

VARIATIONS IN VISCOSITY OF CLAY-WATER SUSPENSIONS OF GEORGIA KAOLINS

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ABSTRACT

The viscosity of clay-water suspensions is an important factor in determining commercial uses of Georgia Kaolins. Impurities, such as montmorillonite type minerals, in these basically kaolinite clays play a part in causing variations in viscosity. However, seemingly pure kaolinite clays also show variations which seem to be related to morphology and degree of crystallinity. Studies are underway to determine the various factors involved.

INTRODUCTION

The sedimentary kaolin deposits in Georgia stretch along the fall line, the old shore line of the Gulf of Mexico, from Augusta on the East through Macon to Columbus on the West. The kaolins are principally the clay mineral kaolinite with small quantities of other clay minerals, halloysite, and montmorillonite, along with iron oxides, titanium in one form or another, mica, and quartz occurring as impurities. It is not uncommon to find extensive deposits that are better than 95 percent kaolinite.

Commercial use is made of these clays in many ways. The paper trade, using the clay either for a coating pigment or as a filler, is the largest single user. Ceramics and refractories account for large tonnages, and other filler uses for rubber, plastics, oilcloth, wallpaper, insecticides, some paints, to name but a few, make up the balance.

Almost all these uses require some processing of the kaolins before utilization. The processing may take the form of degrading, classification as to particle size, bleaching to improve brightness, and physical changes of form such as drying and pulverizing, or a combination of several of these. The condition of the crude clay as well as the desired properties of the processed clay determine the economic factors in selecting the deposits to work.

In general terms, if the clay is fairly free from grit and not too good in color, it can be used as a carrier for insecticides or some filler uses. If not too high in grit and of good color, the filler uses are increased. If grit and color are fair and there are not too many natural fluxes, the clay can be used for refractories. If the color is quite good, it may be suitable for ceramic whiteware uses. However, both these latter uses are also governed by a property called green strength. This is the ability of the clay when incorporated in a whiteware or refractory body to contribute to the handling properties of the unfired body. This green strength characteristic seems

to be related, moreover, to the viscosity of the clay-water suspension. In general, the higher the viscosity, the better the green strength.

If the color and grit are good and the viscosity is low, then the clay is suitable for being made into a paper coating clay.

Since there are available in Georgia vast quantities of kaolins of low grit, good color, and sufficiently low content of natural fluxes, the viscosity property is probably the most important in determining the ultimate use.

As one might expect, since there is one requirement for high viscosity of the clay-water system to be suitable for a ceramic or refractory clay, and another for a low viscosity to be suitable for a paper coating clay, nature has provided a considerable amount of in-between material. In addition, she was not too careful in how these materials were mixed in the kaolin beds. Most deposits have considerable variation from point to point.

In an attempt to determine the causes of this variation in viscosity, a study was undertaken by the Clay Minerals Project, of the Engineering Experiment Station of the Georgia Institute of Technology. It was hoped that, if the causes could be found, perhaps some method of processing could be suggested which would permit better utilization of this basic Georgia mineral.

EXPERIMENTAL PROCEDURE

Viscosity Characterization

First, it was necessary to find some way of characterizing the viscosity effect. This is no simple measurement in a system as complicated as a clay-water suspension which may be almost Newtonian, dilatant, or thixotropic, depending upon concentration.

A method, although not perfect, that seemed to be adequate for purposes of this study consists of expressing the viscosity of a clay in a water suspension in terms of the percent solids of the clay, dispersed to maximum fluidity, necessary to give an arbitrarily selected viscosity reading when measured at a fixed rate of shear.

A Brookfield viscometer gives the means of measuring the viscosity at a fixed rate of shear, and the relationship

$$\frac{1}{\sqrt{\eta}} = K_1 C + K_2$$

enables one to make a systematic approach in finding the percent solids necessary to give the selected viscosity value.

With a # 2 spindle at 30 RPM on the Brookfield and with 200 centipoise selected as the value of viscosity used to characterize the viscosity effect, it was found that clay-water systems ranging from 20 percent solids to 75 percent solids would produce this viscosity. This represents a rather extreme range, for at the higher solids concentration given the more viscous material would be practically a solid; while at the lower concentration given, the less viscous material would flow like water.

It has been felt that this variation in viscosity characteristic among the kaolins could be explained on the basis of particle size distribution alone. That is, that the more viscous materials were finer in particle size. However, although this does certainly play a part, there are kaolins of similar particle size distribution that differ widely in viscosity, so further investigation seemed desirable.

Examination of Processed Clays

The first attempt that was made to seek a clue as to the reason for this vast range of viscosities was to examine a large number of clays by means of the electron microscope. These were commercial samples that the experiences of the companies had found to be suitable for certain applications. At least some of these applications were determined by the viscosity of the clay in water suspension.

Previous experience in examining kaolins by means of the electron microscope had indicated the desirability of dividing the clay into size fractions. This is brought about by the fact that there is a change of morphology in kaolinite with particle size.

The very smallest kaolinite particles, those below about 0.5 microns, always look like flat pseudo-hexagonal plates, as seen in Figure 1. This shape continues in some kaolins up to around 2 microns, as seen in Figure 2. In the six years that this laboratory has been examining Georgia kaolins by means of the electron microscope, a single crystal larger than about 2 microns has not been found. In the sizes above 2 microns, a composite particle shape is found. This is illustrated by the two views of an about 7 microns piece. Figure 3 shows a "top" view of the particle. It is seen that the construction is a sheet composed of a mosaic of the hexagonal plates while Figure 4, a "side" view of the same particle rotated through about 90°, shows that these mosaic sheets are stacked in layers like a pack of cards. This construction continues up to the larger sizes as indicated by Figure 5, an optical micrograph of a particle over 100 microns in length.

Because of this morphological change, therefore, the clays selected for study were first fractionated into size groups. One group was $\frac{1}{2}$ micron and less, another a fraction of those sizes between about 1 and 2 microns, and the last a fraction between 8 and 10 microns.

The results of the examination of the commercial clays is as follows:

If the clay was one where a low viscosity was necessary, such as a paper coating clay, the particles in the size range from 1 to 2 microns were mostly the single, flat, pseudo-hexagonal type as seen in Figure 2. The larger pieces were cylindrical "stacks" of sheets showing regular outlines, as illustrated in Figure 6. Of course, since these processed clays are also controlled as to particle size, there were very few of these larger pieces.

On the other hand, in the clays whose use depended on having high viscosity, such as the whiteware and refractory clays, only the smaller particles were single plates. In the size range from 1 to 2 microns, the basic shape

was mostly irregular "stacks." As can be seen in Figure 7, the basic crystal plates that make up these sheets that are stacked together are much smaller than the overall size of the sheet. The pieces larger than 2 microns were also the irregular type of "stacks" shown in Figure 8 rather than the "cylindrical" type.

Based on this examination, then, the belief is that the nature of the particles in the 1 to 2 micron range is a clue to viscosity characteristic of the clay in water suspension. Perhaps this fits into the feeling that the viscosity of a suspension is a summation of three contributions: the first, the energy needed to shear the suspending liquid; the second, the energy required to rotate the particles in a velocity gradient; and the third, the additional energy required because of the interaction of the particles with each other. This third effect might well be increased by the irregular shaped particles that were noted in the 1 to 2 micron and larger size range.

Examination of Crude Clays

The study was then continued using crude kaolin samples. It must be remembered that the previous series was of processed clays, where the years of experience of the producers in selecting the crudes from which to process the product, as well as the processing itself, may have played its part. Still using the experience of the producers as a guide in selecting samples this time, two general types of crude kaolins were studied. The first type was one found by the producers to be too viscous for paper but not viscous enough for ceramic use; the second was too viscous for any use.

The crude kaolins described as being too viscous for any use seemed all to be of the type that contained a considerable percentage of montmorillonite. This was indicated by the messy look of the fine fraction when viewed by means of the electron microscope, as shown in Figure 9, and by X-ray diffraction using the glycol technique.

The in-between viscosity material presented a more varied aspect. Some definitely seemed to have a small content of montmorillonite. On the other hand, some resembled in particle shape distribution the ceramic and refractory type clays of the previous study.

As an additional study, these clays were examined by means of X-ray diffraction techniques to determine the degree of crystallinity of the kaolinite. That is the method of characterizing the crystallinity in terms of the random $\frac{nb}{3}$ shifts that occur in the crystal lattices.

The results are, to date, not conclusive because of difficulty in resolving some of the lines taught by Brindley to be the criterion as to good or poor crystallinity. However, for those clays where montmorillonite was not a factor in explaining the increased viscosity, there was an indication that they were comprised of the more poorly crystallized material.

This suggests, remembering the results of the previous study, that the degree of crystallinity has a relationship with the size of the actual crystal

pieces that are formed. It would seem that the more poorly crystallized material did not form as large crystal plates. However, the evidence for this is far from conclusive even from this study, which is based solely on Georgia kaolins.

CONCLUSIONS

In conclusion, therefore, it seems that there is a definite relationship between the particle shape distribution and the resulting viscosity of a clay-water suspension made from a Georgia kaolin. In addition, there is an indication that this particle shape distribution is related to the degree of crystallinity of the kaolinite. The more poorly crystallized material does not form as large individual crystal plates and the increase in the composite, irregular stack form both in the larger sizes and in the 1 to 2 micron range produces an increase in the viscosity of the clay-water suspension.

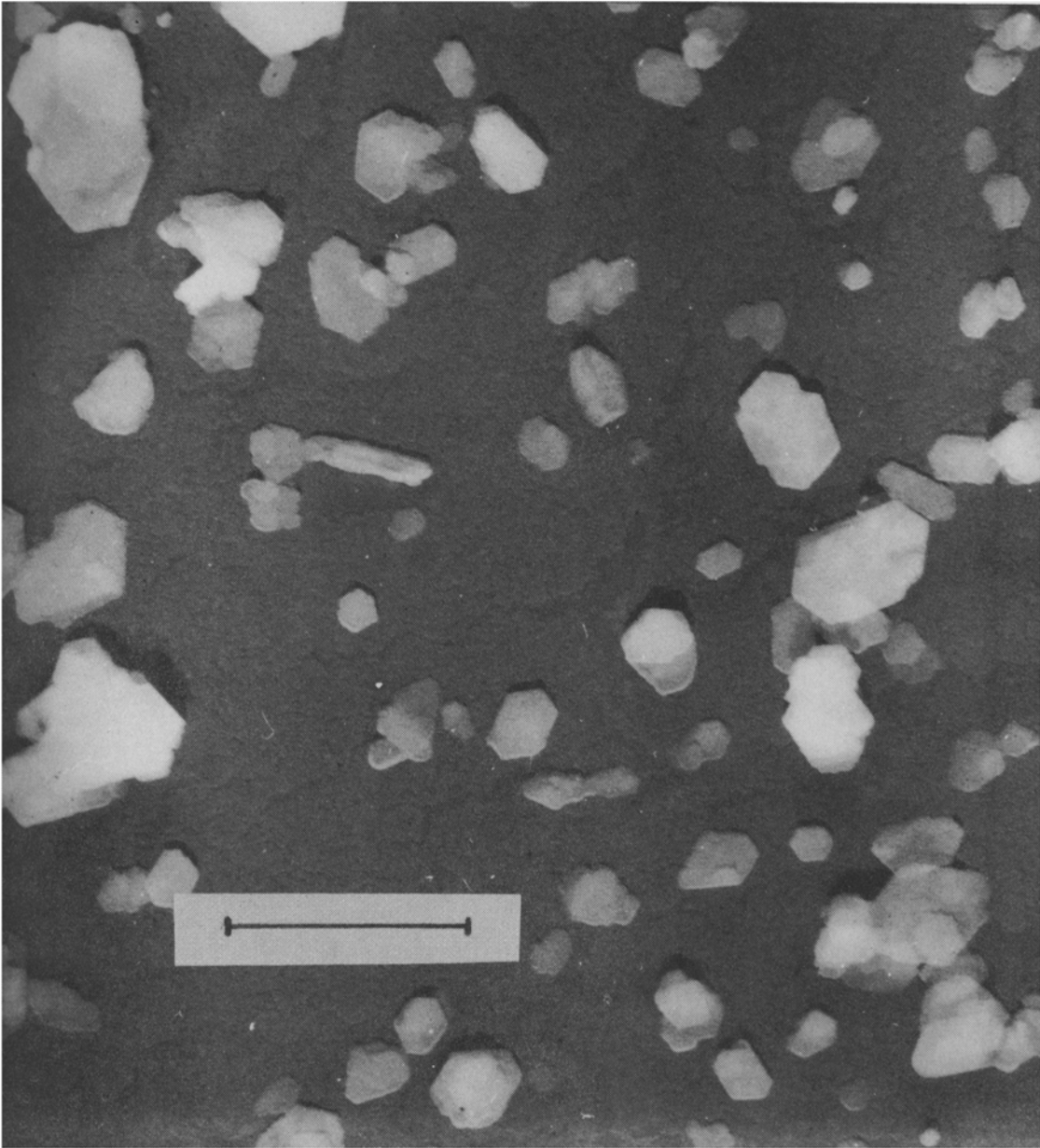


FIGURE 1.— An electron micrograph showing the particle shape of the below 0.5 micron size fraction of a Georgia kaolin. This represents the usual appearance of this size fraction in all types of kaolins. This is a negative print and the line shows the size of 1 micron at this magnification.

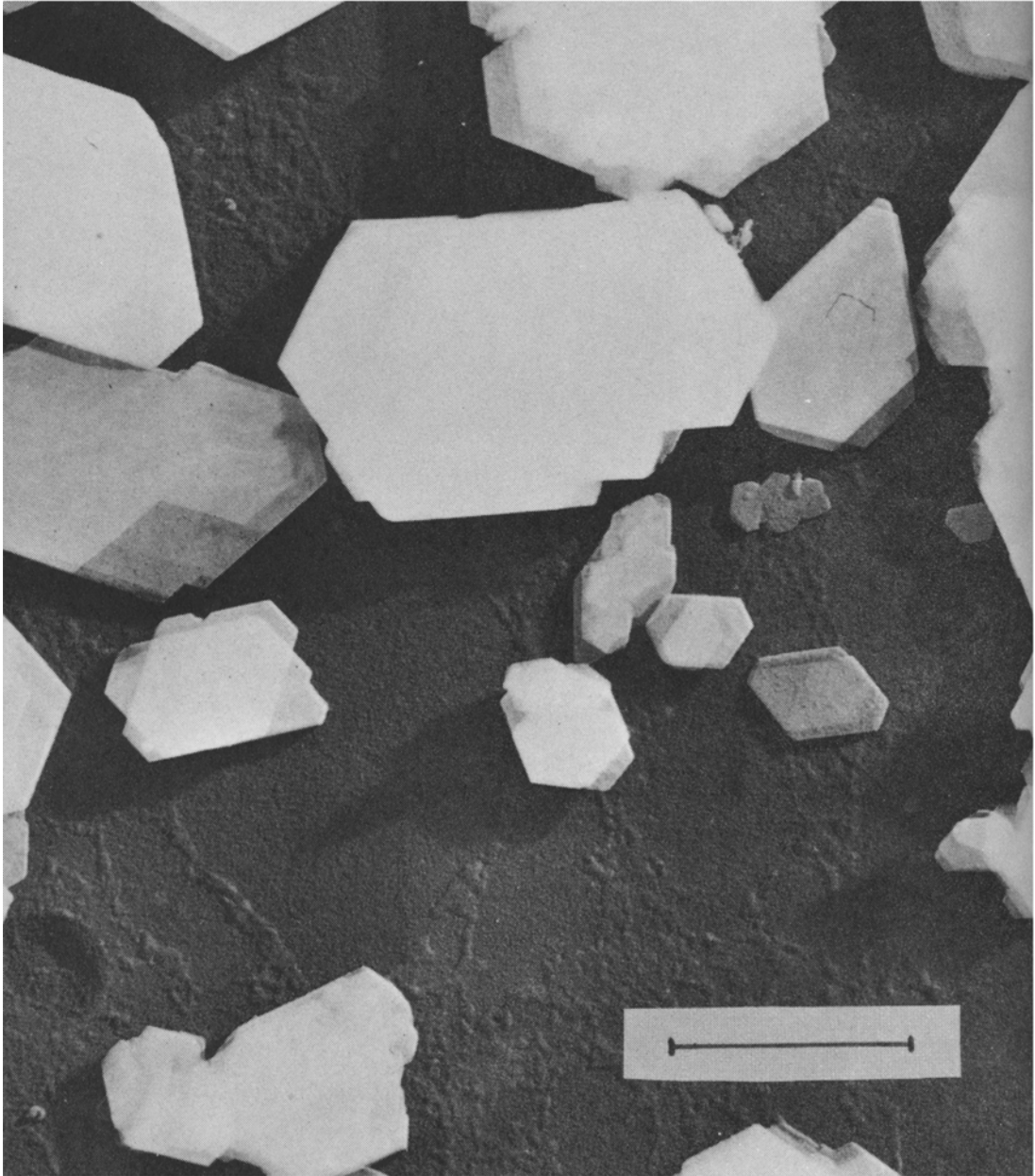


FIGURE 2.— An electron micrograph showing the particle shape of the 1-2 micron fraction of a well-crystallized, low viscosity Georgia kaolin. Note the relatively large, symmetrical crystal plates. Negative print with line showing the size of 1 micron.

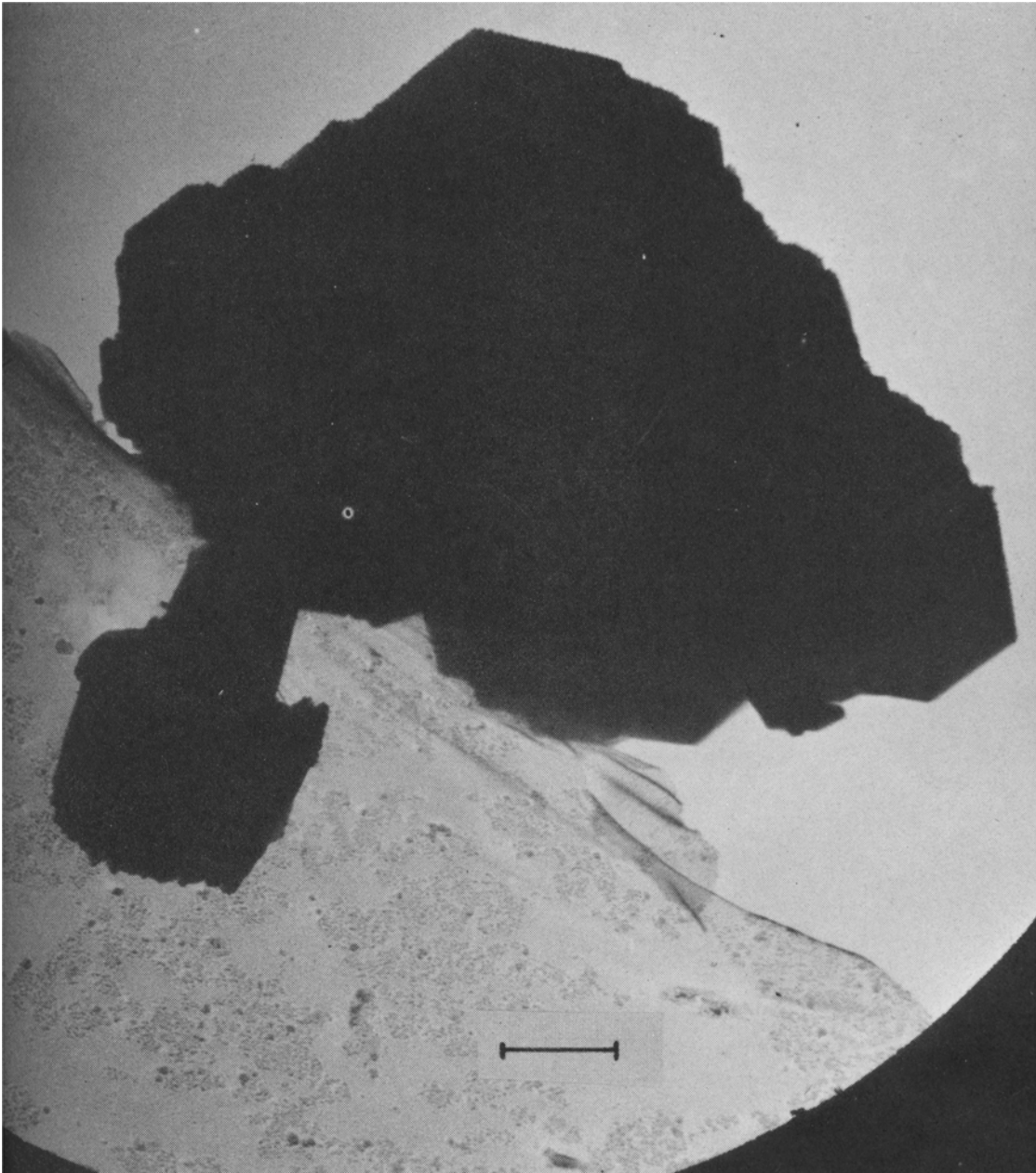


FIGURE 3.—First of two electron micrographs of the same larger-than-2 micron kaolinite particle. This “top” view shows that the construction of these pieces is a sheet made up of a mosaic of the pseudo-hexagonal plates seen in the views of the smaller size fractions. Positive print with line showing the size of 1 micron.

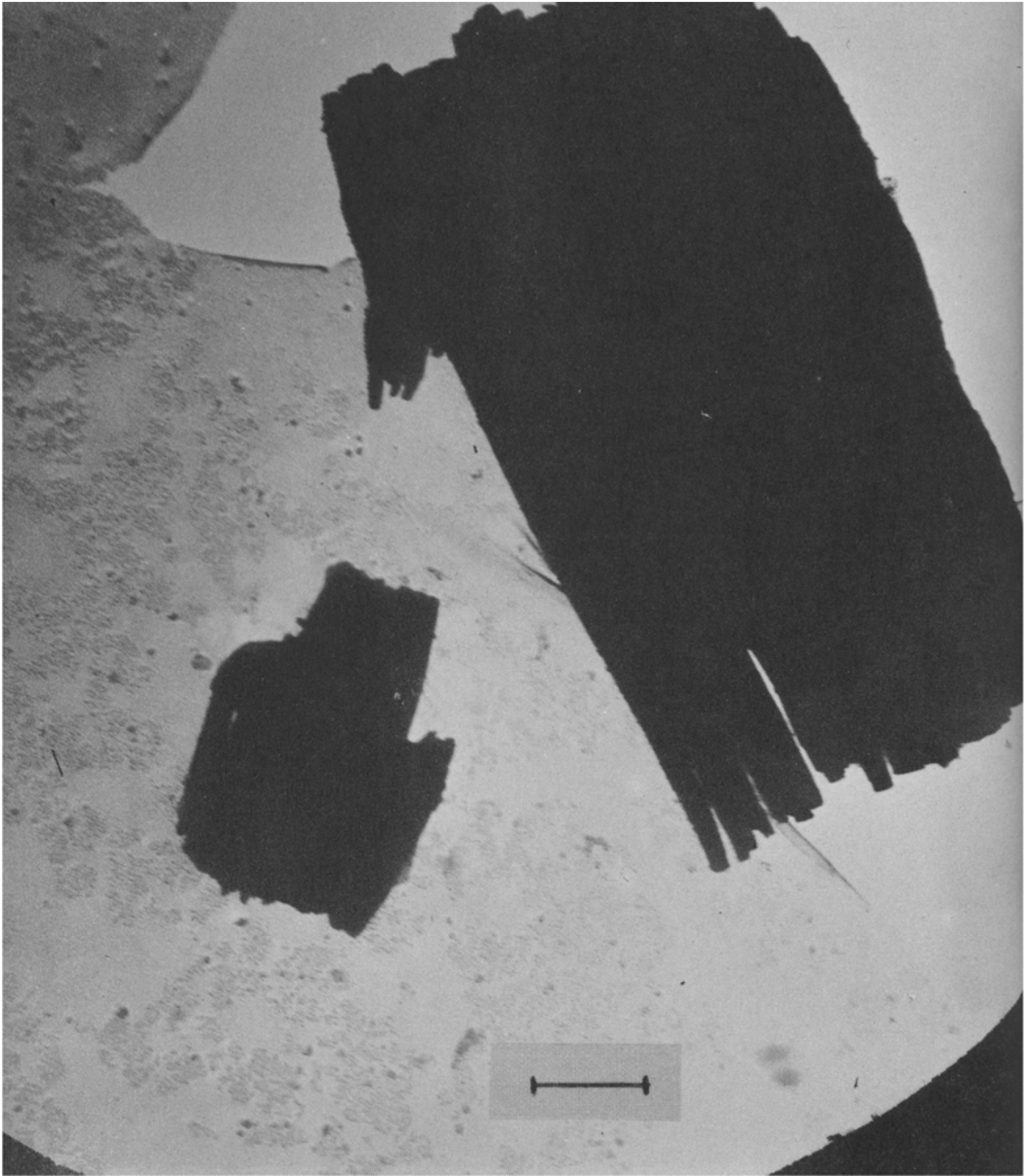


FIGURE 4.— Second of two electron micrographs of the same larger-than-2 micron kaolinite particle. This “side” view, with the particle rotated through about 90 degrees from its position in Figure 3, shows that the mosaic sheets are stacked in layers like a pack of cards. Positive print with line showing the size of 1 micron.



FIGURE 5.—An optical micrograph of a kaolinite “stack” over 100 microns in length. Although the resolution in this view is not sufficient to show the details, this piece is made up of hundreds of layers arranged as is shown in Figure 4.

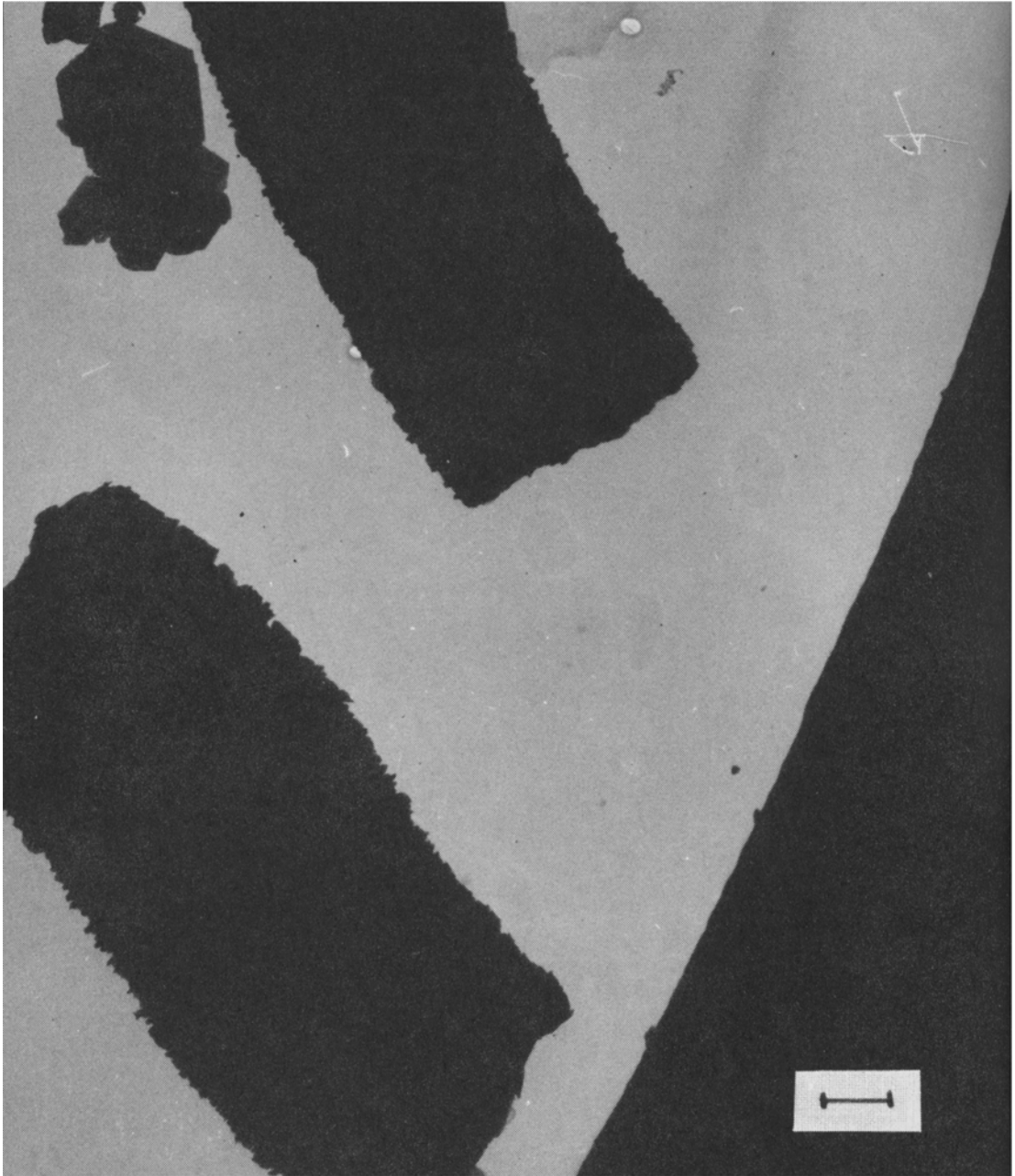


FIGURE 6.— An electron micrograph showing the “cylindrical” type stacks of kaolinite that are found in the larger-than-2 micron size range of a well crystallized, low viscosity Georgia kaolin. Positive print with line showing the size of 1 micron.

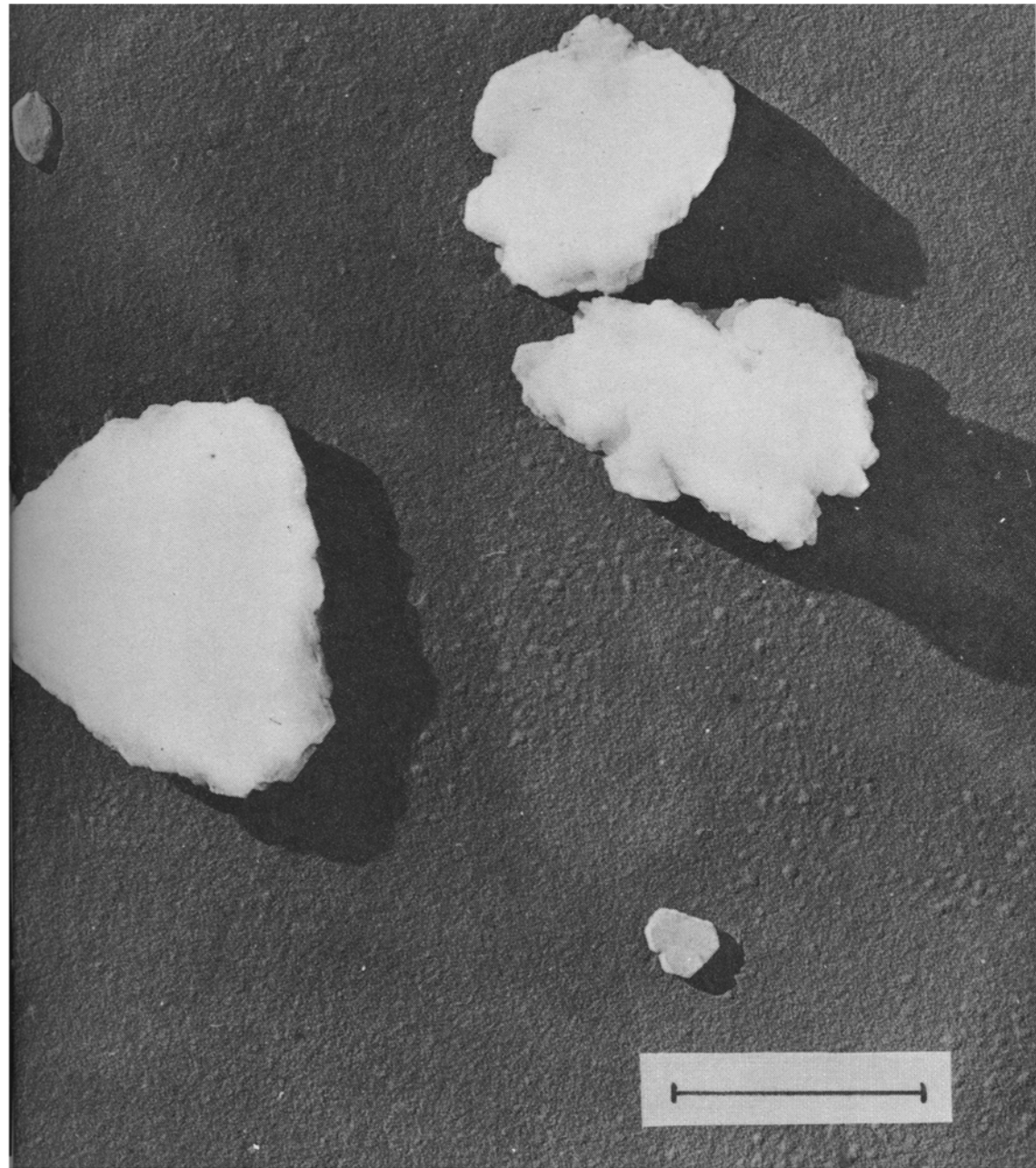


FIGURE 7.— An electron micrograph showing the nature of the particles of kaolinite in the 1 to 2 micron size fraction of a poorly crystallized, high viscosity Georgia kaolin. Compare with Figure 2. Negative print with line showing the size of 1 micron.

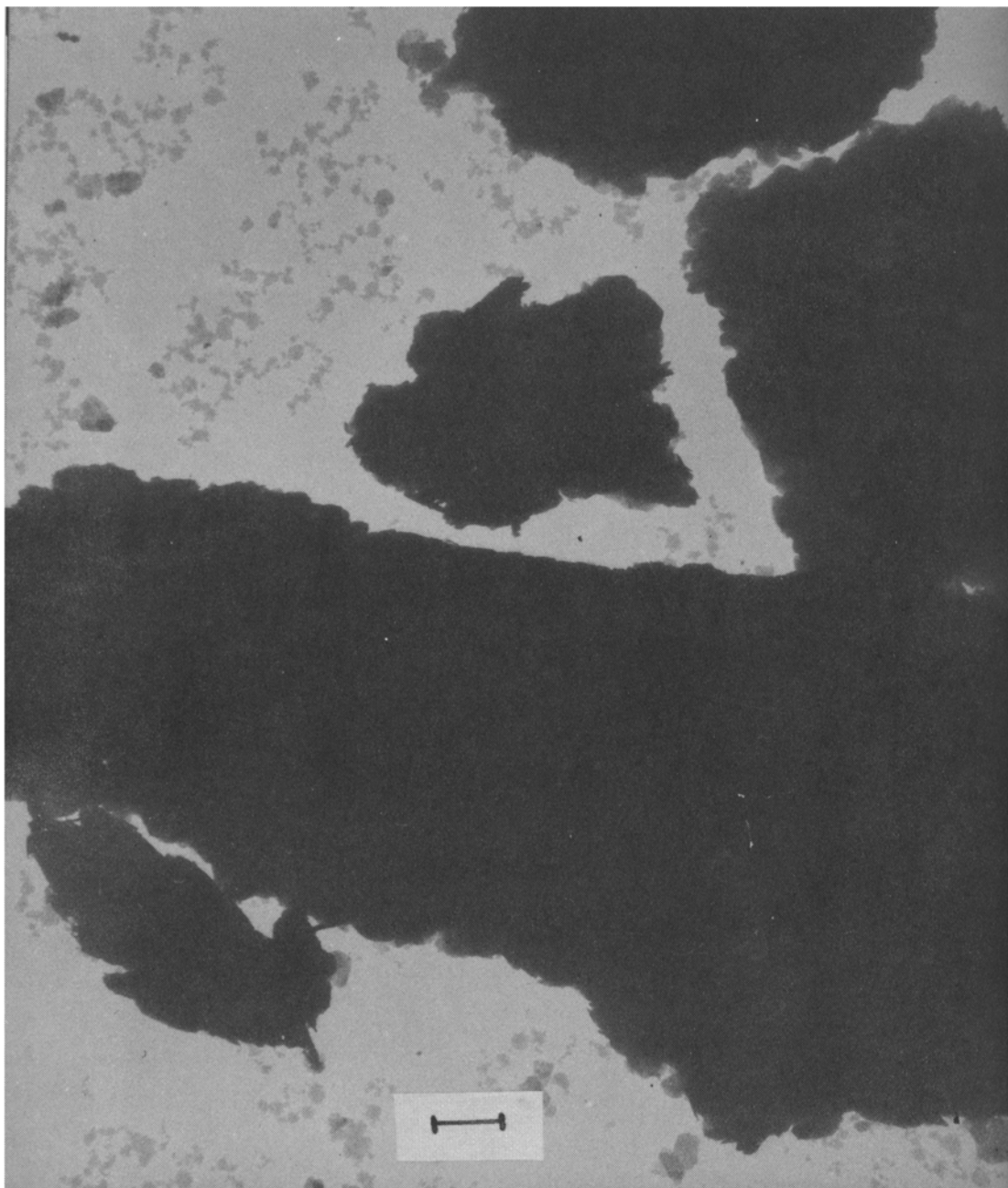


FIGURE 8.—An electron micrograph showing the nature of the larger-than-2 micron size fraction of a poorly crystallized, high viscosity Georgia kaolin. Compare with Figure 6. Positive print with line showing the size of 1 micron.

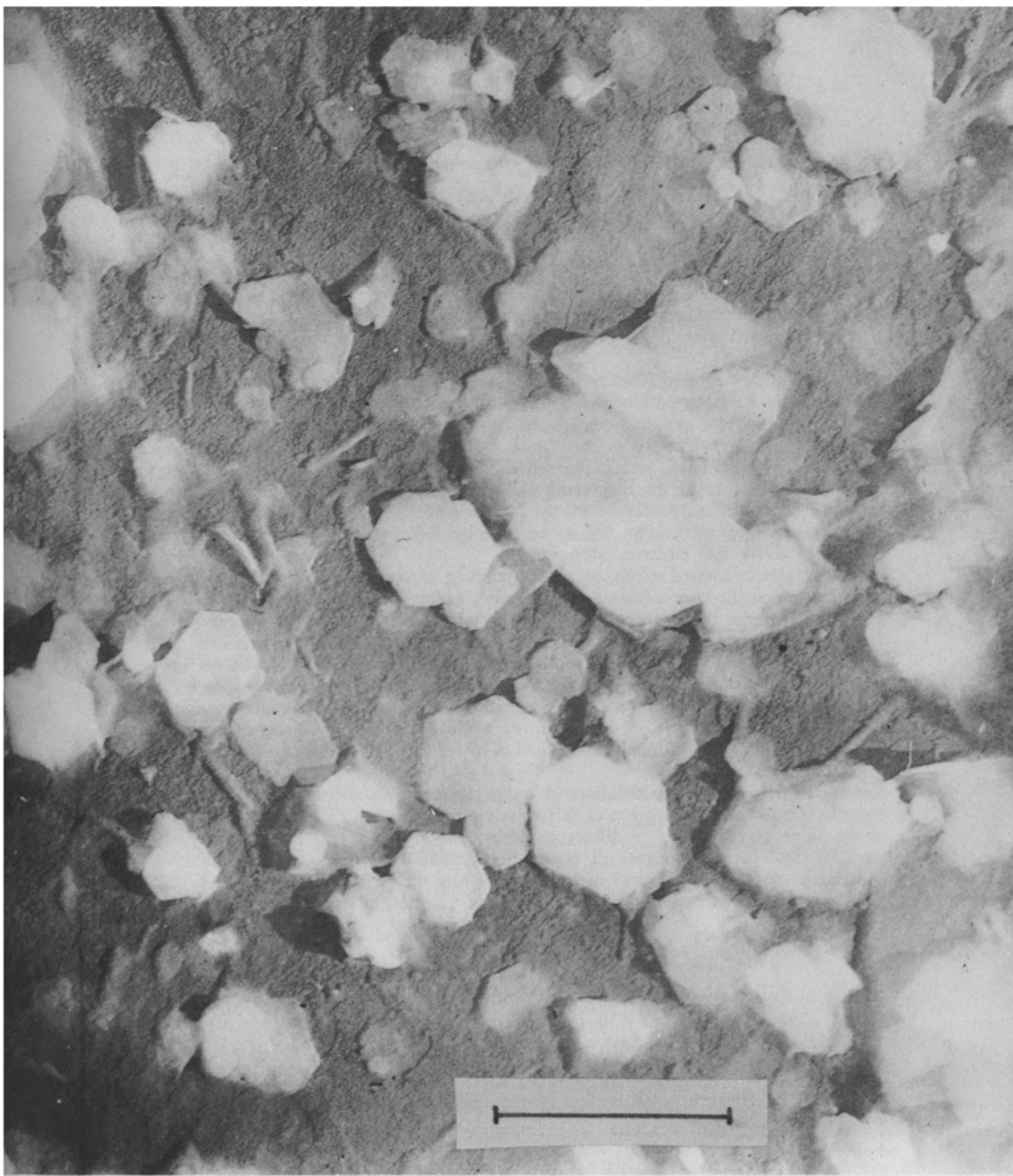


FIGURE 9.—An electron micrograph of the less-than-0.5 micron size fraction of a Georgia kaolin that contains a small percentage of montmorillonite. Negative print with line showing the size of 1 micron.