

# CORRELATION OF PAPER-COATING QUALITY WITH DEGREE OF CRYSTAL PERFECTION OF KAOLINITE

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## ABSTRACT

Several kaolinite samples were selected for x-ray diffraction studies on the basis of their paper-coating ability. The evaluation of the kaolin clay for paper coating was based on a series of empirical tests including viscosity, resistivity, brightness, and particle-size distribution. The crystallinity of the kaolinites was determined by use of x-ray powder diffraction patterns. In all samples that were good paper coaters, the crystallinity was well developed. Other samples which were poor paper coaters either had poor crystallinity, or, if they had good crystallinity, contained montmorillonite. Crystallinity is not a function of the size fraction. Generally, if the crystallinity is good in the raw sample, then the crystallinity is also good in the  $< 0.25$  micron fraction.

Suitability of kaolinite clay for paper coating varies directly with the perfection of crystallinity and indirectly with the montmorillonite content. Both of these variables can be determined by use of x-ray diffraction data.

## INTRODUCTION

Many people know that clay is used in ceramics but relatively few realize that it is an essential ingredient in paper, both as a filler and as a coating pigment. Paper is essentially a thin sheet of interlaced cellulose fibers which has many voids and surface irregularities in the sheet. The sheet surfaces are made smoother by coating them with a slurry of kaolin (sometimes containing other pigments) in an adhesive solution such as starch. The clay is trapped between the cellulose fibers, giving a closer-textured surface and improving the smoothness, brightness, and opacity. For high-quality papers, a thin film of finely divided clay or other mineral pigment is spread on the surface of the filled sheet and this greatly improves ink absorption, makes the sheet smoother and brighter, and increases the opacity.

Kaolinite clays are excellent pigments for both filler and coating purposes. Several characteristics of clays make them an outstanding raw material in the paper-making field; these are softness of texture, optimum particle shape, chemical inertness, high brightness, good ink absorption, low viscosity, controllable particle-size ranges, easy application of concentrated clay systems to paper, and economy of application.

Several empirical tests are run on the raw clay to determine whether or not it can be used as a paper-coating clay. These tests include viscosity, particle-size distribution, brightness, disintegration, moisture determination, pH, screen residue, and abrasion index. Many of these tests are interdependent; i.e., viscosity is dependent on particle size, brightness is related to moisture content, etc. The

mineralogical composition is important because the presence of a small amount of montmorillonite or other minerals can alter many of the empirical test results. Particle shape is an important factor and this property can be related to the "crystallinity" or degree of crystal perfection of kaolinite and even more directly to particle size distribution in relation to the 2 micron size.

The purpose of this paper is to show the relationship of viscosity, particle-size distribution, resistivity measurements, and brightness to the degree of crystal perfection in kaolinite. Brindley and Robinson (1946) showed that there are structural variations within the kaolinite unit layer and significant variations in the stacking of the unit layers one upon the other. Murray (1954) pointed out specific examples of some kaolin minerals having differing degrees of crystal perfection.

Eleven samples of domestic kaolins from different mines and properties of the Georgia Kaolin Company, one sample from another Tuscaloosa formation deposit, and one sample of a residual kaolin were included in this study. These samples are designated as follows and will be referred to by letter hereafter in this report.

A, B, C, D, E, F, G, H, I, J—Kaolin, Tuscaloosa formation (Cretaceous); K—Kaolin, lower Wilcox formation (Eocene); L—Kaolin, Tuscaloosa formation (Cretaceous); M—Residual paper-coating kaolin.

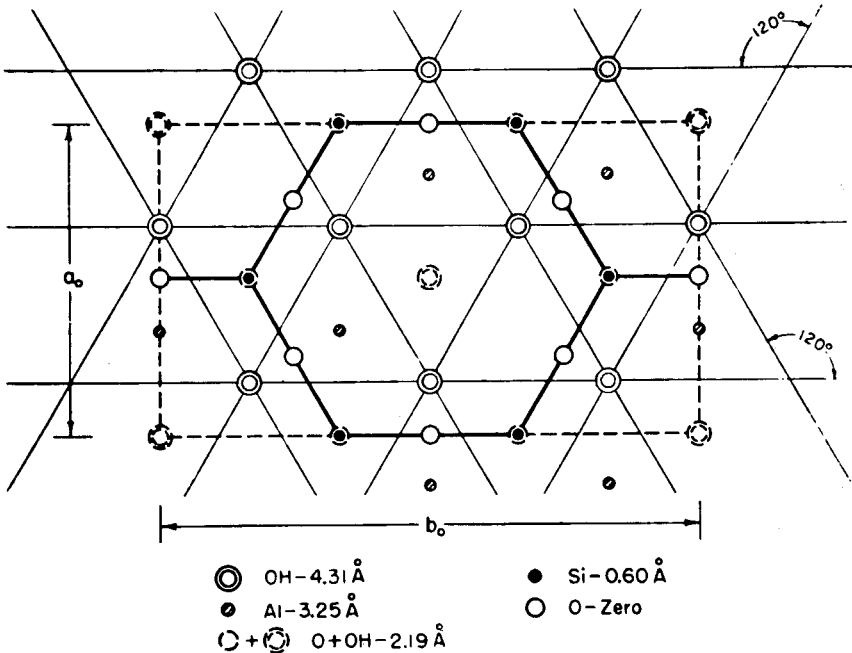


FIGURE 1.—Diagrammatic sketch of kaolin layer projected on (001) plane showing the three possible directions along which the O-OH relationship of the adjacent layer could be satisfied.

## DEGREE OF CRYSTAL PERFECTION

The unit layer of kaolinite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) consists of a silica sheet and gibbsite sheet joined together by shared oxygen atoms and hydroxyl groups. The clay mineral kaolinite is composed of several of these unit layers superposed one upon the other, and is triclinic with one layer per unit cell (Brindley, 1951).

In the kaolin minerals the successive unit layers are arranged such that the oxygen atoms and (OH) groups of adjacent layers are paired (Fig. 1). As is shown on Figure 1 the oxygen atom—(OH)-group relationship can be satisfied in a variety of ways. A displacement of one unit layer relative to the neighboring layer parallel to either the  $a$  or  $b$  axis generally breaks up the pairing of the oxygen atoms and (OH) groups. In certain instances, however, this relationship can be maintained; for example, in shifts parallel to the  $b$  axis with lengths of  $b_0/3$  where  $b_0$  is the cell dimension. These shifts change the type of x-ray diffraction pattern that is obtained (Johns, 1953, p. 188, fig. 1). At one extreme the layers are arranged in a regular manner and the x-ray reflections are sharp, numerous, and well resolved. At the other extreme the layers are arranged in a random fashion and the x-ray reflections are broad, less numerous, and poorly resolved. Summaries of the details of the reflections that are affected by these shifts are given by Brindley (1951) and Murray (1954).

The kaolins which were used for the study show a wide range of crystal perfection. Some are extremely well crystallized and others are poorly crystallized. Figure 2 shows a typical x-ray diffractometer trace of a well-crystallized kaolin

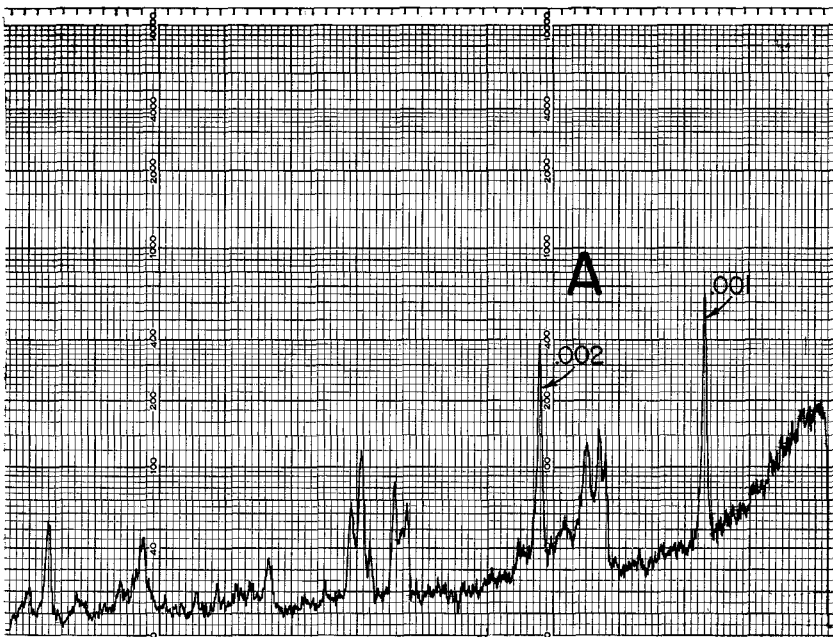


FIGURE 3. — X-ray diffractometer trace of poorly crystallized kaolinite.

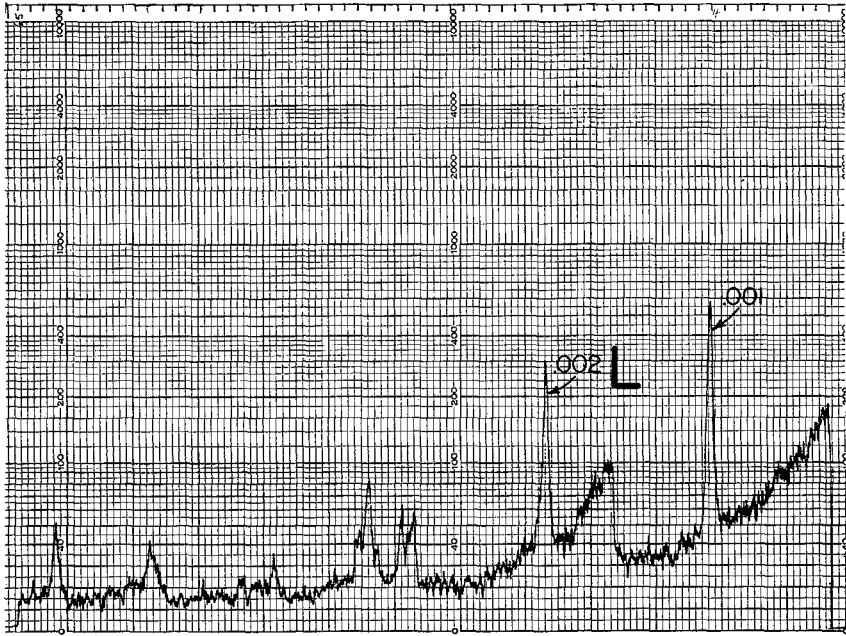


FIGURE 2.—X-ray diffractometer trace of well-crystallized kaolinite.

and Figure 3 a poorly crystallized kaolin. From these and other diffractometer traces of the kaolins a diagrammatic representation was prepared (Fig. 4). The kaolin clays are arranged in order of their crystallinity.

### DISCUSSION OF EMPIRICAL TEST RESULTS

For the past three years the degree of crystal perfection of the Georgia Kaolin Company clays has been determined and it has been noted that usually the clay that has a high degree of crystal perfection is a good paper coater unless it contains an impurity such as quartz or montmorillonite. Therefore a study was undertaken to test the degree of correlation that exists between crystal perfection and the empirical tests of viscosity, resistivity, brightness, and particle size.

Viscosity is a measure of the resistance of a fluid or fluid mixture to flow. Flow properties of coating clays are of importance in that they affect the functioning of the coating operation. Clark viscosity measurements (Clark, 1949-50) were made on aqueous suspensions containing 71 percent solids dispersed to maximum fluidity with tetrasodium pyrophosphate. A Brookfield viscosimeter was used to measure the flow properties. The Clark viscosity values in percent solids are plotted on Figure 5A.

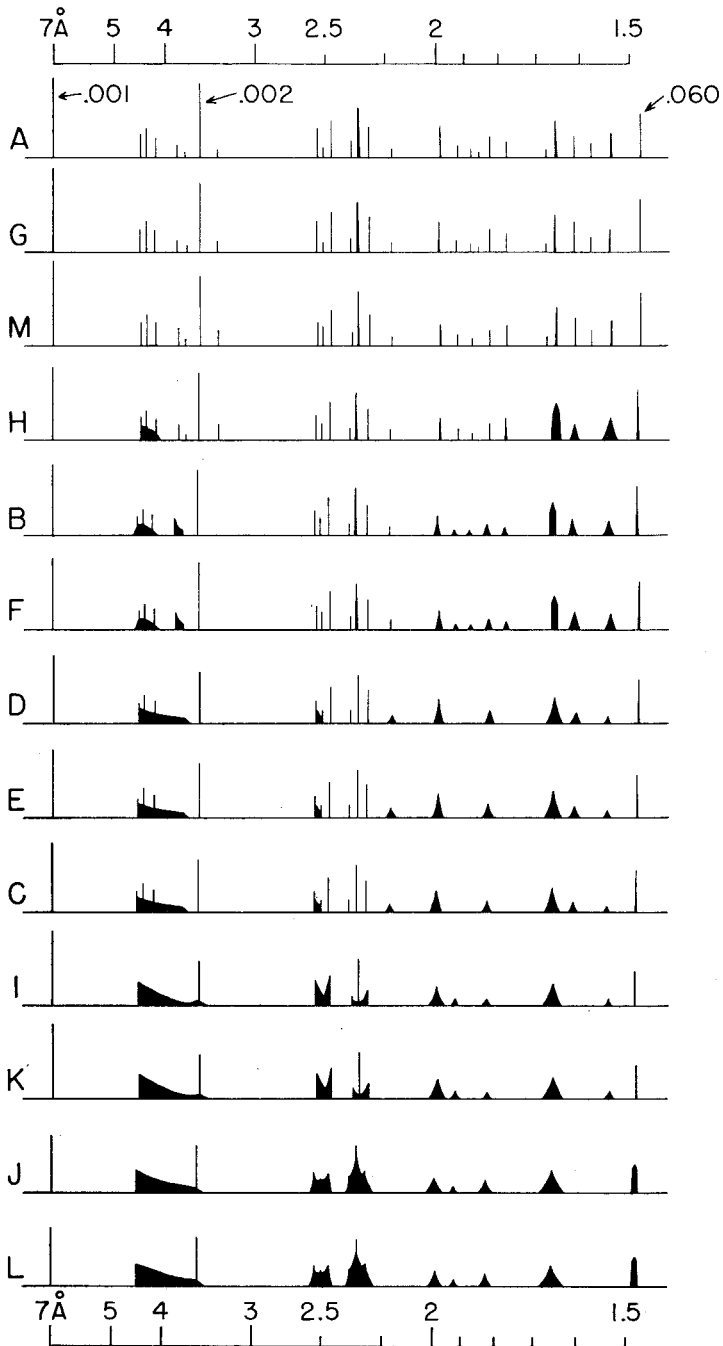


FIGURE 4.—X-ray powder diagrams of samples of kaolinite used in this study arranged in order of crystallinity.

A good correlation exists between viscosity and degree of crystallinity. In general the clays with a high degree of crystal perfection are least viscous and those with a poor degree of crystal perfection are most viscous. Samples M, D, C, and J correlate poorly because these clays contain montmorillonite which increases their viscosity. A partial explanation of the correlation between degree of crystalline perfection and viscosity is given by electron micrographs. When the diffraction patterns indicate a high degree of crystallinity, the micrographs usually show a high degree of geometric crystallinity or blockiness (thickness) of kaolin plates (Fig. 6). The poorly crystallized kaolins are com-

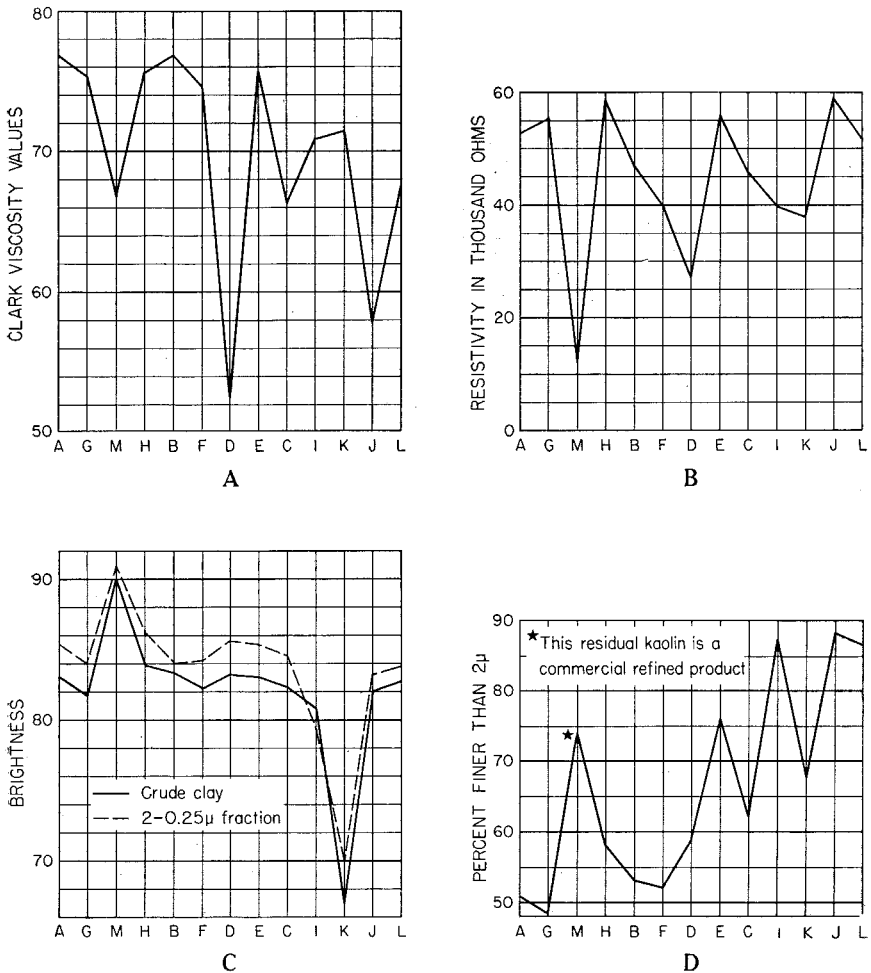


FIGURE 5.—Plots of empirical tests versus crystallinity of clays. (A) Viscosity, (B) Resistivity, (C) Brightness, (D) Size.

posed of thinner plates (Fig. 7) and therefore many more individual edges and corners are available to cause friction and give higher viscosity. Perhaps a greater concentration of valence forces in these poorly crystalline kaolins could provide a higher electrokinetic component of viscosity. Viscosity in kaolin slips involves more than just friction between particles, and considerations of particle shape, mineral composition, particle size, and other factors must be recognized.

Woodward and Lyons (1951) have shown that the 2-micron diameter is a morphological dividing line in kaolins and this certainly should affect viscosity. Below 2-micron diameter the particles are plates and might be expected to show dilatancy at high concentrations and high rates of shear. Above 2 microns the particles are thick stacks and should tend to develop shear blockage.

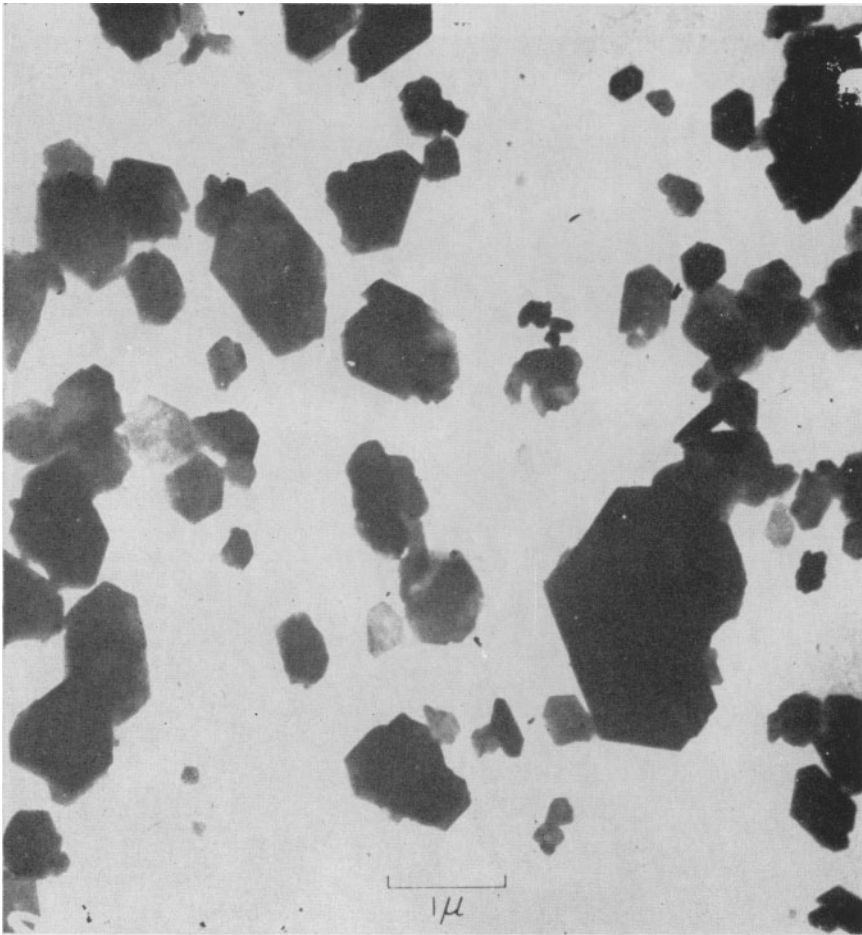


FIGURE 6. — Electron micrograph of well-crystallized kaolinite.

Resistivity is a measure of the electrical conductance of the clay-water system. The measurement is made in ohms at 28° C with an Industrial Instruments, Inc., conductivity bridge, Model RC. The results of this test, expressed in ohms, are plotted on Figure 5B.

Correlation between the degree of crystal perfection and resistivity is poor because the resistivity depends more on the presence of ionizable salts and impurities than on whether or not the kaolin is well crystallized. However, crystallinity may be a factor in the resistivity values, because one would expect that a poorly crystallized kaolin containing more broken bonds and unsatisfied valence charges would give a lower resistivity value than a well-crystallized kaolin.

Clay brightness was determined with a General Electric Reflection Meter which is designed to measure the brightness or reflectance of white or near-white pigments to blue light. The results are expressed as percentage reflec-

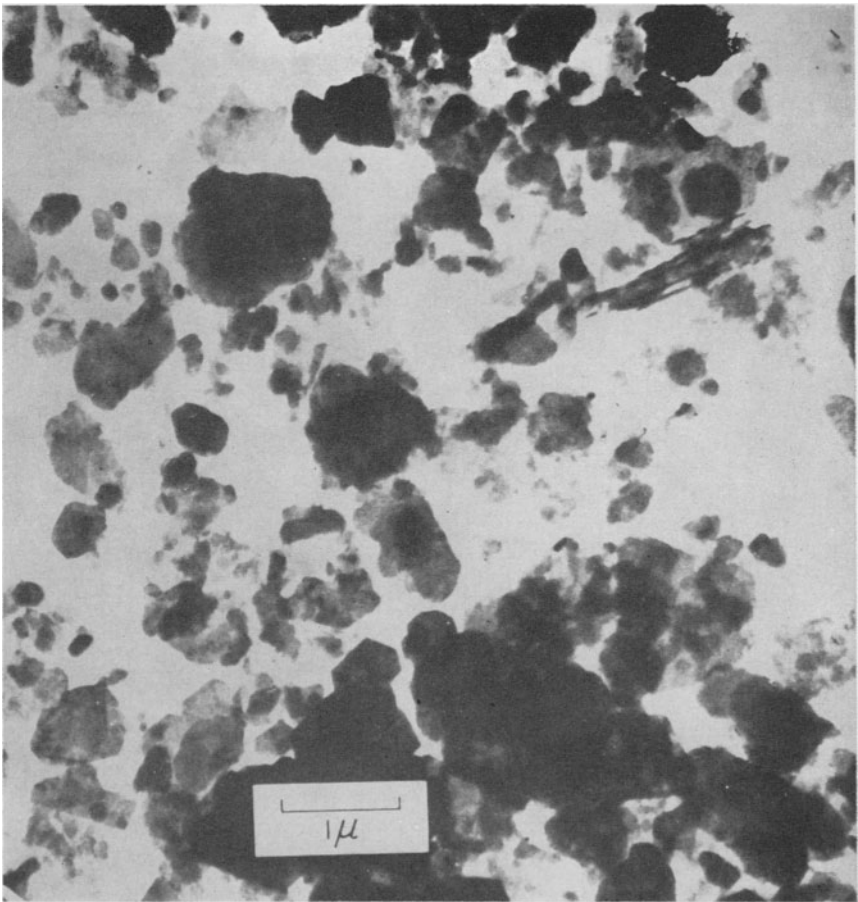


FIGURE 7.— Electron micrograph of poorly crystallized kaolinite.



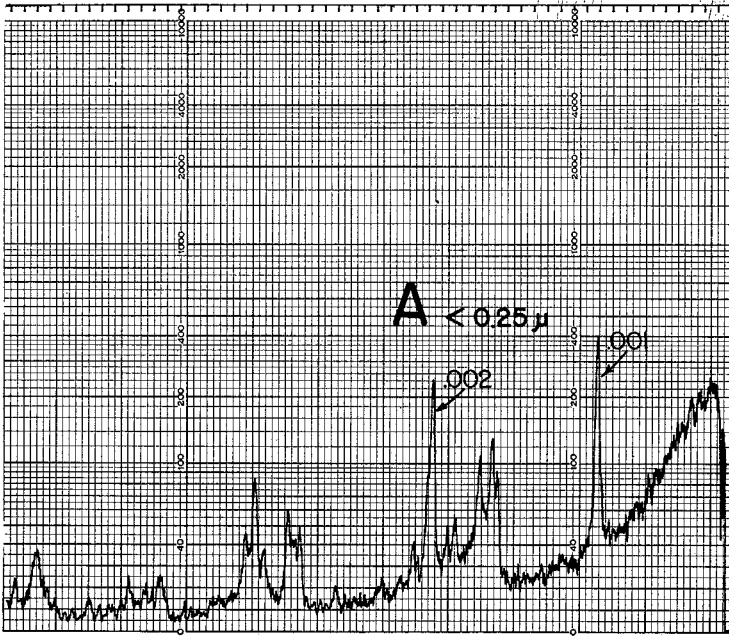


FIGURE 8.—X-ray diffractometer trace of well-crystallized  $< 0.25$  micron fraction of kaolinite.

tance measured against magnesium carbonate at an effective wave length of 458 millimicrons. The procedure for this test is outlined by Lester and Lyons (1947) and Millman (1948). The values for brightness of crude clay and the 2 to 0.25 micron fraction are shown on Figure 5, C. In all cases but one, the brightness value is higher for the 2 to 0.25 micron fraction relative to the crude clay. Much of the colored impurity is present in the coarse and very fine fractions and by using only the 2 to 0.25 micron fraction the color of the clay is improved.

Correlation between brightness and degree of crystal perfection is moderately good but again impurities such as iron oxides exert the prime control over brightness values. However, the poorly crystalline kaolins would be expected to contain more impurities on their surfaces because of more available valence charges.

Particle-size determinations were made by a centrifugal-Casagrande hydrometer method. As has been pointed out recently by Woodward and Lyons (1951) and Koenig and Lyons (1955), the 2-micron diameter in clays is the important size break or control point. The values on Figure 5, D are given as percent finer than 2 microns.

The correlation between particle size and degree of crystal perfection is excellent. Sample M, a residual kaolin, should be disregarded because the original sample was a refined product. In general the coarser the particle size the

better the crystal perfection. This does not hold true within one individual kaolin sample, however. Sample A, which has a high degree of crystal perfection in the crude sample, also has a high degree of crystal perfection in the  $<0.25$  micron fraction of the sample (Fig. 8). In every sample studied, if the original crude clay shows a high degree of crystal perfection the fine clay fraction also shows a high degree of crystal perfection, and if the original crude clay shows a poor degree of crystal perfection then the fine clay fraction shows a poor degree of crystal perfection.

The correlation between particle size of a kaolin clay and degree of crystal perfection is understandable because the better-crystallized kaolins commonly tend to form larger stacks in which the component plates seem to be regularly arranged and are mechanically more durable. This may be significant in terms of the mechanism of the interfacial bonding between the plates which form the stacks. It is very possible that the failure of poorly crystallized kaolins to form adequate and well-constituted stacks may be a manifestation of their failure to form well-crystallized or highly ordered plates. It appears that many of the papermaking use properties of kaolin clays have their origin to a considerable degree in an orderly arrangement of the atoms in the kaolinite unit cell.

#### ACKNOWLEDGMENTS

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