INTERRELATIONSHIPS OF PHYSICAL
AND CHEMICAL PROPERTIES OF KAOLINITES

by

W. M. BUNDY,* W. D. JOHNS,† and H. H. MURRAY*

ABSTRACT

RANK-CORRELATION coefficients are utilized to show relationships between physical and chemical properties of Georgia and English kaolins. Montmorillonite impurity in the Cretaceous kaolins shows high level correlations with magnesium, iron, silica–alumina ratio, CEC, water sorption, surface area, sediment volume, and Brookfield viscosity. Cation exchange capacity of these kaolins is believed to be related primarily to montmorillonite impurity. Low shear viscosity measurements show a strong correlation to properties indicative of montmorillonite. Correlations with viscosity are believed to be related primarily to surface area and particle packing. Packing volume exerts a dominant effect on high shear rheology. Differences in particle shape are not of sufficient magnitude to show a significant effect on rheology. A strong inverse relationship of vanadium with high shear viscosity indicates that the wetting effect of vanadium organic complexes or adsorption of $(VO_4)^{-3}$ tetrahedra at gibbsite edge faces may be mechanisms for viscosity reduction. Brightness and whiteness are related to titanium and iron-bearing impurities as well as the amount of particles having optimum diameters for light scattering. Well-crystallized kaolinites are believed to have been derived primarily from feldspar. Muscovite alteration may be retarded where well-crystallized kaolinites occur. To account for the inverse relation of vanadium with crystallinity, it is suggested that complex vanadium ions may act as growth poisons.

INTRODUCTION

KAOLINITE is rapidly growing in importance as a raw material for a plethora of industries. Although a common component of plastic, ink, paint, ceramic and rubber products, filling and, particularly, coating of paper are the dominant uses of well-crystallized Georgia kaolins. For paper coating, economy demands preparation of concentrated kaolinite suspensions where rheology becomes critically important. Of almost equal significance are color characteristics, and white kaolin coatings with a blue to violet hue are commonly required and psychologically preferred for print contrast on high grade paper.

Increasingly stringent requirements by the paper and printing industries necessitates increasingly stringent controls on kaolinite products. Although numerous work has been conducted on Georgia kaolins, reasonable methods for commercial control of optical and rheological properties still elude adequate understanding. Murray and Lyons (1956, 1960) have studied the

* Georgia Kaolin Company, Elizabeth, New Jersey.
† Department of Geology, Washington University, St. Louis, Missouri.

relationship of crystallinity to numerous kaolinite properties. Hinckley (1961) conducted an extensive investigation of Georgia kaolins, and collated highly statistical data on many physical and chemical variables. This study was carried out exclusive of optical and rheological considerations. Ormsby, Shartsis, and Woodside (1962) studied the relationships between particle size, surface area, exchange capacity, and crystallinity, whereas Ormsby and Marcus (1964) investigated the relationship of these properties to rheology. The present investigation is an attempt to elucidate more clearly inter-relationships of many kaolin variables with attention being drawn to optical and rheological properties.

CHOICE AND CHARACTERIZATION OF MATERIALS

Five distinct kaolins were selected for study showing significant differences in crystallinity and coincident variations in chemical and other physical properties. These clays include four secondary, or sedimentary Georgia kaolins, and one primary English kaolin. Because these clays represent extremes in geological origin, it is believed that the inclusion of both types may enable a more lucid understanding of kaolinite deportment.

The Georgia kaolins occur within the sands of the Upper Cretaceous Tuscaloosa formation as irregular lenticular bodies. Sediments of the Tuscaloosa formation are believed to have been derived from crystalline rocks occupying the site of the present Piedmont. Eroded material was transported by streams, and deposited along the Cretaceous coastline. Although it is generally agreed that kaolinite has been derived by the alteration of feldspars and micas, it is not clear whether kaolinization was dominant in the Piedmont area or after transportation and deposition. It is probable, however, that kaolinization was a continuous phenomenon, and occurred from the source area to the site of deposition. Bates (1964) has presented a candid review of the origin of these deposits.

The English primary kaolin is a product of hydrothermal alteration of granite. Kaolinite has been derived primarily from feldspars, and crystallinity, seemingly, is a function of proximity to former hydrothermal solution channels (Exley, 1964).

Each of the clays was classified by centrifugation to coarse, medium, and fine fractions, which generally delineate types being used by the paper coating industry. These particle sizes, originally, were chosen as the basis for a study of paper coating properties (Bundy, Johns, and Murray, 1965) whereas the present investigation is confined to the interrelationships of kaolin properties.

Table 1 shows data for the five kaolinites including particle size, crystallinity index, and mineralogical composition other than kaolinite.

There is a general, but not lucid, indication of increasing crystallinity with decreasing particle size within each clay type. Ormsby, Shartsis, and Woodside (1962) studied Georgia kaolins, and fractionated each sample into six different size classifications. Their data unequivocally demonstrate an increase

TABLE 1.—PARTICLE SIZE, CRYSTALLINITY, AND MINERALOGICAL COMPOSITION
OF KAOLINS

Sample	Particle size % > 1 μ	Crystallinity index	Mineralogical composition other than kaolinite	
			X-ray	Electron micrographs
English	43 69 79	0.77 0.51 0.45	Muscovite Quartz	Montmorillonite
Georgia A	37 66 86	0.42 0.40 0.41	Anatase	Montmorillonite
Georgia B	34 66 88	0.12 0.02 0.05	Anatase	
Georgia C	40 60 72	0.03 0.05 0.00	Anatase	Montmorillonite
Georgia D	22 22 40	0.00 0.00 0.05	Anatase	Montmorillonite

in crystallinity with decreasing particle size within a single sample. In contrast, among kaolinite types, in the present work, there is a general increase in particle size with increase in crystallinity.

Although about 5% muscovite was resolved in English kaolin by X-ray diffraction, none was resolved in Georgia kaolins. Under the petrographic microscope, however, 325 mesh residues show that some muscovite is present in all of the kaolin samples.

Georgia kaolins normally contain 1.0 to 2.0% anatase, a strong discolorant, whereas English kaolins show a paucity of titanium-bearing minerals. Apparently, iron is the most abundant and strongest discoloring agent in English kaolins.

Of considerable significance to the present study is the occurrence of minute quantities of montmorillonite in all but one of the kaolins. Approximately 5% montmorillonite must be present before X-ray diffraction can be used as an identification technique. Approximation of the content of montmorillonite, which occurs as minute, lath-shaped particles, can be obtained from shadowed electron micrographs. Edge faces of kaolinite rarely are coated with montmorillonite, and this is an indication of the reason for montmorillonite occurrence in both fine and coarse kaolinite fractions. These approxi-

mations of montmorillonite content show high level correlations with chemical components related to 2 : 1 clay minerals, and will be discussed below.

METHODS OF ANALYSIS

Physical and chemical properties determined for each kaolinite sample are shown below:

Chemical composition	Hercules viscosity
Cation exchange capacity (CEC)	Particle size ($\% > 1.0\ \mu$)
Charge density	Shape factor (S.F.)
Surface area	Brightness
Relative sediment volume	Whiteness
Water sorption	Crystallinity (Xtly)
Brookfield viscosity	

Chemical analyses were carried out with wet chemical and spectrographic procedures by Maynard Coller and R. K. Leininger of the Indiana Geological Survey. X-ray emission procedures were also utilized.

Cation exchange capacity was measured by a sodium exchange procedure and was conducted by Dr. Edward Jonas at the University of Texas. Charge density was calculated as the ratio of CEC in meq/g to surface area as m^2/g after the fashion of Greene-Kelly (1962).

Surface area was determined by a glycerol adsorption technique similar to procedures described by Diamond and Kinter (1956) and Woodside and Ormsby (1960). In addition to these procedures, a calibration curve was constructed with B.E.T. nitrogen adsorption data relating surface area to glycerol retention. The B.E.T. standard samples were included for comparison with each glycerol measurement.

Relative sediment volume of kaolinite suspensions was measured in accordance with the procedure outlined by Hagemeyer (1960) using the Baroid filter press. Water sorption determinations were conducted by the procedure described by Keeling (1958).

Rheological measurements were obtained at 69% solids with the exception of the fine fraction of English clay, which was determined at 65% solids. Low shear viscosity was determined with a Brookfield viscosimeter at 100 RPM, and high shear viscosity with a Hercules viscosimeter in the range of 200 to 1100 RPM at a cycle time of 20 sec. The pH's of the suspensions were controlled between 6 and 6.5.

Particle size was determined by the hydrometer-centrifugal sedimentation procedure, and is reported as equivalent spherical diameter. Oden's correction was applied to compensate for homogeneous sedimentation.

Shape factors were obtained from shadowed electron micrographs using the following relationship:

$$\text{Shape factor (S.F.)} = C/(AB)^{1/2}$$

where C is the particle thickness, and A and B represent maximum and

minimum diameters. These determinations were carried out for each discrete kaolinite particle and averages computed for each clay sample. Electron micrographs were prepared by John Brown of the Georgia Institute of Technology.

Brightness and whiteness were measured with a General Electric Recording Spectrometer using a MgO reference. Brightness was determined as per cent reflectance at a wavelength of 457 μ. Difference in reflectance at 400 and 700 μ is designated, arbitrarily, as a whiteness measurement. Whiteness increases as the calculated value approaches zero.

Potential variations in kaolinite crystallinity are clearly described in the original work of Brindley and Robinson (1946) whereas Murray (1954) defined examples of kaolinites showing differing degrees of crystallinity. The empirical method for measuring crystallinity suggested by Johns and Murray (1959) was used in the present study. The measurement serves as a crystallinity index and permits quantitative comparisons.

Correlations of data were obtained by means of rank correlation coefficient (Volk, 1956):

$$R = 1 - \frac{6\Sigma d^2}{n(n^2 - 1)}$$

where R is the rank correlation coefficient, d is the difference between each pair of rankings, and n is the number of pairs ranked. The possible values of R range from -1.0 to $+1.0$. Where the value is 1.0, there is a highly probable relationship. At 0.0, there is no correlation, and at -1.0, an inverse or discordant relationship is probable. For fifteen pairs of rankings, as in the present study, a minimum value of about 0.5 must be obtained to be at the 95% confidence level, and a minimum value of about 0.6 for the 99% level.

Profusion of data preclude extensive discussion of each relationship, and many of the observations are clearly subjects for further investigation. Relationships which are unique to Georgia kaolins are occasionally over-shadowed by seemingly anomalous trends with English kaolins. It is hoped that this approach will facilitate a better overall understanding of kaolinite deportment and will preclude erroneous interpretation that conceivably can be offered by the study of a single source of kaolinite.

EXPERIMENTAL RESULTS

Rank correlations for the physico-chemical properties of kaolinites are shown in Fig. 1. Relationships of elemental constitutents show wide significance, and are useful for the evaluation of non-kaolinite components, distribution of elements, and crystal growth phenomena. Particularly noteworthy are, not only the mutual correlations of magnesium, iron, and silica–alumina ratio, but corresponding relations with CEC, surface area, sediment volume, Brookfield viscosity, and water sorption. Considering magnesium as a component which may be most specific to montmorillonite, it is not surprising that qualitative correlations are obtained with montmorillonite as

	MgO	Fe₂O₃	SiO₂/Al₂O₃	K₂O	TiO₂	V₂O₅	CEC	Charge Density	Surf. Area	Sed. Volume	H₂O Sorption	Brookfield	Hercules	% >2μ	S.F.	T̄	D̄	Brightness	Whiteness	Xtly
MgO	•	.84	.76	-.23	.14	-.33	.85	.36	.79	.52	.86	.83	.36	-.35	-.05	-.24	-.18	-.52	-.53	-.19
Fe₂O₃	.84	•	.82	-.43	.14	-.12	.83	.14	.91	.53	.92	.84	.42	-.39	-.33	-.55	-.46	-.52	-.66	-.45
SiO₂/Al₂O₃	.76	.82	•	.09	.23	-.43	.75	.32	.67	.54	.74	.84	.67	-.27	-.12	-.12	.03	-.36	-.46	-.04
K₂O	-.23	-.43	.09	•	-.74	-.14	-.18	.56	-.51	-.23	-.54	-.18	.18	.66	.18	.69	.76	.71	.77	.84
TiO₂	.14	.14	.23	-.74	•	.09	-.01	-.69	.24	.44	.23	.12	-.18	-.68	.44	-.35	-.37	-.76	-.63	-.34
V₂O₅	-.33	-.12	-.43	-.14	.09	•	-.08	-.04	-.19	-.44	-.18	-.25	-.78	.15	-.12	.02	-.33	.37	-.05	-.61
CEC	.85	.83	.75	-.18	-.01	-.08	•	.51	.83	.50	.84	.84	.35	-.36	-.42	-.33	-.31	-.39	-.46	-.25
Charge Density	.36	.14	.32	.56	-.69	-.04	.51	•	.10	-.07	.18	.26	.30	.25	-.35	.25	.39	.36	.33	.32
Surf. Area	.79	.91	.67	-.51	.24	-.19	.83	.10	•	.67	.98	.91	.45	-.62	-.40	-.59	-.63	-.48	-.59	-.39
Sed. Volume	.52	.53	.54	-.23	.44	-.44	.50	-.07	.67	•	.70	.80	.65	-.63	.01	-.46	-.32	.00	-.06	.20
H₂O Sorption	.86	.92	.74	-.54	.23	-.18	.84	.18	.98	.70	•	.93	.54	-.66	-.12	-.55	-.55	-.47	-.59	-.30
Brookfield	.83	.84	.84	-.18	.12	-.25	.84	.26	.91	.80	.93	•	.65	-.63	-.35	-.49	-.32	-.32	-.38	-.16
Hercules	.36	.42	.67	.18	-.18	-.78	.35	.30	.45	.65	.54	.65	•	-.42	-.14	-.28	.03	.33	.29	.43
% >2μ	-.35	-.39	-.27	.66	-.68	.15	-.36	.25	-.62	-.63	-.66	-.63	-.42	•	.22	.80	.70	.27	.35	.38
S.F.	-.05	-.33	-.12	.18	.44	-.12	-.42	-.35	-.40	.01	-.12	-.35	-.14	.22	•	.50	.52	-.14	.07	.25
T̄	-.24	-.55	-.12	.69	-.35	.02	-.33	.25	-.59	-.46	-.55	-.49	-.28	.80	.50	•	.86	.18	.37	.39
D̄	-.18	-.46	.03	.76	-.37	-.33	-.31	.39	-.63	-.32	-.55	-.32	.03	.70	.52	.86	•	.33	.52	.66
Brightness	-.52	-.52	-.36	.71	-.76	.37	-.39	.36	-.48	.00	-.47	-.32	.33	.27	-.14	.18	.33	•	.96	.81
Whiteness	-.53	-.66	-.46	.77	-.63	-.05	-.46	.33	-.59	-.06	-.59	-.38	.29	.35	.07	.37	.52	.96	•	.87
Xtly	-.19	-.45	-.04	.84	-.34	-.61	-.25	.32	-.39	.20	-.30	-.16	.43	.38	.25	.39	.66	.81	.87	•

.83 99% confidence level   .63 95% confidence level

FIG. 1. Correlations of kaolinite properties.

approximated from shadowed electron micrographs. Strong correlations with iron indicate that a large percentage of iron in Georgia kaolins is associated with or derived from montmorillonite.

Correlations of cation exchange capacity (CEC) with magnesium, iron and silica–alumina ratio strongly indicate that the CEC of the kaolinites under study are primarily related to montmorillonite impurity. Based upon the assumption that the CEC is due primarily to montmorillonite, Hinckley and Bates (1960a, b), in the investigation of 108 Georgia kaolin samples, indicate that montmorillonite content ranges from 0.01 to 6.47%. In the present study, the smallest CEC value for Georgia kaolinites showing no detectable mag-

nesium is 0.29 meq/100 g, having a surface area of 15 m²/g. Assuming a linear relationship, such a kaolinite would require a surface area of approximately 50 m²/g to show an exchange capacity of 1 meq/100 g. If the montmorillonite impurity, arbitrarily, is assumed to have an exchange capacity of 100 meq/ 100 g, only 1% montmorillonite need be present to give an exchange capacity of 1 meq/100 g. On this assumption, and inasmuch as the maximum CEC determined was 3.87, only a less than X-ray detectable montmorillonite content need be present to account for the entire exchange capacity.

Although difficult to interpret because of montmorillonite impurity, this study, as well as others (Ormsby and Shartsis, 1962), shows a strong correlation between CEC and surface area If it is assumed that CEC is primarily a function of isomorphous substitution in kaolinite, as many workers believe (Schofield and Samson, 1954; Robertson, Brindley, and MacKensie, 1954; Sumner, 1963), a strong inverse relationship would be expected with factors of shape. On the other hand, if CEC is primarily a function of broken bonds, positive relations would be expected with factors of shape. Inasmuch as these variables do not show significant correlations, it is assumed that montmorillonite eclipses the intrinsic, but negligible, contribution of kaolinite.

Charge density, ratio of CEC to surface area, shows a low level correlation with CEC. On the other hand, lack of correlation with surface area indicates that montmorillonite has no significant effect on charge density. Concordancy with potassium is anticipated inasmuch as Greene-Kelly (1962) shows that muscovite has a much higher charge density than either kaolinite or montmorillonite, and arises from abundance of tetrahedral aluminum (Jonas, 1960). Greene-Kelly demonstrates that comparable charge densities are shown by kaolinite and montmorillonite. Lack of correlation with silica–alumina ratio may be indicative of abundant tetrahedral aluminum present in the muscovite impurity, as suggested by Bates (1964).

The relatively strong inverse relation between charge density and titanium is of particular interest. Titanium shows a strong tendency to be concentrated in the fine particle fraction, primarily as anatase, as opposed to the concentration of muscovite in coarse fractions. Association of titanium with fine kaolinite particles has been demonstrated also by Nagelschmidt, Donnelly, and Morcom (1948). Positively charged sols of anatase can be formed in acid systems. In such systems, both titanium and hydrogen are the stabilizing ions (Weiser, 1935) and should be precipitated by negatively charged kaolinite surfaces. Adsorption of colloidal titanium by kaolinite might be expected to inhibit growth without a coincident effect on crystallinity. In addition, nucleation sites on kaolinite surfaces provide a mechanism for growth of minute crystals (Bundy and Conley, 1962). These phenomena may account for the increased concentration of titanium in fine kaolinite particle sizes.

Lack of correlation between titanium and CEC as well as between charge density and particle size, however, indicates that titanium is not functional, *per se*, in decreasing surface charge. At pH 7, where the exchange capacity is determined, the positive charge on anatase may be expected to be neutralized

or reversed. The good inverse relationship of titanium with potassium strongly suggests that the titanium-charge density correlation is coincidental. The increased surface area provided by colloidal anatase may also affect some decrease in charge density.

Surface area, relative sediment volume, and water sorption are interrelated, and show common correlations to magnesium, silica–alumina ratio, iron, CEC, and Brookfield viscosity. Of all the correlations obtained, the most positive relationship is between surface area and water sorption. This would seem to indicate that carefully controlled water adsorption measurements may be a reasonable method of surface area determination for kaolinites. Keeling (1958) has shown a strong correlation of nitrogen adsorption measurements with water adsorption. Sediment volume is closely related to these properties and is discussed in detail under the section on rheology.

Brookfield viscosity, a low shear measurement, shows strongly concordant relations to magnesium, iron, silica–alumina ratio, CEC, surface area, and water sorption, all of which seem to bear close correspondence to montmorillonite content. The adverse effect of montmorillonite on rheology of kaolinite suspensions has been emphasized by Lyons (1958), Murray and Lyons (1956), Woodward (1955), and Swanson and Hemstock (1956). Correlation with sediment volume and reciprocal correlation with particle size are expected trends based upon previous work (Weyl and Ormsby, 1960; Phoenix, 1963). Such relations seem to indicate the dominant importance of surface area and attendant particle packing characteristics to low shear rheology. These observations are in accord with Ormsby and Marcus (1964) who indicate that such data support the generally accepted thesis that flow properties are largely controlled by surface area.

Particle packing, presumably, is a function of surface energy and particle size and shape distribution. Weyl and Ormsby (1960) have pointed out that for particles having the same size and shape, sediment volume and viscosity will increase with increasing surface energy. Michaels (1958) has described the effect of surface forces on viscosity of clay–water systems. Attraction at clay surfaces may include van der Waals or dipole interactions representing short range forces. Repulsive forces between clay particles are long range and are caused by ionic charges. Both types of forces may exist simultaneously causing particles to repel when far apart and attract when close together. It is apparent that attraction between particles will increase resistance to flow.

If repulsive forces dominate, as for dispersed kaolinite systems, effective particle volume can be substantial, and increases with decreasing particle size. Although for idealized and Newtonian systems, the unique importance of particle volume to viscosity is shown by the Einstein equation for concentrated suspensions of spheres:

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

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.

Because the surface area of anisodimensional particles is substantially larger than for equal volume spheres, surface forces assume a proportionate increase in importance. Under conditions of turbulent flow, the plate-shaped kaolinite particles may undergo random rotations and assume an effective volume far in excess of the same particles under conditions of laminar flow.

Optimization of particle size distribution is an essential character for maximum packing density and minimum viscosity (Phoenix, 1963; Millman, 1964). Thus, removal of ultrafine particles from the highly polydisperse Georgia kaolins, gives rise to increased packing volume and the consequent increase in viscosity:

Sample	$\% < 0.5\,\mu$	Relative sediment volume	Hercules viscosity (poises)
Control	47	1.59	1.9
Defined	37	1.69	8.0

Although packing volume is generally satisfactory for low shear flow characteristics, concentrated kaolinite suspensions become dilatant at high shear. At low shear preferential orientation of particles is, generally, adequate to maintain minimum packing volume. At high shear disruption of preferred orientation causes an increase in packing volume and viscosity. In this connection, Warkentin and Yong (1962) studied the shear strength of kaolinite–water systems under varying conditions of flocculation and dispersion. Their data indicate that shear strength increases with increasing void volume. Thus, edge-to-face flocculation shows greater shear strength than dispersed systems, and is minimum for face-to-face flocculation.

The lack of direct correlation of surface area with Hercules viscosity, in the present study, indicates that surface forces are not uniquely functional, as for low shear flow, in the control of high shear rheology. The strong correlation of sediment volume with Hercules viscosity indicates the dominant significance of the combined physical and chemical characteristics of kaolins which influence packing volume.

Although it is generally accepted that particle shape exerts a major influence on rheology (Michaels, 1958), factors of shape, in the present study, do not correlate with rheology. Shape factor values range from 0.125 to 0.291. It is emphasized, however, that the factors of shape are averages, and do not reflect size and shape distribution. Differences in shape characteristics, however, are apparently not of sufficient magnitude to exert a significant differential effect on rheology.

The good correlation of Hercules viscosity with silica–alumina ratio and lack of correlation with either magnesium or potassium indicate a generally

adverse effect on rheology by both montmorillonite and muscovite. As shown by Swanson and Hemstock (1956), as much as 5% quartz, apparently, does not have an adverse influence on flow properties, whereas as little as 1% montmorillonite and 2% mica seriously effect viscosity. Increased viscosity, presumably, results from the high surface area of montmorillonite and the high surface energy of muscovite.

The inverse relation of vanadium with Hercules viscosity is unanticipated. Vanadium organic complexes, however, are commonly associated with clay minerals (Rankama and Sahama, 1950; Breger, 1963). Vanadium porphyrins, for example, show substantial interfacial activity (Dunning, Moore, and Denekas, 1953) and potentially may act as efficient wetting agents for kaolinites. Alternatively, Rankama and Sahama point out that pentavalent vanadium has a pronounced tendency to form $[VO_4]^{-3}$ tetrahedra in mineral structures. Such polyvalent anions can be highly effective in the deflocculation of kaolinite suspensions, for example, sodium polyphosphates and silicates, which also exist as tetrahedra. Van Wazer and Besmertnuk (1950), Michaels (1958), and Lyon (1963) believe that phosphate tetrahedra are adsorbed at the gibbsite edge faces of kaolinite. Retention of these anions at normally neutral or cationic sites leads to a strong electrokinetic potential causing spontaneous deflocculation.

Factors of shape, average thickness $\bar{T}$, and average diameter, $\bar{D}$, show expected correlations with particle size and surface area. Non-correlation with shape factor (S.F.) may be ascribed to a general trend toward a proportionate increase in diameter with increase in thickness. The positive relationship of potassium to diameter and thickness may be considered as coincidental, and related to the concentration of muscovite in coarse fractions.

Brightness and whiteness show similar relationships and are primarily related to titanium- and iron-bearing impurities. Magnesium, surface area, and water adsorption also show inverse correlations, and are probably related insofar as they reflect the presence of a high, iron-bearing montmorillonite. Correlations with particle diameter and crystallinity are discussed under crystallinity.

Inasmuch as various size fractions of the spectrum of Georgia kaolin types, including so called "hard" and "soft" varieties (Hinckley, 1961) and English primary kaolins have been combined for common correlations as discussed above, results of the present study would not necessarily be expected to correspond to investigations confined to Georgia kaolins. For example, although there is a clear tendency for increased vermicular crystal content with increase in crystallinity for Georgia kaolins (Hinckley, 1961), English kaolins show far superior crystallinity and no vermicular crystals. English kaolinites contain particles unusually large in diameter, whereas poorly crystallized Georgia kaolins are unusually small in diameter. Thus, the good correlation between crystallinity and average diameter is not surprising, and is expected inasmuch as the a and b crystallographic axes seem to be preferred growth directions. The lack of correlation between shape factor and

average thickness with crystallinity is indicative of the non-uniformity of growth habits between kaolinites of differing origins.

The good correlation of crystallinity with potassium is not readily amenable to interpretation. The assumption that potassium reflects the presence of mica is based upon correlation with the microscopic observation of relative mica content. Hinckley (1961) obtained inconsistent correlations for mica and potassium with crystallinity. Furthermore, potassium does not always correlate with mica. Potassium shows correlations with either mica or iron or both. Because pyrite is commonly observed in the Georgia kaolin deposits, the relationship of potassium to iron may indicate the presence of a sulfate mineral such as jarosite. In the present study, however, there is an indication of decrease in iron with increase in potassium, and it is believed that it is safe to assume that potassium is largely associated with mica.

Jonas (1964) has observed that kaolinites derived from muscovite in Georgia kaolins show a b-axis disorder, and that well-crystallized kaolinites are alteration products of feldspar. On the other hand, Sand (1956) believes that mica is an essential intermediate product in the alteration of feldspar to kaolinite. Jonas, however, presumably is referring to primary mica. In this connection, Exley (1964) shows the approximate mineralogical analysis of the St. Austell granite of southwest England:

$$30\text{--}35\% \text{ quartz}$$
$$20\text{--}30\% \text{ potash feldspar}$$
$$20\text{--}25\% \text{ plagioclase}$$
$$3\text{--}6\% \text{ biotite}$$
$$5\text{--}10\% \text{ muscovite}$$
$$<3\% \text{ accessories}$$

It is apparent from this analysis that kaolinite has been derived primarily from feldspar. Inasmuch as beneficiated English kaolins may contain as much as 5% muscovite, it would seem that relatively little kaolinization of muscovite has occurred. English primary kaolinites show substantially higher crystallinity values than the best crystallized Georgia kaolins.

As shown by the strong correlation of potassium with particle size, muscovite tends to be concentrated in coarse fractions. Hinckley (1961) has shown the strong tendency toward increase in vermicular crystal content with increase in crystallinity, and Jonas (1964) has observed that vermicular crystals are invariably well crystallized. It seems, therefore, that the correlation of potassium with crystallinity may be coincidental, and that muscovite may be relatively stable under conditions propitious to the formation of well-crystallized kaolinite.

The inverse relationship of crystallinity with vanadium is a completely unanticipated correlation. Vanadium occurs at levels ranging from 1 to 4 parts per thousand. Although this relation may be coincidental, the high level of correlation indicates a variable worthy of consideration. Its relation to high shear viscosity is particularly noteworthy and has been discussed

above. There is no relationship of vanadium with particle size, surface area, montmorillonite, or mica, and indicates general dissemination throughout the kaolin.

It is noted by Rankama and Sahama (1950) that feldspars are virtually devoid of vanadium. In contrast, micas commonly show V^{4+} and V^{5+} in replacement for Fe^{3+} and Al^{3+}. The possibility of certain vanadium compounds acting as growth poisons for development of well-crystallized kaolinites is indicated by recent work on crystal growth. Sears (1958) discusses information on a class of poisons consisting of complex inorganic ions which are active at concentrations of 10^{-5} to 10^{-6} molal. This hypothesis conceivably could account for the observations by Jonas that a b-axis disorder occurs in kaolinites derived from micas. Absence of vanadium in feldspars would support the contention of development of well-crystallized kaolinite from feldspars regardless of intermediate alteration phases. It might be expected that iron and titanium would show a similar relationship, and although correlations at the 95% confidence level were not obtained, relatively high inverse relations with crystallinity do occur. Murray and Lyons (1960) have observed correspondence between increase in crystallinity and decrease in iron and titanium.

As in the present study, increase in whiteness and brightness with crystallinity has been observed in kaolinites by Murray and Lyons (1956). It is surprising, however, that a similar correlation of crystallinity with iron and titanium does not occur. Iron- and titanium-bearing constituents are the primary discolorants in Georgia kaolins, and removal of relatively small percentages give substantial improvement to optical characteristics (Duke, 1960; Conley, Golding, and Taranto, 1964). Iron extraction from kaolinite is normally carried out by reduction of Fe^{3+} to Fe^{2+} by sodium dithionite in acid solution. A correlation, however, is not obtained between amount of extracted iron and color improvement. Inasmuch as reoxidation gives rise to color degradation of the clay, it is probable that reduction to Fe^{2+} without extraction is instrumental in color improvement (Conley, 1965).

As indicated above, inverse relationships for crystallinity with iron and titanium do exist not too far below the 95% confidence level. It is suggested, however, that particle diameter may be highly functional in controlling the relationship of crystallinity with whiteness and brightness. The average particle diameter of clays used in the present study ranges between 0.4 and 0.8 micron. As mentioned above, particle diameter increases with increasing crystallinity. Because these kaolins are highly polydisperse, an abundance of particles occur having diameters less than half the wavelength of light. As shown by the universal scattering curve, Rayleigh scattering becomes operative at these small particle diameters, where selective scattering occurs and optical efficiency is low (Barnett, 1949). By the same token, an abundance of particles with diameters above the wavelength of light gives rise to reduced scattering efficiency, but is constant and generally superior to Rayleigh scattering.

SUMMARY AND CONCLUSIONS

Correlations of physical and chemical properties of Georgia sedimentary kaolins and English primary kaolins were carried out to show interdependencies of many variables. Approximations of montmorillonite content from shadowed electron micrographs show correspondence to variables that can be logically ascribed to montmorillonite. Mutual correlations between magnesium, iron, silica–alumina ratio, CEC, water sorption, surface area, and Brookfield viscosity, indicate the strong influence exerted by small quantities of montmorillonite.

Strong correlations of CEC with magnesium, silica–alumina ratio, and iron, indicate that the CEC of the kaolinites under study are primarily related to montmorillonite impurity. Charge density is similar for kaolinite and montmorillonite. Increase in charge density with increase in potassium is ascribed to the presence of a high aluminium muscovite.

It is suggested that the minute particle size of anatase contained in the kaolin may be related to nucleation and growth control exerted by charge sites on kaolinite crystals. Growth or adsorption of anatase at charge sites may inhibit growth of kaolinite crystals. Because of the strong inverse relation of titanium to potassium, the inverse relation of titanium to charge charge density is believed to be coincidental.

Excellent correlation of water sorption with surface area indicates that carefully controlled water sorption measurements may be a reasonable method for surface area determination.

Low shear viscosity measurements show a high level correlation with montmorillonite content, and such viscosity measurements seem to be related, primarily, to surface area and particle packing. For high shear viscosity, packing volume exerts a dominant influence. Differences in particle shape are not of sufficient magnitude to show a significant effect on rheology. The combined influence of montmorillonite and muscovite seems to adversely affect high shear rheology.

The inverse relationship of vanadium with high shear viscosity offers an area of interesting speculation. Alternative suggestions as to the mechanism of viscosity reduction by vanadium include:

1. the presence of vanadium organic complexes which may act as efficient wetting agents,
2. adsorption of polyvalent anions which may act to increase electrokinetic potential enabling more efficient deflocculation.

Brightness and whiteness are primarily related to titanium- and iron-bearing impurities. Titanium seems to be present primarily as anatase, whereas abundant iron is associated with or derived from montmorillonite. Those clays which contain a maximum number of particles in the optimum size range for light scattering are generally associated with well-crystallized kaolinites. There is a tendency toward increase in particle diameter with increase in crystallinity. There is some indication that well-crystallized

kaolinites are derived primarily from feldspars, and that muscovite alteration has been retarded where well-crystallized kaolinites occur. A highly suppositional suggestion is offered that complex vanadium ions may act as growth poisons to account for the inverse relation of vanadium with crystallinity.

It is apparent from these observations that much additional work is needed to define the genesis of the physical and chemical properties of kaolinites. The strong contribution exerted by small quantities of montmorillonite commonly may preclude definition of intrinsic kaolinite properties. Such a problem is particularly obvious in the case of ion exchange and rheological investigations. Methods for the efficient extraction of non-kaolinite minerals, particularly montmorillonite, are needed for fundamental investigations.

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