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W. B. Jepson

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Kaolins: their properties and uses

By W. B. Jepson

Central Laboratories, English China Clays p.l.c., St Austell, Cornwall PL25 4DJ, U.K.

The main commercially important kaolin resources are the primary deposits in Cornwall and the sedimentary deposits in South Carolina and Georgia in the U.S.A. Annual world production is about 18 Mt (1 t = 10^3 kg). In 1981 the U.K. production was 2.6×10^6 t of which about 77 % represented paper filler and paper coating grades. About 15 % of the U.K. production is used in ceramics.

The kaolin extracted from the commercial deposits contains kaolinite as the major component together with ancilliary minerals. The kaolinite particles take the form of pseudo-hexagonal platelets with widths that vary from 10 to 0.1 μm and less.

Surface chemical properties have been widely researched. There is no uniformity of view on the origin of the cation exchange capacity. Aqueous suspensions of kaolin are flocculated at low pH. This can be understood in terms of the positively charged edges and the negatively charged faces of the platelets. The deflocculation of kaolin under alkaline conditions is important, and is assisted by adding a polyanion.

The Kubelka–Munk equations have provided a useful basis for interpreting the optical properties of kaolins in terms of an absorption coefficient (k) and a scattering coefficient (s). The parameter k is a bulk property and is interpreted in terms of light absorption by ancilliary minerals, by coatings of hydrated iron oxides on the kaolinite particles and by transition metals in the kaolinite structure. The parameter s depends on the size distribution of the platelets and the manner in which they are packed together.

The rheological properties of deflocculated suspensions of kaolin in water are important in modern paper coating applications. The relation between the bulk physical properties of kaolin and rheology is complex. Viscosity at low rates of shear increases with increasing specific surface area of the kaolin. Viscosity at high rates of shear depends on the shapes of the particles and their packing.

The extraction and production of kaolins are described for both primary and sedimentary deposits. The main use of kaolin is as a paper filler and a paper coating pigment. The various filler and coating grades are indicated, and effect of kaolin properties on coated sheet properties is discussed. Kaolin is a major component in most ceramic bodies. Examples of formulations are given. The manufacture of sanitaryware and tableware is discussed in terms of kaolin properties. Kaolin is used as an extender in aqueous based paints and as a filler in rubber and synthetic polymers.

1. BRIEF OUTLINE OF HISTORY

By the 16th century, Chinese porcelain was so highly regarded in Europe that many attempts were made to produce it from local materials. In the early 18th century a Jesuit missionary, Father Francis d'Entrecolles, working in China, observed the processing of the raw materials and the manufacture of the several porcelains. He wrote to his superior in Paris giving details (Pounds 1948) and supplied specimens of the two constituents, petunse and kaolin.

The samples were passed to a French scientist, Baron de Reaumur, who demonstrated that two types of porcelain could be produced, a soft paste and a hard paste, depending on the firing conditions. The hard paste porcelain was similar to that produced in China. Howe (1914) gives an excellent description of the methods used by the Chinese to produce their raw materials. A sample of what is thought to be the original petunse provided by d'Entrecolles is held by the

British Museum (BM 60022). Keller *et al.* (1980) describe kaolin from the locality of the original Kauling mine.

The word kaolin is used as an alternative name for the clay material known as china clay. The description china clay is retained in the United Kingdom and the description kaolin in most other countries including the United States of America.

William Cookworthy is credited with the discovery of the china clay and china stone deposits in Cornwall. He recognized their properties and identified them with the materials described by d'Entrecolles. Cookworthy took out a British patent and started a small porcelain factory in Plymouth. The history of the growth of the pottery industry in Staffordshire is well documented (Barton 1966; Wedgwood & Wedgwood 1980). Earthenware and bone china bodies were developed and hard porcelain manufacture declined.

The early 19th century saw the introduction of china clay as a filler in the manufacture of paper. It was also used in the textile industry as a constituent of size to add 'body' to cotton goods and to whiten them. The first coated papers were produced around 1900 to meet the demands from improved methods of printing.

2. Terminology and crystal structure

Kaolin is tentatively defined by the International Committee on Correlation of Age and Genesis of Kaolin as 'an earthy rock characterized by a significant content of kaolin minerals' (Keller 1978). The kaolin minerals include all the dioctahedral 1:1 layer aluminosilicates (Bailey 1980). Of the many theoretically possible structures, kaolinite is the only known 1-layer form; dickite and nacrite are the only known 2-layer forms.

A platelet of kaolinite is made up of layers about 7.2Å† thick that are continuous in the *a* and *b* directions (excluding twinning) and stacked in a given order along the *c*-axis. In reality there are varying degrees of disorder in the layer stacking. Brindley (1980) has reviewed the various experimental and interpretational approaches and emphasized the important papers by Plancon & Tchoubar (see, for example, Plancon & Tchoubar 1977) whose models include stacking faults by linear displacements, rotation of layers and displacement of Al cation vacancies. The number of layers per domain was calculated from the breadth of the 001 X-ray reflection. Values varied from 25 layers for a French kaolinite to 75 layers for a Georgia kaolinite. The layer stacking imperfections are seen by electron microscopy as folds, voids or other inclusions (Tchoubar *et al.* 1982).

Material extracted from commercial deposits contains kaolinite as the major component together with ancilliary minerals that vary with the type and quality of the deposit. The extracted material is known and well understood as kaolin or china clay; usage is followed below although this conflicts with the geological definition. There is no known large scale exploitation of either dickite or nacrite. This account excludes certain industrial minerals which contain kaolinite as a major component. These include ball clays (Watson 1982*a*), flint clays (Keller & Fitzpatrick 1981) and the refractory clays (Dickson 1982). Halloysite is also excluded.

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† 1 Å = 10^{-10} m = 10^{-1} nm.

3. DEPOSITS

The most important kaolin resources are in Cornwall in SW England and in S Carolina and Georgia in the United States of America. Other important resources are found in the Amazon basin in Brazil, in Brittany and in the Aquitaine basin in France, in Bavaria and Bohemia, in Spain and in parts of eastern Europe, particularly Russia. There are unexploited deposits in South East Asia including Australia; it remains to be seen whether certain rheological problems can be overcome to permit their use in paper coating (O'Neill 1983).

The deposits in SW England are described by Bristow (1968, 1977) and the deposits in Georgia are described by Patterson & Murray (1975) and Hurst *et al.* (1979). Keller (1977*a*) has described the fabric of kaolin deposits throughout the world.

Kaolin deposits are classified (Keller 1978; Bristow 1980) into primary and secondary or sedimentary deposits. Those in SW England are primary deposits, probably formed by a combination of weathering and hydrothermal alteration of granite (Bristow 1977). On a mass basis, the commercial product represents about 15% of the whole, with the balance largely present as quartz, feldspars and unaltered granite. Those in S Carolina–Georgia are sedimentary deposits; they have been transported from their place of origin and the recovery of commercial product can exceed 90%. The kaolinitic sands are closely related to sedimentary kaolins but the kaolinite content is much lower, about 10–15%. Some of the Spanish and German deposits are of this type.

4. COMMERCIAL ASPECTS

The total annual world production of kaolin is about 18 Mt (Watson 1982*b*). In 1981 the U.K. production was 2.6 Mt, of which 2.2 Mt were exported principally to Europe. Markets in Europe for paper grades of kaolin have been reviewed (Anon 1982). About 5.2 Mt of refined kaolin were produced in the U.S.A. in 1981. Some 90% of this was produced in Georgia. Harben (1979) reviews production in Georgia and Clark (1982) reviews kaolin markets in the U.S.A.

The main use of kaolin is as a filler and as a coating pigment in the production of paper. Some 78% of the U.K. production is used in this sector. About 15% of the U.K. production is used in the production of ceramic articles, mainly in sanitaryware, tableware and wall tiles. The balance of 7% is used in a variety of lesser applications of which those in paints, plastics and rubber predominate.

5. PROPERTIES

(*a*) *Shape and size*

The shape and size distribution of kaolin is important in its commercial uses, particularly in paper filling and paper coating. It affects the mechanical, optical and printing properties of the finished sheet of paper. Particle size is expressed as e.s.d. (equivalent spherical diameter) (Allen 1975) even though the kaolin particles are in the form of platelets and not spheres. Particle size distribution is normally measured by sedimentation from a deflocculated suspension in water. Measurements below 0.15 μm are best made with a centrifuge. Commercial instruments have been developed for routine measurements (Sennett *et al.* 1974; Allen 1975). The cumulative mass per cent below 2 μm value is often used as a control in production.

Transmission electron microscopy of a fraction of a kaolin under 5 μm e.s.d. prepared from a Cornish primary deposit shows it to be largely composed of pseudo-hexagonal plates. In this fraction the plate widths would vary from an upper limit of about 8 μm down to at least 0.1 μm. The aspect ratio, which is the ratio of plate width to thickness, would vary through the size distribution from about 10:1 at the coarse end to about 50:1 at the fine end (Noble & Golley 1970, unpublished work).

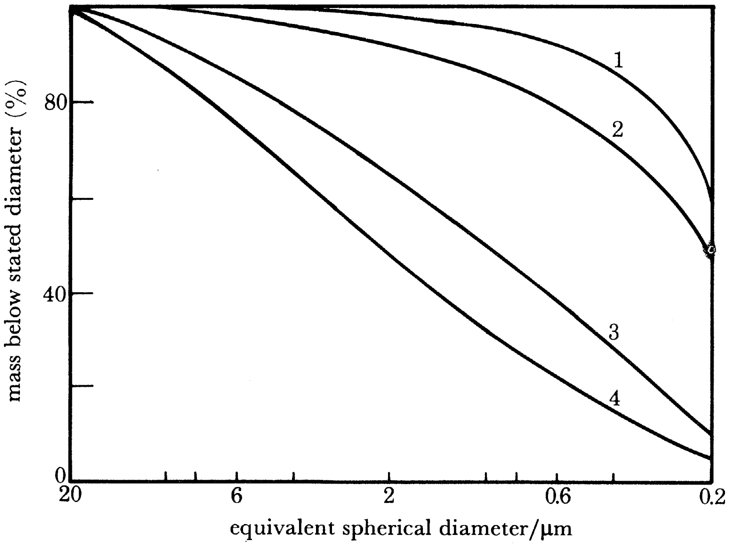

Figure 1. Cumulative particle size distribution curves of kaolins. Curves (1) and (2), sedimentary kaolins from East Georgia; curve (3), sedimentary kaolin from Central Georgia; curve (4), primary kaolin from Cornwall.

Kaolins refined from the central Georgia sedimentary deposits show a number of important differences (Conley 1966). In an under 5 μm e.s.d. fraction from a 'coarse' deposit the particles are much closer to hexagonal in shape. The plate widths again extend to at least 0.1 μm but the particles are now much smaller. The aspect ratios lie between 6:1 and 10:1 and vary little through the size range. If a fraction exceeding 5 μm e.s.d. is examined by scanning electron microscopy, many exfoliated booklets of kaolinite are seen; they are up to 50 μm thick and up to 20 μm across (Morris *et al.* 1965; Olivier & Sennett 1973). They are alternatively described as vermicules or stacks. They are porous and numerous slit-like voids can be seen between the kaolinite platelets making up each booklet. Keller (1977*b*) reviews their formation and origin. In commercial production the fraction over 5 μm e.s.d. is used either as a component of paper filling grades or is broken down mechanically (Whitley & Iannicelli 1972; Murray 1976) to produce grades called 'delaminated kaolins'. Booklets are also found in the kaolin deposits of SW England. They seem to break down readily during normal production and are not a significant component of the commercial products.

Examples of cumulative size distributions of kaolins refined from deposits in Cornwall and Georgia are shown in figure 1. The two kaolins from the East Georgia deposits (1 and 2) are finer than the kaolin from Central Georgia (3) which in turn is finer than that from Cornwall (4).

If a kaolin between narrow size limits is prepared by repeated sedimentation and then examined by transmission electron microscopy, the range of plate widths can be compared with the equivalent spherical diameter. For the primary kaolins, the centre of the plate width distribution exceeds the e.s.d. of the fraction by a factor of between 2 and 3. These measurements are tedious and time consuming. Encouraging progress is now being made in the application of electrically induced birefringence methods to the sizing of anisometric particles in the colloidal size range (Oakley & Jennings 1982). By assuming a thin disc model and a log-normal size distribution, a number-diameter distribution can be calculated. These methods are likely to find wide applicability once comparative measurements have been made on a range of samples and any limitations have been identified.

The microstructural features of kaolinite particles are receiving attention. Deposition of gold from the vapour phase has been used to decorate the faces; it reveals a multiplicity of micro steps (Thompson *et al.* 1981). Edges of the platelets, when examined at a magnification of about 1 million, show a frayed appearance. These findings are significant when judging the worth of calculations based on model particles to interpret the colloidal properties of kaolin suspensions in water.

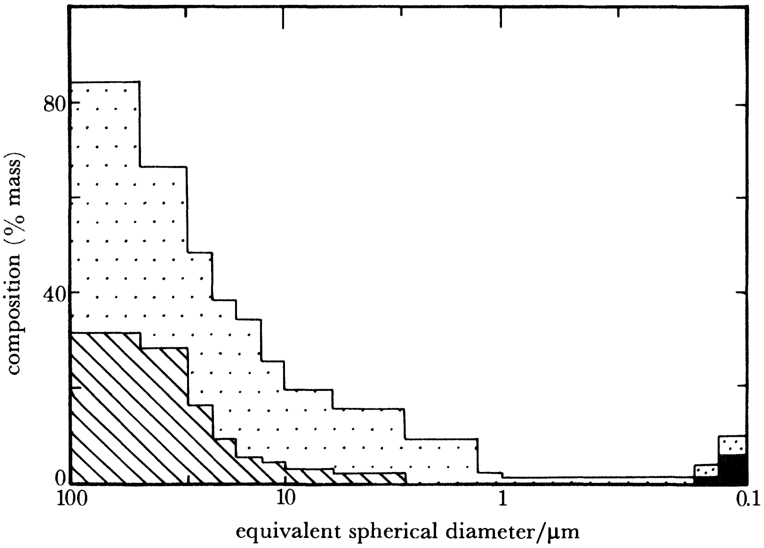

FIGURE 2. The variation of mineralogy of a Cornish kaolin with particle size. Oblique lines: feldspar and quartz; dots: mica; solid region: smectites; non shaded region: kaolinite.

(*b*) *Elemental and mineralogical composition*

The mineralogy of a primary kaolin varies with particle size. In the experiment shown in figure 2, a fraction under 50 μm was prepared from matrix and divided into 15 fractions by sedimentation from a deflocculated suspension. The mineralogical composition of each fraction was then determined by X-ray powder diffraction. The main ancilliary minerals are quartz, micas and feldspars. Small amounts of smectite are sometimes found in the finest fractions. The kaolinite content increases with decreasing particle size and this is the basis of much of the commercial production.

The mineralogical and partial elemental compositions of two refined kaolins, approximating to a commercial filler grade and a commercial coating grade, are shown in table 1. The finer fraction has the greater kaolinite content and the smaller mica content. The analytical TiO_2 content of each fraction is small. Anatase is sometimes found in kaolins derived from primary deposits overseas. The amount depends on the parent granite but is generally below 0.5% by mass.

The mineralogical compositions of the Georgia kaolins vary much less with particle size. The crude kaolin contains small amounts of mica, quartz, anatase and other ancilliary minerals amounting to perhaps 10 % by mass (Hurst *et al.* 1979; Van Olphen & Fripiat 1979). Indicative mineralogies and partial elemental compositions of two Georgia kaolins are shown in table 2. Anatase is a major impurity but mica is present in only small amounts.

Kaolinite prepared from a geode source gave a chemical analysis close to the theoretical value and has been suggested as a reference kaolinite mineral (Keller *et al.* 1966). Research samples are best selected and prepared under laboratory conditions from matrix. Large samples may contain a mixture of polymorphic types (Keller & Haenni 1978).

TABLE 1. ANALYSES OF KAOLINS PREPARED FROM CORNISH MATRIX

	composition (% mass)	
	under 20 μm	under 10 μm
kaolinite	83	90
mica	14	8
feldspar	2	1
Fe_2O_3	0.9	0.6
TiO_2	0.05	0.06
K_2O	1.9	1.1

TABLE 2. ANALYSES OF TWO KAOLINS (UNDER 10 μm) PREPARED FROM GEORGIA MATRIXES

	composition (% mass)	
	central Georgia	east Georgia
kaolinite	> 95	> 95
mica	≈ 1	≈ 2
Fe_2O_3	0.25–0.60	0.8–1.5
TiO_2	1.0–2.0	1.5–3.0
K_2O	≈ 0.1	0.2

The identification and measurement of the ancilliary minerals in kaolin by X-ray powder diffraction together with quantitative elemental analysis by x.r.f. are essential prerequisites to any investigation. A major advance took place in the early 1970s when transmission electron microscopes equipped with an analytical facility became commercially available. The presence of iron in the kaolinite structure, previously inferred from lengthy Mossbauer experiments with magnetically extracted samples (Malden & Meads 1967), was confirmed (Jepson & Rowse 1975). There was a wide variation in Fe:Si atom ratios between individual kaolinite particles extracted from a small matrix sample. In the Georgia kaolins almost all of the Fe found by elemental analysis is contained in the kaolinite structure. Mossbauer and electron spin resonance spectroscopy have provided valuable information. Most of the iron in the kaolinite structure is present as Fe(III) isomorphously replacing Al(III) in octahedral sites (Angel & Hall 1972; Jefferson *et al.* 1975; Meads & Malden 1975; Hall 1980; Komusinski *et al.* 1981).

The association of mica with kaolinite has been inferred from analytical electron microscopy (Jepson & Rowse 1975). Ultramicrotomy and high resolution electron microscopy (Lee *et al.* 1975) showed it to be present as occlusions within the kaolinite layers in the samples examined.

Most of the titanium found by elemental analysis of refined Georgia kaolins is present as anatase with only minor amounts in the kaolinite structure (Dolcater *et al.* 1970; Jepson & Rowse 1975; Sayin & Jackson 1975; Rengasamy 1976). Small amounts of rutile are sometimes found. Transmission electron microscopic examination of refined Georgia kaolins (under 5 µm) shows the anatase to be present as particles about 0.1 µm across. Probe analysis shows some combined iron, hence the term 'titanoferrous impurities'.

(c) *Surface chemistry*

The crystal structure of kaolinite suggests that the octahedral basal surface of a platelet should be gibbsite-like and should present close packed hydroxyl groups; the tetrahedral basal surface of the platelet should be silica-like and present siloxane bonds. At the edges of a platelet, the lattice is disrupted and a broken bond surface should be exposed.

(i) *Contamination of surfaces*

Surfaces of kaolinite platelets found in nature deviate from the above. They are contaminated (Jefferson *et al.* 1975; Angel & Vincent 1978) with hydrated iron oxides which may be present either as particles, several 100 Å across, or as an amorphous coating combined with other elements and perhaps occupy localized areas. The hydrated iron oxides are removed during commercial production by leaching with sodium dithionite (Conley & Lloyd 1970). The surfaces are also contaminated with organic material and values up to 0.05%, expressed as carbon, are not unusual (Ferris & Jepson 1972). Commercial kaolins may contain residual organic compounds added as flocculants or deflocculants during processing.

(ii) *Cation and anion exchange*

The cation and anion exchange properties of kaolinite have been widely researched. Present day views have developed from the work of Schofield (1949), Schofield & Samson (1953) and Van Olphen (1951, 1964). If a well chosen and carefully prepared sample of kaolin is repeatedly washed with 1 M NaCl at pH 7, for example, then certain cations, the exchange cations, predominantly Ca^{2+} and Mg^{2+} ions, are displaced. If the sample is allowed to equilibrate with 0.01 M NaCl at pH 7 it is found that some Na^+ ions are associated with the kaolin. If the sample is rinsed with water most of the Na exchange ions are retained by the kaolin. The amount is typically about 20 µmol Na per gram of sample which is equivalent to about 1 Na atom per 100 Å^2 of surface using the BET (Brunaeur, Emmett and Teller) nitrogen area. Figure 3 shows that Na^+ ion adsorption increases with increasing pH (Ferris & Jepson 1975). The adsorption around pH 3 is sometimes larger than zero (figure 3), and seems to depend on sample and preparative technique. Kaolins also show a small anion adsorption that decreases with increasing pH (figure 3).

There are three different views on the origin of the cation adsorption. The first is that isomorphous replacement of Al for Si in the kaolinite structure produces an excess of negative electrical charge. Only 1 Si atom in 400 would need to be replaced by 1 Al to give a cation adsorption of 20 µmol Na per gram. It has not been possible to demonstrate this deviation from stoichiometry either by wet chemical analysis on a bulk sample or by probe analysis of individual kaolinite particles (Jepson & Rowse 1975). Work by Weiss (1959) and Weiss & Russow (1963) suggested that the isomorphous substitution was confined to the silica tetrahedral layer. Comments by Uytterhoeven (1963) and by Bolt (1963) are pertinent. The second view attributes either some or all of the cation adsorption to the presence of small amounts of expanding minerals. Lim *et al.* (1980) examined 7 Georgia kaolins and apportioned the cation adsorptions, which varied from 30 to 90 µmol Cs per gram, to contributions from 2:1 layer minerals and from isomorphous substitution of Al for Si in the kaolinite structure. The external surface cation adsorption ranged from zero to 10 µmol Cs per gram. Talibudeen & Goulding (1983) measured differential heats of K^+–Ca^{2+} exchange on a number of kaolins and inferred the presence of vermiculite, micaceous and smectite layers in association with the kaolinite. The third view (Ferris & Jepson 1975) is based on studies of two kaolins prepared under laboratory conditions. It suggests that the kaolinite particles are coated with a gel-like material, rich in silica, which dominates the cation adsorption. This view does not exclude isomorphous substitution.

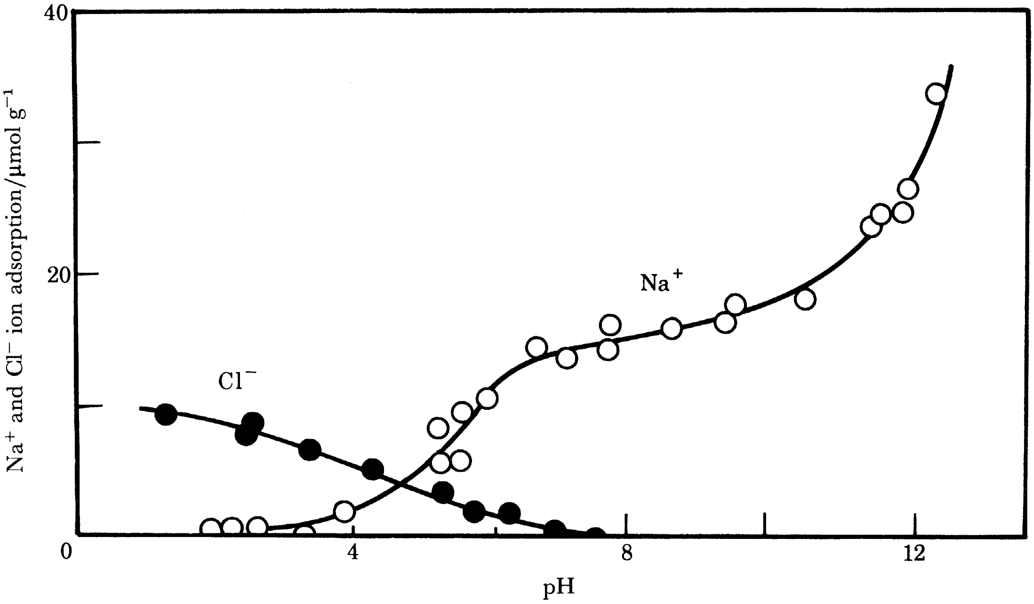

FIGURE 3. Change of Na^+ ion and Cl^- ion adsorption on kaolin with pH. Electrolyte: 6×10^{-3} mole dm^{-3} NaCl. After Ferris & Jepson (1975). Reproduced with permission from *J. Colloid Interface Sci.*

The anion adsorption and some of the cation adsorption are attributed to adsorption at the particle edges (see § 5(*a*)). The model proposed by Schofield & Samson (1953) which incorporates earlier suggestions by Van Olphen (1951) is still accepted. Under acidic conditions the edges are positively charged through protonation of hydroxyl groups attached to Al atoms exposed at the platelet edges. Above about pH 7, by analogy with gibbsite, protonation becomes negligible. As the pH is increased so the exposed edge silanol groups start to dissociate and the cation adsorption increases. The paper by Van Olphen (1964) on the flocculation of clay suspensions gives a deeper insight.

Rand & Melton (1977) have made rheological measurements using aqueous suspensions of kaolins in the homoionic Na-form and inferred that the platelet edges have an apparent isoelectric point of 7.3. In other work the zero point of charge of the platelet edges has been estimated by combining separate data for silica and for alumina; Williams & Williams (1978) suggest a value of pH 7.2.

The following simple description emerges. Each platelet carries a negative charge on one or both of its faces which will be of constant charge (isomorphous replacement or adsorbed 2:1 layer mineral models) or of constant potential (gel coating model). The negative charge on the faces increases with increasing pH (gel coating model). The particle edges are positively charged at low pH, pass through an isoelectric point and become negatively charged at high pH. The model is supported by experiments with radioactively tagged cations followed by autoradiography at the electron microscope level (Fordham 1973).

(iii) *Colloid chemistry*

Kaolin suspensions have the interesting and important property of being dispersed (deflocculated) under alkaline conditions (say pH 9) and being coagulated (flocculated) under acidic conditions (say pH 4). This is readily understood in terms of the simplified account given above of the electrical charges carried by the kaolinite platelets. Stability calculations have been made by using double layer theory for different H^+ ion (pH 4–10) and electrolyte concentrations (10^{-2} to 10^{-4} mol dm^{-3}). Idealized geometry is used and electrical potentials are assigned to the edge and face surfaces (Flegmann *et al.* 1969; Williams & Williams 1982). Face-to-face interaction showed a high primary maximum in all environments. At pH 6 there is no energy barrier to either edge–edge or edge–face interactions. At pH 4 there is a slight barrier to edge–edge interactions which decreases with increasing salt concentration. At pH 10 there are moderate energy barriers to both edge–edge and edge–face interactions. These findings are in broad accord with practical observations.

Electron microscopy, freeze drying and critical point drying methods have been used to examine the spatial relations between the particles of kaolinite in floccules and in filter cakes. Results by O'Brien (1971, 1975), by Lanier & Jones (1979) and by Lockhart (1980) are in broad agreement. The flocculated kaolin fabric consists of abundant stepped clusters of plates in face–face contact with some zones of edge–face oriented plates randomly arranged in a porous 3-dimensional network. Lockhart (1980) uses the term 'microporous honeycomb'.

The flocculation of kaolin is important in commercial production. On lowering the pH of a deflocculated suspension, the platelets interact to form aggregates that grow into flocs by collision and by 'sweeping' up individual platelets. After flocculating and thickening, the kaolin is separated from most of the aqueous phase by filtration. The permeability of a kaolin depends quite markedly on its size distribution and on the pH of the suspension. The permeability of a Cornish coating grade (see table 1) increases by a factor of about 2.5 on decreasing the pH of the suspension from 8 to 4. In commercial production, the kaolin slurries are often filtered at elevated pressures to lower the final water content of the filtercake. In terms of mechanism the cake consolidates until its strength increases to the new applied pressure.

The deflocculation of kaolin under alkaline conditions is important in both the production and use of kaolin, and is explained by the stability calculations described above. Dispersion or separation of the particles is assisted by stirring to impart some shear which dislodges smaller particles from larger particles. It is also helped by adding a polyanion which adsorbs on the platelet surfaces and increases their negative charge.

Intermediate situations exist and are important in the casting of shapes in the ceramic industry (Bailey 1976). Casting rate and cast properties depend on achieving and maintaining the intermediate condition of 'under deflocculation'.

(iv) *Further discussion of kaolinite surfaces*

Experimental work with kaolin normally involves some pretreatment to remove adsorbed impurities. This may include leaching with sodium dithionite, contacting with hydrogen peroxide solution followed by washing with dilute hydrochloric acid (Schofield 1949) until the concentration of aluminium in solution reaches some small and arbitrary limit. Such an approach ignores the solubility of kaolinite in water and fails to recognize that the dissolved aluminium and silicon will eventually attain equilibrium values. Small concentrations of aluminium and silicon in solution do not of themselves guarantee that dissolution and readsorption processes are not taking place. Bolland *et al.* (1976), in work that merits detailed study, attempted to reduce dissolution and contamination with soluble Al species by conducting their experiments around 0 °C.

The above general approaches contain the implicit assumption that the pretreatments reveal the ideal kaolinite surfaces and that these surfaces persist during the subsequent experiments. This has never been convincingly demonstrated.

An alternative approach (Ferris & Jepson 1975) is to prepare the sought size fraction with a hydrocyclone, and hence add no chemical other than water. The experimental objective then becomes that of characterizing the surface of the naturally occurring material. There are prospects that the surface compositions of kaolinite platelets will be determined by using the newer techniques of electron spectroscopy and some progress is being made (McBride 1976, 1978; Koppelman & Dilland 1977; Dilland & Koppelman 1982).

TABLE 3. OPTICAL PROPERTIES OF TWO COATING GRADES OF KAOLIN

	kaolin C	kaolin G
$B(\%)$	86.8	86.8
$k/(\mathrm{cm^2\ g^{-1}})$	23.8	28.5
$s/(\mathrm{cm^2\ g^{-1}})$	2400	2850

(*d*) *Absorption and scattering of light*

The optical properties of kaolins are important in most of the commercial uses. They are usually interpreted in terms of an absorption coefficient (k) and a scattering coefficient (s) by using the Kubelka-Munk (K.-M.) theory (Kerker 1969; Starr & Young 1975).

The parameter k is a property of the kaolin itself and can be modified by chemical treatment or by beneficiation to remove coloured impurities. It can be determined by measuring the diffuse reflectance of light of a particular wavelength, generally 457 nm, from a series of paper sheets containing different loadings of kaolin.

The parameter s depends on the difference in refractive index between the kaolin and the medium, generally air. It also depends on the shape and size distribution of the particles and, in particular, on their state of aggregation. Conceptually it is useful to regard the pores in, for example, a compacted powder or a coating on paper as the light scattering units.

If a sample of flocculated kalin is powdered and compacted into a disc in a reproducible manner and the diffuse reflectance is measured at 457 nm, the powder brightness B (Windle & Gate 1968) is obtained. The value is expressed on an absolute basis as a percentage and is measured relative to a subsidiary standard which has been calibrated in a laboratory approved by the International Standards Organization.

Having already determined k the value of s can be calculated by using the K.-M. equations. Table 3 shows values for a coating grade (C) prepared from a Cornish deposit and a premium coating grade (G) prepared from a blended Georgia crude by refining and flotation. It is seen that sample G has a higher value of k and hence greater light absorption. It is however finer than sample C and when compacted shows more light scatter as evidenced by the greater value of s. It is interesting that in this example the greater value of k is offset by the greater value of s so that the powder brightnesses are equal (N. A. Climpson & J. H. Taylor 1972, unpublished work).

If a series of kaolins with different size distributions is examined, the calculated values of s can be related to some measure of average particle size. One common choice is the d_{50} value which is the e.s.d. corresponding to the 50 % value on the cumulative size distribution curve. It is found that s increases from about 1500 cm^2 g^{-1} for d_{50} equal to 3 μm up to a maximum of about 2900 cm^2 g^{-1} for d_{50} equal to 0.5 μm. It then decreases as d_{50} decreases further. With k set equal to 23.8 cm^2 g^{-1} the above values of s would give powder brightnesses of 83.7 and 88.0.

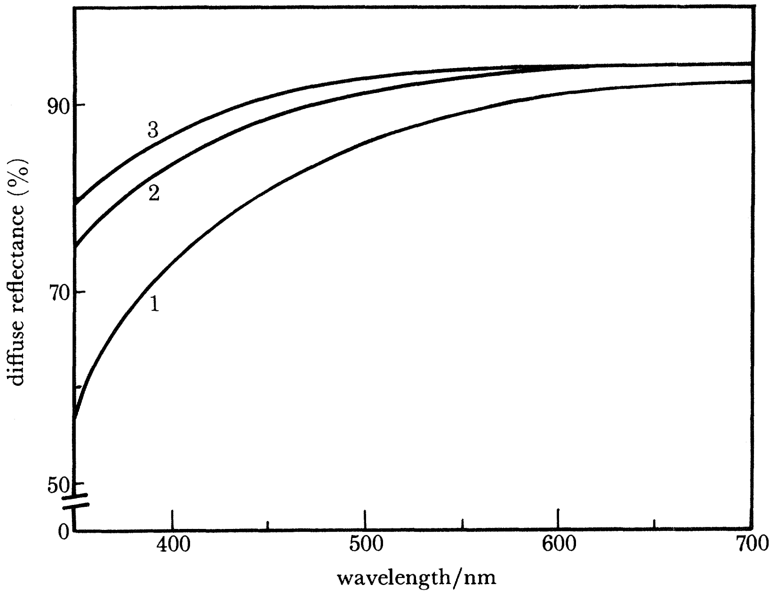

Figure 4. The change in the diffuse reflectance of light from several kaolin compacts plotted against wavelength. Each sample had been refined to under 10 μm. The ordinate is in absolute units. Curve (1), sedimentary kaolin from Georgia; curve (2), primary kaolin from Cornwall; curve (3), primary kaolin from Cornwall after leaching with sodium dithionite.

The optical properties of papers have been widely researched with both real and model systems. Ultra-microtomed sections have been used to make direct measurements of the size and distribution of the scattering elements (Climpson & Taylor 1976; Lepoutre 1976; Borch & Lepoutre 1978; Starr & Young 1978; Alince & Lepoutre 1980*a*, *b*). The scattering coefficient of a coating of kaolin and adhesive on paper is well below the value for the power compact because the particles are laid down from a deflocculated suspension. They adopt a preferred orientation broadly parallel to the base sheet and are more closely packed; some of the pore volume is occupied by adhesive. The values of s for the samples C and G in table 3 when coated on paper would each be about 800 cm^2 g^{-1}.

Figure 4 shows the change of diffuse reflectance with wavelength. The kaolins were prepared from flocculated suspensions. Reflectance decreases with decreasing wavelength and falls markedly in the ultraviolet region despite the increasing contribution there from scattering.

Ancilliary minerals (micas, tourmaline, titanoferrous impurities) and coatings of hydrated iron oxides on the kaolinite particles contribute substantially to the light absorption which arises from charge transfer (c.t.) transitions involving metal–ligand and metal–metal transfers (Weyl 1959; Robbins & Strens 1972; Karickhoff & Bailey 1973; Faye *et al.* 1974).

If the sample shown as curve (2) in figure 4 is leached with sodium dithionite and then filtered, dried and recompacted, the reflectance follows curve (3). This is because hydrated iron oxide coatings are dissolved. The analytical Fe_2O_3 content only fell from 0.54 to 0.52 % by mass. It seems that quite large amounts of iron can be tolerated provided they are in the kaolinite structure. Some coating grades analyse about 2 % Fe_2O_3. Provided the iron atoms are well separated from each other the c.t. reinforcement is limited.

Figure 4 also shows the reflectance curve (1) of a Georgia kaolin. When the sample was beneficiated by flotation and the reflectance redetermined, the experimental curve was close to curve (2). The analytical Fe_2O_3 content of 0.90 % showed little change but the analytical TiO_2 content fell from 1.70 to 0.60 %. This illustrates the major effect of titanoferrous impurities on light absorption.

The naturally occurring organic material adsorbed on the surfaces of the kaolinite particles also contributes to light absorption and oxidative treatments are sometimes used in processing to improve powder brightness. Ozone (Allegrini *et al.* 1970; Cecil & Jacobs 1971; Malden 1972), hydrogen peroxide (Bundy & Berberich 1969), potassium permanganate (Duke 1967) and sodium hypochlorite (Iannicelli *et al.* 1972) have been used.

(*e*) *Rheology*

When a kaolin is stirred under appropriate conditions into an aqueous solution of tetrasodium pyrophosphate (TSPP) that contains a small sodium hydroxide addition, a solids content of about 70 % by mass (or 47 % by volume) can be reached. The optimum TSPP addition is about 0.3 % and the optimum pH is about 8. The suspension can be easily poured when freshly made and has a viscosity of about 500 m Pa s at a shear rate of 30 s^{-1}.

The deflocculation of kaolin with TSPP and the higher polyphosphates (Michaels 1958; Lyons 1964; Millman 1964) is due to Ca^{2+} and Mg^{2+} exchangeable cations being displaced from the kaolin surface by Na^+ ions and forming complexes with the polyphosphate ions in solution. Additionally, polyphosphate ions are strongly adsorbed on the kaolin surface, probably at exposed Al atoms on the platelet edges and at steps on the platelet surfaces. The negative charges built up together with the mechanical shear applied during mixing causes the particles to separate. The system is unstable and the polyphosphates slowly hydrolyse to orthophosphate. Complex aluminium phosphates also form (Dennison & Toms 1967).

Some kaolin slurries that have been prepared by using a polyphosphate will form a gel structure within a few hours if left undisturbed (Dennison & Toms 1967; Mallett & Craig 1977) which can give discharge problems when the kaolin is transported as a deflocculated slurry. Gelation is retarded or stopped by adding sodium polyacrylate along with the polyphosphate when the kaolin is dispersed in water. The polyacrylate may adsorb in the form of a looped configuration, which gives steric stabilization and prevents bridging of the particles (Ottewill 1978).

In paper coating a mixture of the deflocculated kaolin and an adhesive is applied to one or both sides of the paper web and dried. The rheological properties of this mixture or coating colour are very important in modern coating processes. Rates of shear can reach 10^6 s^{-1} along the line of contact of the blade with the paper in blade coating. Dilatency or shear thickening can develop to the extent that the coating colour assumes a rigid form as long as the high rate of shear is applied. If this were to occur in commercial practice, coat weight and smoothness would be adversely affected and printing properties would be degraded. The rheology of kaolin–water mixtures is also important during normal operation. An excessively dilatent suspension can give screening problems.

The relation between bulk kaolin properties and coating colour rheology is complex (Beazley 1972). The important variables seem to be specific surface area, particle shape and particle packing. Viscosity at low rates of shear increases as the specific surface area increases. The shear rate at which shear thickening becomes significant depends on the aspect ratios of the particles and their packing. Anisometry seems important. In general, the platier the particles then the lower the rate of shear at which shear thickening is first observed. Thus a suspension of kaolin that contains many thin particles with large diameters has a greater viscosity than a suspension of the same solids that contain 'blocky' particles with a range of sizes. In a well packed assembly, voids between the spheres of rotation of the larger particles are occupied by smaller particles and this is continued through the size distribution.

Expanding 2:1 layer minerals have an adverse effect on rheology. They are sometimes present in amounts of up to several per cent in kaolins. Processes have been developed to remove or modify chemically the expanding minerals; for example, they can be concentrated in the finest fraction of the size distribution and then removed in a continuous centrifuge (Lyons 1950; Brociner 1971). Alternatively they can be converted to a non-swelling form by adding a solution that contains positively charged aluminium–hydroxy species to a suspension of the kaolin in water and then by raising the pH to about 7. Coagulation occurs and the smectite layers become attached to each other and to the larger kaolinite platelets (McCartney & Yeo 1965; Adams *et al.* 1977; Kunkle & Kollmar 1977, 1978).

In ceramic production which involves plastic forming, particles of high aspect ratio play an important role in providing cohesion and strength. For such applications 2:1 expanding minerals at small concentrations are beneficial and the kaolin matrix is selected accordingly.

6. Commercial production

(*a*) *From primary deposits*

The extraction and production of refined kaolins from primary deposits are described (Menadue 1979). Powerful jets of water are directed at the working faces in the pit to break up the kaolinized granite or matrix. The washing streams gravitate to centrifugal gravel pumps which lift the suspension to spiral classifiers and then to hydrocyclones which produce an overflow containing particles mainly below 53 μm in size. The underflow contains quartz sand as the major component.

The product, which has a pH of about 4.5 and is naturally flocculated, is stored in tanks and allowed to thicken. It is then pumped to a refining plant where a deflocculant is added. Subsequent refining exploits the increase of kaolinite content with decreasing particle size as shown in figure 2. The slurry passes to refining tanks operated in series to give a product with about 12% over 10 μm and 45% under 2 μm and essentially 100% by mass under 20 μm (table 1).

The fraction under 20 μm is suitable as a feed for a paper filling grade or a ceramic clay, although in practice kaolin slurries from several pits are blended together in a central plant. Paper coating grades are further refined in solid bowl centrifuges which typically give a product with about 99.5% under 10 μm and 75% under 2 μm (table 1). The oversize fraction may be further beneficiated by flotation. The refined clay from either stage is flocculated by adding sulphuric acid. Paper grades are generally leached with sodium dithionite and most of the ferrous salts brought into solution are removed during filtration.

The slurry is allowed to thicken and is then filter pressed. In the production of a paper coating grade, a mixture of filter cake and dried clay is passed through a pug mill (Brociner 1970) to improve certain properties, particularly rheology. Product forms include powder, lump containing about 10% water and deflocculated slurry at 65% solids and above. Filler clay product from a tube press (Gwilliam 1971) contains only about 17% water and can be shipped directly without thermal drying.

(*b*) *From sedimentary deposits*

The sedimentary deposits include sedimentary kaolins and kaolinitic sands. The extraction and production of refined kaolins from sedimentary deposits are described (Anon 1955; Murray 1963, 1976; Coope 1979; Harben 1979; Hurst *et al.* 1979). The simplest and cheapest production route uses the airfloat process. The matrix is crushed, dried and ground. It then passes into an air stream of constant velocity. Grit and coarse kaolin particles remain behind. The product is used as a low cost filler where brightness and viscosity are not important.

Most of the kaolins used in the paper industry are produced by wet refining. The kaolin matrix is mined by drag line or front-end loader, crushed and made down with added deflocculant as a suspension in water. The matrix may be slurried at the mine and transported as slurry by pipeline to a central plant. It is degritted, screened and then classified through continuous centrifuges to the sought particle size distribution. The coarse middle Georgia crudes, as mined, have a particle size of 60–70% under 2 μm and are classified to 80–90% under 2 μm for the coating grades. The east Georgia crudes have a particle size of 90% under 2 μm as mined and do not require the same classification.

Subsequent processing involves flocculation, leaching with sodium dithionite followed by dewatering with either parallel plate filter presses or rotary vacuum filters. The kaolin may be thermally dried after extrusion in the form of noodles or it may be deflocculated and the slurry then spray dried for bulk shipment. There is an increasing emphasis on shipment as a deflocculated slurry.

7. DEVELOPMENTS IN SEPARATION

In the production routes outlined above, the kaolin is beneficiated by size separation or refining. Micromineral separation methods have been introduced to remove some of the unwanted minerals from the refined kaolin. In particular, the introduction of flotation and of high extraction magnetic filtration (HEMF) has been of great commercial significance. It has been possible to extend reserves, to reduce overall production costs and to produce new grades. One major application of HEMF has been the removal of titanoferrous and micaceous impurities from Georgia kaolins.

(*a*) *Magnetic separation*

High extraction magnetic filtration was developed between 1963 and 1968 and put into full commercial production by the Kaolin Industry of Georgia between 1973 and 1975 (Kolm 1975; Kolm *et al.* 1975; Iannicelli 1976; Dawson 1977). A slurry of deflocculated kaolin is passed through a canister packed with ferritic steel wool and surrounded with water cooled copper coils through which electric current is passed. The magnetic field in empty space is 2T.

Particles with the greatest volume magnetic susceptibilities and hence analytical Fe_2O_3 contents are retained on the filter. The supply of electric current is halted at intervals and the steel wool is flushed with water to remove the retained impurities.

(*b*) *Discrimination between surfaces*

(i) *Froth flotation*

Froth flotation (Greene *et al.* 1961; Greene & Duke 1962; Cundy 1968) is used to remove titanoferrous impurities from appropriate Georgia kaolin feeds. The analytical TiO_2 content is reduced to about 0.6 % and the shade is improved for the reasons discussed in § 5(*d*). About 500 Mt of high brightness coating grades are produced each year by flotation.

Froth flotation has also been applied to the processing of primary kaolins (Clark 1971). The oversize fraction from the refining stage has hitherto been of limited use as a filler grade because of its relatively high feldspar and quartz content (see § 6(*a*) and figure 2). In the flotation process, the kaolinite and mica particles are separated and represent a valued starting material for several commercial grades.

(ii) *Selective flocculation*

In selective or differential flocculation (Yarar & Kitchener 1970; Kitchener 1972) a small quantity of a polymeric flocculant is added to an aqueous suspension of kaolin. The titanoferrous impurities are selectively flocculated to form aggregates and then flocs (Maynard 1974). The method has been used commercially to beneficiate kaolins refined from East Georgia crudes.

(iii) *Selective coagulation*

When a kaolin is deflocculated with a substantial excess of sodium hexametaphosphate and the suspension is left undisturbed, some of the titanoferrous impurities coagulate and settle out preferentially (Maynard *et al.* 1969). The method was operated commercially for some years before being replaced by selective flocculation.

A later example of selective coagulation is described by Nott & Price (1978*a*, *b*). A suspension of freshly prepared magnetite is added to the deflocculated kaolin slurry. The magnetite particles and the titanoferrous impurities mutually coagulate and are removed by magnetic separation. It seems that almost all of the titanoferrous impurities can be removed under laboratory conditions. Cook & Cobb (1982) describe later developments.

8. USE IN PAPER

Kaolin is used as a filler and as a coating pigment in the production of paper. Major sectors in terms of kaolin consumption are the supercalendered (SC) papers used in the production of large circulation magazines and the light weight coated (LWC) papers used in the production of mail order catalogues. In the SC papers the filler may represent up to 25 % of the total substance. A LWC paper composed of a base sheet of 38 g m^{-2} with a coating of 8.5 g m^{-2} on each side contains about 33 % kaolin. Coat weights (pigment plus binder) may reach 35 g m^{-2} for the high quality art papers.

(*a*) *As a filler*

In papers made from chemical pulp the filler is added to provide opacity and to reduce the cost of the furnish. In the SC papers made from mechanical pulp, the filler again reduces furnish costs and more significantly improves paper gloss and printability.

Excellent accounts of papermaking are given by Casey (1960), Britt (1970) and Macdonald & Franklin (1970) while detailed aspects are described in the specialist publications of the Technical Association of the Pulp and Paper Industry in the U.S.A. (see, for example, Britt 1975; Davison 1982; Tanaka *et al.* 1982).

Filler grades are controlled in terms of particle size, powder brightness and abrasion index. In the U.S.A. they range from the air-floated grades to the wet refined grades including those grades produced mainly for coating applications.

The optical properties of a paper sheet are interpreted (Robinson 1976) by using the Kubelka–Munk equations (§ 5(*d*)). The absorption coefficient k is the algebraic sum of the values for the fibre and filler and is easily interpreted. The interpretation of s is more complex (Bown 1981, 1983) because the filler prevents some of the external fibrillation collapsing on to the fibre surfaces and disrupts the fibre–fibre bonding. Because fibres are held apart, the filler reduces the sheet strength and increases the bulk of the fibre network. The strength of a paper sheet, whether burst or tensile, decreases with decreasing filler particle size at a given loading (Beazley & Petereit 1975).

(*b*) *As a coating pigment*

Paper and board are coated with a mixture of pigment and adhesive to cover a relatively rough substrate. The adhesive (or binder) in the coating colour bonds the pigment particles to themselves and to the base sheet when the coating is dried. The appearance of the paper is improved and a smooth and receptive surface is provided for ink transfer in printing. The coated paper is generally calendered to improve its smoothness and gloss. Kaolin is the major pigment used in coating followed by calcium carbonate. Titania and calcined kaolins (Jones *et al.* 1982) are sometimes added to improve opacity. A mixed coating pigment system of kaolin and calcium carbonate may be used to reduce costs. Dean (1979) gives an excellent introduction to the aqueous coating of paper and board.

European coating grades are controlled in terms of particle size, powder brightness and rheology. There are many unspecified properties that have become established through usage and that contribute to the required consistent performance. In the U.S.A. over 10 coating grades are produced by the different companies. They range in particle size from 73–95% below 2 μm which reflects the wide variation in size distribution of the available curves (see figure 1). They are classified in three groups: regular; delaminated (see §5(*a*)); and high brightness (see § 6(*b*)).

The two major factors that determine the properties of a coated paper are the shape and size distribution of the pigment and the mass of the coat applied. Gloss, brightness, opacity and smoothness all generally improve with increasing coat mass and with decreasing particle size. A very finely sized kaolin can give problems. For example, the amount of adhesive needed to bond the platelets to themselves and to the base sheet increases with increasing fineness. The ultrafine grades impart excellent gloss but may give coatings deficient in opacity because the voids formed between the platelets are below the size required for optimum light scattering.

The ultrafine grades can also give a 'closed' coating which leads to difficulties when the paper is printed by offset lithography.

One recent development has been the deliberate narrowing of the size distribution of a platey Cornish kaolin to give an improved coating grade for LWC papers produced for rotogravure printing (Brociner & Beazley 1980). For this application the coating must be sufficiently compressible to permit contact with the inked cells during impression.

The smoothness of a coated paper is of importance and there is increasing interest in the mechanism of imbibition of coating colour and aqueous phase by the base sheet and the immobilization of solids that results (Baumeister & Weigl 1980; Baumeister & Kraft 1981; Kent 1983). Macroscopic roughness is determined by the shrinkage of the coating and the rate of the capillary imbibition and affects printing properties. Microscopic roughness is determined by the dimensions and orientations of the pigment particles and influences specular reflectance and hence gloss (Oittinen 1981).

9. Use in ceramics

Kaolin is a major component in most ceramic bodies. It is used in the production of sanitaryware, tableware, fine china, electrical porcelain, wall tiles and floor tiles. Introductory accounts are given by Rado (1969) and by Worrall (1982) while Konta (1980) discusses the properties of ceramic raw materials. Certain grades of china clay are calcined to about 1400 °C, ground and graded to give products used in the manufacture of kiln furniture and of moulds for use in investment casting.

Table 4. Illustrative ceramic body formulations

	composition (% mass)				firing temp/°C	
product	kaolin	ball clay	feldspathic flux	silica	biscuit	glost
hard porcelain	50–55	0	15–25	20–30	900	1400
soft porcelain	40	10	20–30	20–30	1230	1100
bone china†	25	0	25	0	1270	1120
vitreous sanitaryware‡	28	24	18	30	1200	—
earthenware	25	25	10–20	30–40	1170	1060
lime earthenware white tiles§	25	25	0	40	1080	980

† Also contains 50 % by mass bone ash.
‡ Nepheline syenite is the normally preferred flux.
§ Also contains 10 % by mass calcium carbonate.

Illustrative formulations are given in table 4, together with firing temperatures. The sanitaryware and tableware sectors are the most important in terms of kaolin consumption.

(a) *Kaolin requirements*

Kaolins with consistent properties are required in the production of tableware and sanitaryware (Bailey 1965). Historically, single pit clays were used. In the mid-1950s standardized ceramic grades were introduced: kaolins from four or five pits are refined and blended to give the sought properties. The two papers by Clark (1957, 1963) that discuss this change and the need for consistent properties make interesting reading.

Kaolins for sanitaryware are controlled in terms of analytical Fe_2O_3 and K_2O contents, particle size distribution, strength and rheological properties.

Kaolins for tableware are again controlled in terms of particle size, chemical composition and strength. Casting properties are also controlled because some shapes are still made by casting. The plastic properties of the kaolin are particularly important in bone china and hard porcelain formulations which contain little or no ball clay. There are other unspecified properties which have become established through usage.

(*b*) *Use in vitreous sanitaryware*

Shingler (1979) has given an excellent review of production methods. In simple terms the ceramic shape or cast is produced by pouring the deflocculated slip (see table 4) at a total solid content of about 72% by mass into a plaster mould. A filtercake builds up on the plaster surface. When the required thickness is reached, the mould is inverted and the excess slip is allowed to drain. The cast is allowed to dewater in the mould. It is then removed and its surface is cleaned by sponging and holes are cut in the shape for waterways and for fittings. The cast is then dried, sprayed with glaze and fired.

The rheological properties of the casting slip are closely controlled. The deflocculant addition is carefully adjusted to be less than the amount required for optimum deflocculation (Bailey 1976). Recent technical developments have included battery casting (Gemmell 1981) and pressure casting (Ahlgren 1976), which have been successful in reducing production costs.

(*c*) *Use in tableware*

Examples of formulations and firing schedules are given in table 4. The glost temperature is that of the second firing after the glaze has been applied. Hard porcelain is made by one company in the U.K. and is the normal high quality product on the Continent, particularly in W Germany. Soft porcelain is not as strong or as translucent as hard porcelain. It is the general quality of much of the continental tableware. The body is more plastic and easily formed than hard porcelain but generally has an inferior colour. Bone china (Franklin & Forrester 1975; Rado 1981) is almost exclusively made in the U.K.; it is strong and translucent. Earthenware is produced in a wide range of qualities. It is not as strong as vitreous ware and has a lower chip resistance. The high content of plastic clay makes for easy fabrication. Opaque and transparent glazes are used.

Most tableware is produced by shaping a plastic mass in or on a plaster mould. Round items, including the majority of plates and saucers, are made in this way. Cups are made in a similar fashion with the handles being added later. Items with complicated shapes are cast from slip. The articles are dried before the subsequent stages of firing, glazing and decorating. These techniques require the constituents to be mixed, usually without the addition of deflocculants, at a relatively low solids content. The slurry is then filtered in a plate press, after which the cakes are fed to a deairing pug which extrudes a large diameter slug from which plastic body is passed to the 'making' machines.

A number of European companies now produce flatware directly from spray-dried granulate (Hahn 1978) which is metered into a press. The method has the advantage of complete automation of the 'making' machine and eliminates the need to dry the ware. A further way of eliminating the filterpress is to 'dry mix' the body constituents (Nilsson 1976). The components which must be free from contaminants, are blended and then made down to a well-controlled moisture content; production then follows the conventional route.

In translucent ceramics (hard porcelain, soft porcelain and bone china), light absorption depends on the concentrations of transition metal ions and which are largely derived from the kaolin. The Kubelka–Munk equations (Kerker 1969) have been applied (Hogg 1979). Values of s are interpreted in terms of light scattering from pores.

10. Use as an extender

Hydrous and calcined grades of kaolin are used as extenders in the paint and polymer industries. Properties of importance are fineness, aspect ratio and whiteness.

In paints, the requirements include some of those sought in the grades used in paper coating. Optical properties of brightness and opacity in the finished paint are important, as are physical properties such as scrub resistance and crazing resistance.

In plastics and rubbers, various other parameters may be important. Surface finish may be improved by fine well dispersed fillers, electrical properties enhanced by calcined clays, and rigidity, and other physical properties such as impact resistance may be significantly modified.

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