection coefficient corresponds to significant increases in brightness and opacity.

Void development in paper coatings via amine-modified kaolin arises, in part, from a random orientation of platelets. Characteristically, as shown in Figure 10, coating grades of kaolin give a desirable high degree of preferred orientation, with clay platelets being parallel to the plane of the sheet. This system corresponds to relatively dense packing.

A scanning electron micrograph of a coating containing the amine-modified clay is shown in Figure 11. A random structure of loosely packed platelets gives a system of relatively high void volume. Lepoutre (1978) showed that when water is removed rapidly from a clay-water system the filter cake reflects the random orientation of platelets in suspension. Because of the flocculation of fine particles and inefficient packing, increased permeability permits faster dewatering.

Shrinkage forces exerted during the drying of coat-

ings are correspondingly reduced due to the lower zeta potential of the amine-treated kaolin. Presumably, the looser packing depicted in Figure 11 results from this phenomenon. Thus, the more open structure of amine-treated kaolin paper coatings arises from rapid dewatering and consequent random orientation along with looser packing stemming from lower zeta potential.

Climpson and Taylor (1976) showed that the optimum diameter of voids in coatings for light scatter is 0.3 to 0.7 μm. The pore structure shown in Figure 11 indicates that many of the voids fall within this optimum size range.

As discussed by Bundy et al. (1983), optimal coating structure significantly increases both brightness and opacity of coated paper, although opacity is more important for lightweight publication coatings in which this pigment has greatest potential. By virtue of the bulkier coating and better fiber coverage, printability is improved for both offset and rotogravure coated papers.

CONCLUSIONS

1. Kaolin floc structures, largely face-to-face with selective aggregation of small diameter platelets on larger plates, are produced by hexamethylenediamine treatment. Rheology of amine-treated kaolins is degraded by zeta potential reduction and by increased particle diameter arising from imbricate structures.
2. Muscovite, because of its higher layer-charge density, is more effective than kaolinite in scavenging colloidal particles on basal surfaces.
3. Amine seems to be adsorbed on both basal and edge surfaces as suggested by face-to-face and edge-to-face flocculation in hexamethylenediamine-treated kaolin. This contention is further attested to by polyester adsorption on edge and basal surfaces of ethylenediamine kaolin.
4. Hexamethylenediamine-modified kaolins are potentially useful in paper coating to produce improved optical properties and printability. By virtue of random orientation and loose packing, porosity in paper coating is increased which in turn improves light scatter for greater brightness and opacity. Increased bulk of coatings gives greater fiber coverage for better printability.

REFERENCES

Benesi, H. A., Sun, Yun Pei, and Loeffler, E. S. (1959) Stabilized pesticidal compositions: *U.S. Patent* **2,868,688,** Jan. 13, 1959, 10 pp.

Bundy, W. M. (1963) Coated mineral filler for organic polymers, and method of forming the coated filler: *U.S. Patent* **3,080,256,** Mar. 5, 1963, 3 pp.

Bundy, W. M. (1965) Hydrophobic organophilic particulate matter: *U.S. Patent* **3,211,565,** Oct. 12, 1965, 2 pp.

Bundy, W. M. (1978) High bulking clay pigments and methods of making the same: *U.S. Patent* **4,075,030,** Feb. 21, 1978, 3 pp.

Bundy, W. M., Harrison, J. L., and Ishley, J. N. (1983) Chemically induced kaolin floc structures for improved paper coating: *TAPPI Coating Conference Preprints,* 175–187.

Climpson, N. A. and Taylor, J. H. (1976) Pore size distributions and optical scattering coefficients of clay structures: *TAPPI Coating Conference Preprints,* 85–94.

Cloos, P. and Laura, R. D. (1972) Adsorption of ethylenediamine (EDA) on montmorillonite saturated with different cations. II. Hydrogen- and ethylenediammonium-montmorillonite: protonation and hydrogen bonding: *Clays & Clay Minerals* **20,** 259–270.

Conley, R. F. and Lloyd, M. K. (1971) Adsorption studies on kaolinites. II. Adsorption of amines: *Clays & Clay Minerals* **19,** 273–282.

Greene-Kelly, R. (1962) Charge densities and heats of immersion of some clay minerals: *Clay Min. Bull.* **5,** 1–8.

Grim, R. E., Allaway, W. H., and Cuthbert, F. L. (1947) Reaction of different clay minerals with some organic cations: *J. Amer. Chem. Soc.* **30,** 137–142.

Lepoutre, P. (1978) Paper coatings: substrates absorbency and coating structure: *TAPPI Coating Conference Preprints,* 61–68.

Norton, F. H. and Speil, S. (1938) The measurement of particle sizes in clays: *J. Amer. Ceram. Soc.* **21,** 89–97.

Solomon, D. H., Swift, J. D., and Murphy, A. J. (1971) The acidity of clay minerals in polymerizations and related reactions: *J. Macromol. Sci. Chem.* **3,** 587–601.

Weiss, A. (1963) A secret of Chinese porcelain manufacture: *Angew. Chem. Int. Ed. Engl.* **2,** 697–703.

Wilcox, J. R. (1961) Modified kaolin as a polyester resin filler: *U.S. Patent* **2,999,089,** Sep. 5, 1961, 4 pp.