EFFECT OF IMPURITIES ON THE RHEOLOGY
OF TWO KAOLINS

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ABSTRACT

TWO KAOLINS were given five successive processing steps designed to remove a number of impurities: (1) removal of nonclay and soluble fractions; (2) removal of organic material; (3) removal of iron oxides; (4) removal of allophane; and (5) removal of three-layer lattice minerals. After each of these steps, consistency curves were obtained for each of the clays at both 6.5 and 9.0 pH on slurries containing up to 50 weight % solids.

Photomicrographs and electron micrographs showed that Ka-7 from Bath, South Carolina, contained generally smaller particles than Ka-2 from Macon, Georgia. Lowering the pH from 9.0 to 6.5 in Ka-2 produced no change in plastic viscosity at the lower concentrations and a decrease of about 30 per cent at higher concentrations after processing step 1. A comparison of the same evaluations of step-1–treated Ka-7 showed that the decrease in pH reduced the plastic viscosity by 50 per cent at 5 per cent clay concentration and increased the plastic viscosity by 100 per cent at 35 per cent clay concentration. After complete processing, lowering the pH from 9.0 to 6.5 increased the plastic viscosity at all concentrations for both kaolins by 5–20 per cent. At a clay concentration of 30 per cent, complete processing decreased the plastic viscosity of Ka-2 from 0.4 to 0.02 poise and of Ka-7 from 0.4 to 0.06 poise. Ka-7 showed progressive viscosity changes due to the processing, while Ka-2 showed only a marked change in viscosity for processing step 5. The rheological changes of Ka-2 and Ka-7 with processing are supported by the X-ray diffraction data at the various processing stages. X-ray diffraction data confirm that processing step 5 effectively removed a three-layer lattice expandable mineral from Ka-2, while processing step 3 effectively removed a different three-layer expandable mineral from Ka-7.

INTRODUCTION

THE RHEOLOGICAL properties of kaolins reported in the literature vary by several orders of magnitude for similar concentration and pH conditions. Since these differences could not reasonably be ascribed to size, shape or counter-ion variations of the fundamental kaolin particles, it is assumed that such rheological variations result principally from impurities present. Impurities associated with a kaolin could be both organic and inorganic, water soluble and insoluble, crystalline and amorphous, discrete and coatings.

The objective of this study was to evaluate the effect of naturally occurring

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organic matter, free iron oxide, amorphous aluminosilicates (allophane) and some three-layer lattice clay minerals on the rheological properties of two kaolins. Inasmuch as the effect of allophane was of particular interest, A.P.I. Kaolins nos. 2 and 7 were originally chosen to represent low and high allophane content respectively. In this work the alumina and silica extracted in $2\frac{1}{2}$ min from the kaolin by a boiling 0.5 N NaOH solution was called allophane (Hashimoto and Jackson, 1960). Later work has shown that neither of these two kaolins contains more than 1 or 2 per cent allophane, but that A.P.I. Kaolin no. 7 itself has a lower degree of crystalline order and a much faster dissolution rate in the boiling caustic than A.P.I. Kaolin no. 2 (Langston and Jenne, 1964).

LITERATURE REVIEW

Organic matter is the only one of the impurities considered in this study whose effect on the rheological properties of kaolin has been reported in the literature. Henry (1955) concluded that much of the increase of plasticity of commercial clays, as a result of weeks or months of aging under moist conditions, results from microbiological growth. Johnson and Norton (1941) presented data showing much higher apparent viscosities for " Florida Clay " after treatment with H_2O_2, although the difference is more likely to have been due to the dilute NaOH wash (to provide sodium saturation) and to the additional blunging and screening treatments given the H_2O_2-treated samples that would have produced differences in shape and size of the particles. They did, however, observe that as increments of NaOH were added to the electrodialyzed specimen, the apparent viscosity increased in the pH range of 6.5–9.0 and then decreased at pH 12 to the same value that was obtained between pH 5.9 and pH 6.0. This " hump " in the apparent viscosity vs. pH curve did not occur in the H_2O_2-treated electrodialyzed sample. It could be induced by adding a distilled water extract of lignite to the sample; subsequent removal of the lignite by H_2O_2 treatment removed the " hump ". According to these authors, " The samples in this region exhibit a pronounced thickening during the period in which the viscosity readings are taken. This phenomenon is a type of ' rheopexy '. The thickening of the slip has been known to continue to increase even after from 10 to 15 hours of operation in the modified MacMichael viscometer . . ." They suggested that the sharpness of the peak in the apparent viscosity vs. pH curve would tend to indicate the degree of purity of the sample relative to organic material. Mitchell and Henry (1943) reported that the viscosity was greatly increased in a " soft " Georgia kaolin by H_2O_2 treatment. Mitchell and Poulas (1959) reported that in five of seven Georgia kaolins the viscosity was decreased by H_2O_2 treatment and that, in the other two, there was not much change; however, only the samples that were treated for organic matter removal were blunged, and an evaluation of the effect of the H_2O_2 treatment itself was not obtained.

No references have been found showing the effect of iron oxides on the

rheological properties of kaolins. However, Hauser and Reed (1937) found that 2.47 per cent positively charged iron oxide (dialyzed) mixed with electro-dialyzed bentonite resulted in a gel with a thixotropic setting time in excess of 130 hr and that additional ferric oxide lowered the thixotropic setting time to a few minutes. They cite a private communication to the effect that positively charged aluminum oxide (alumina gel) produced a similar effect.

EXPERIMENTAL

Materials

Two samples of raw kaolins from the A.P.I. series of reference clays were obtained from Wards Natural Science Establishment and used in this study. The preliminary A.P.I. reports on project 49 describe Kaolinite-2 as coming from the Birch Pit near Macon, Georgia, and Kaolinite-7 as coming from the Dixie Rubber Pit near Bath, South Carolina.

According to Kerr, Main, and Hamilton (1951), the impurities found in Kaolinite-2 include: quartz, halloysite, sericite, leucoxene, and carbonaceous material; the impurities found in Kaolinite-7 include: quartz, vermiculite, feldspar, mica (sericite), titanium-bearing minerals (ilmenite or rutile, sphene altering into leucoxene), and some zircon.

Processing of the Materials

Pretreatment.—Any carbonates, sulfates, or manganese dioxide present in the raw clays were removed with a 1 N sodium acetate treatment, buffered at pH 5. The procedure of blending the sample in the sodium acetate solution, followed by wet sieving (to separate the +2-mm fraction), allowed the non-clay and soluble fractions to be discarded. The clay fraction was recovered by centrifugation. Each sample was processed through three extraction cycles with the slurry being heated at about 80°C for 15 min before centrifugation (Jackson, 1956, paragraph 2–6). The centrifuged solids were then washed twice with 1 N NaCl to remove the acetate ions and then washed with distilled water, using sufficient methanol to maintain the clay in a flocculated state, until the decanted liquor gave a negative chloride test with $AgNO_3$. In both cases the supernatant was passed through No. 03 filter candles to ensure that no clay was lost. The recovered washed solids were then dried at 60°C, crushed to −100 mesh, and stored. The resulting samples were numbered Ka-2 I and Ka-7 I.

Organic Matter Extraction.—In each case the organic matter present in the samples was removed by subjecting the solids from treatment I to a H_2O_2 treatment (Jackson, 1956, paragraph 2-15). These extractions were carried out using a total of 40 ml. of 30 per cent H_2O_2 per 10 g of clay solids in 400-ml.

beakers in a hot water bath. After the peroxide treatment the samples were washed, dried, and crushed as described in the preceding paragraph. The resulting samples were numbered Ka-2 II and Ka-7 II.

Iron Oxide Removal.—The solids from treatment II were subjected to three successive iron oxide extractions (Jackson, 1956, paragraph 2–56). In each of these extractions 10 g of the specimen were placed in a solution of 40 ml. of 0.3 M sodium citrate to which 5 ml. of 1 M sodium bicarbonate was added. Suspensions were heated to 80°C, 1 g of $Na_2S_2O_4$ was added to each and the mixture was then stirred intermittently for 15 min. Ten milliliters of saturated NaCl solution was added to each, and the suspensions centrifuged. Finally, the solids were washed, dried, and crushed as described previously, and the resulting samples numbered Ka-2 III and Ka-7 III.

Allophane Removal.—Amorphous silica and alumina were extracted using the method of Langston and Jenne (1964). This process consisted of placing 3 g of Ka-2 III or 0.3 g of Ka-7 III in 200 ml of boiling 0.5 N NaOH for 12 min, with stirring. After the extraction, the flocculated solids were washed, dried and crushed as previously described. The recovered solids were numbered Ka-2 IV and Ka-7 IV.

Particle-Size Classification and Removal of Three-Layer Lattice Minerals.— Identical particle-size separations on the Ka-2 IV and Ka-7 IV samples were made to obtain clean, narrower size range particles. The separations were carried out in distilled water which contained 2 g of sodium carbonate per 18 l. with a clay concentration of 2 g per l. The coarsest fraction was removed by centrifugation. The limit of the finest fraction was set so that X-ray diffraction studies of orientated and glycolated specimens indicated the presence of only a trace of three-layer expandable minerals. The remaining fractions were washed, dried and crushed as previously described. Since only comparable-sized specimens were desired, accurate particle-size determinations were not made. The finished specimens were numbered Ka-2 V and Ka-7 V.

EVALUATION AND RESULTS

X-Ray Diffraction. The solids from the various extraction processes were studied using the X-ray diffraction techniques that have been previously described by Langston, Trask, and Pask (1958). In their method, oriented specimens are prepared on glass microscope slides. The slides have a density of 20 mg of sample per in.[2] and were successively given treatments of (a) drying at 110°C, (b) glycolation for 1 hr at 65°C, and (c) firing for $\frac{1}{2}$ hr at 600°C. An X-ray diffraction pattern was obtained after each of the treatments. Table 1 shows the effect the different treatments had on some selected characteristic spacings of the various processed solids. Powder patterns were also obtained on −325 mesh material that was dried at 110°C. The diffraction patterns were obtained with a NORELCO diffractometer that was operated using nickel filtered copper radiation at a scan rate of 1° 2θ per min. The

Table 1.—Summary of X-ray Diffraction Results*

Treatment	Orientated, dried 110°C		Orientated, glycolated		Orientated, fired 600°C
Peak	12.6 Å	7.2 Å	17 Å	7.2 Å	9.4 Å
Source of peak	3-Layer	Kaolin	3-Layer	Kaolin	3-Layer
Ka-2 I	500	790	560	740	200
Ka-2 II	380	770	650	790	150
Ka-2 III	d	830	440	830	d 80
Ka-2 IV	560	770	575	780	120
Ka-2 V	0	1010	0	1050	d 7 to 9° 2θ

Treatment	Orientated, dried 110°C		Orientated, glycolated			Orientated, fired 600°C
Peak	10.0 Å	7.2 Å	18.4 Å	10 Å	7.2 Å	10 Å
Source of peak	3-Layer	Kaolin	3-Layer	—	Kaolin	3-Layer
Ka-7 I	13	490	26	0	560	8
Ka-7 II	24	650	26	0	770	20
Ka-7 III	80	800	0	d 12	790	s 40
Ka-7 IV			NO SAMPLE			
Ka-7 V	0	760	12	0	780	d

* Intensities in counts per second
s = sharp
d = diffused

data in Table 1 indicate that kaolin is the major constituent in both of the samples. The stronger reflections for Ka-2 suggest a higher degree of crystallinity. A three-layer lattice mineral, 12.6 Å when dried at 110°C, that expands to 17 Å when treated with ethylene glycol and contracts to 9.4 Å when heated to 600°C is present in Ka-2. It was removed during the particle-size separation step (treatment V). Ka-7 also has an expandable three-layer lattice mineral present. It has a 10 Å spacing when dried at 110°C that expanded to 18.4 Å when treated with ethylene glycol and contracted to 10 Å when fired at 600°C; the latter line, however, was very weak on the Ka-7 I specimen but appeared stronger on the Ka-7 II specimen. This expandable material was no longer present after the iron oxide removal step (treatment III). Some hydrous micaceouslike (10 Å) material appeared in the Ka-7 series after the iron oxide removal processing (treatment III); this was subsequently removed during the particle-size separation step (treatment V). Samples of the Ka-7 IV solids were not available for analysis.

Differential Thermal Analysis Samples were heated at a rate of 12°C per min in equipment where the differences in temperature between the sample and a standard inert material (calcined Al_2O_3) could be measured. A general review of the DTA curves reveals the following: (1) both the exothermic and endothermic effects observed in Ka-2 specimens were stronger than those observed in Ka-7 specimens, and (2) as the material progressed through the various impurity-removal steps, the kaolinite reaction peaks generally became sharper

Table 2.—Plastic Viscosity (Poise) of Kaolin Suspensions*

| | Weight % concentration | | | | | | | | | | | | | |
| | 9.0 pH | | | | | | | 6.5 pH | | | | | | |
Specimen	5	10	20	30	35	40	50	5	10	20	30	35	40	50
Ka-2 I	0.0184	0.0324	0.0515	—	0.830	—	5.48	0.0181	0.0326	0.0763	—	0.414	—	4.93
Ka-2 II	0.0134	0.0203	0.0366	0.331	—	0.714	—	0.0137	0.0214	0.0410	0.319	—	0.230	—
Ka-2 III	0.0139	0.0229	0.0517	0.368	—	0.792	—	0.0162	0.0238	0.0656	0.407	—	0.506	—
Ka-2 IV	0.0130	0.0213	0.0560	0.312	—	0.530	—	0.0126	0.0210	0.0581	0.287	—	0.469	—
Ka-2 V	0.00997	0.0112	0.0149	0.0240	—	0.0402	—	0.0106	0.0128	0.0165	0.0277	—	0.0410	—
Ka-7 I	0.0352	0.0675	0.203	—	0.525	—	—	0.0173	0.0648	0.333	—	0.958	—	—
Ka-7 II	0.0218	0.0298	0.186	0.375†	—	0.479	—	0.0210	0.0304	0.191	0.442*	—	1.58	—
Ka-7 III	0.0142	0.0130	0.0445	0.145	—	0.195	—	0.0156	0.0148	0.0448	0.0891	—	0.114	—
Ka-7 IV	0.0161	0.0283	0.0805	0.144	—	0.338	—	0.0206	0.0294	0.132	0.332	—	1.30	—
Ka-7 V	0.0100	0.0144	0.0207	0.0566	—	—	—	0.0129	0.0162	0.0245	0.0867	—	—	—

* The viscosity of water at 25°C was 0.00893 poise.
† 32%.

more intense with the other smaller thermal effects diminished. This effect was most pronounced for treatment III of the Ka-7 specimen.

Chemical Analysis.—Conventional analytical methods were used to evaluate the silica, alumina, iron oxide, and volatile matter of the various processed solids. There were no significant changes in the contents of either series of specimens (Ka-2 or Ka-7) due to any of the processing steps. Lack of change in the iron contents was confirmed using X-ray fluorescence.

Rheological Measurements.—Viscosity and yield stress measurements on prepared clay-water slurries were made using a modified Precision Inter-chemical coaxial cylinder rotational viscometer. This instrument is equipped with a constant temperature bath, which was maintained at $25° \pm 0.2°C$, a stepwise controller of the rotational speed (0 to 400 rpm), and with a selection of cups, bobs, and torsion springs that produced a working range of shear rates from zero up to 1700 sec^{-1}. It was calibrated against standard viscosity materials obtained from the National Bureau of Standards.

Water suspensions of each of the samples were prepared over the concentration ranges of 5–50 weight % solids as indicated in Table 2. After standing overnight and just before the consistency curves were run, the pH of each slurry was adjusted to either 6.5 or 9.0 pH with a hydrochloric acid or sodium hydroxide solution. After completion of each consistency curve, pH evaluations showed that in no case had the pH varied more than 0.3 pH units. The pH determinations were made with a Beckman Model H-2 pH meter.

Consistency down-curves for each of the suspensions were obtained using a suitable bob, cup, and torsion-spring combination. These curves were obtained by determining a number of points, at 50-rpm intervals. Starting with the viscometer at a steady state at 400 rpm, the rotational speed was decreased and the reading for that speed recorded when the viscometer reached equilibrium, which in most cases required 2 or 3 min. Between the points, in each case, the viscometer rotational velocity was returned to equilibrium at 400 rpm before the next point on the consistency down-curve was determined. From these consistency curves, plots of shear stress vs. shear rate, graphical values were obtained so as to allow calculations to be made of the plastic viscosity, the apparent viscosity at 250 sec^{-1} and yield stress. The results are summarized in Tables 3 and 4 respectively. The data for plastic viscosity vs. clay concentration, for suspensions at pH 9.0, are presented graphically on semi-log paper in Fig. 1.

The data in these tables contain three significant figures that reflect the accuracy of the viscometer. However, there were instabilities in the suspensions, such as tendencies for settling (particularly in the intermediate concentration range) that could not be evaluated. The curves as drawn in Fig. 1 were based on the observed data as well as (1) the known instability in the intermediate concentration range, and (2) the previously reported observations of Langston and Pask (1958). The variability between some of the points and curves drawn in Fig. 1 reflects this known suspension instability.

TABLE 3.—YIELD POINT (dynes/cm²) OF KAOLIN SUSPENSIONS

| Specimen | Weight % concentration | | | | | | | | | | | | | |
| | 9.0 pH | | | | | | | 6.5 pH | | | | | | |
	5	10	20	30	35	40	50	5	10	20	30	35	40	50
Ka-2 I	0	0	1.2	—	657	—	2,340	0	0	7.9	—	1,075	—	3,550
Ka-2 II	0	0	32.2	171	—	442	—	0	0	37.8	164	—	196	—
Ka-2 III	0	0.8	24.3	135	—	289	—	0	1.1	27.5	228	—	374	—
Ka-2 IV	0	0	21.6	235	—	309	—	0	0	15.0	135	—	366	—
Ka-2 V	0	0	1.3	3.0	—	5.9	—	0	0	3.5	8.6	—	12.1	—
Ka-7 I	18.9	103	471	—	3,310	—	—	3.7	64.3	539	—	2,180	2,560	—
Ka-7 II	7.2	73	670	813*	—	2,190	—	29.4	64.6	841	994*	—	2,560	—
Ka-7 III	0	1.6	96	398	—	910	—	4.0	3.5	65.4	368	—	972	—
Ka-7 IV	6.9	17	270	411	—	1,340	—	21.1	84.3	907	1,170	—	2,750	—
Ka-7 V	0.8	1.3	10.9	50	—	—	—	1.6	7.5	43	254	—	—	—

* 32%.

TABLE 4.—APPARENT VISCOSITY (POISE) AT 250 sec^{-1} OF KAOLIN SUSPENSIONS

| | Weight % concentration | | | | | | | | | | | | | |
| | 9.0 pH | | | | | | | 6.5 pH | | | | | | |
Specimen	5	10	20	30	35	40	50	5	10	20	30	35	40	50
Ka-2 I	0.0184	0.0324	0.0564	—	3.47	—	14.8	0.0181	0.0326	0.109	—	4.70	—	19.0
Ka-2 II	0.0134	0.0203	0.166	1.02	—	2.51	—	0.0139	0.0214	0.176	0.975	—	1.01	—
Ka-2 III	0.0139	0.0261	0.148	0.906	—	2.17	—	0.0162	0.0282	0.176	1.32	—	2.26	—
Ka-2 IV	0.0130	0.0213	0.142	1.25	—	1.75	—	0.0126	0.0210	0.118	0.825	—	1.92	—
Ka-2 V	0.00997	0.0112	0.0202	0.0365	—	0.0618	—	0.0106	0.0128	0.0304	0.0622	—	0.0898	—
Ka-7 I	0.110	0.480	2.07	—	13.8	—	—	0.0382	0.322	2.49	—	9.58	—	—
Ka-7 II	0.0510	0.322	2.86	3.58*	—	9.13	—	0.138	0.288	3.56	4.38*	—	11.7	—
Ka-7 III	0.0142	0.0189	0.428	1.73	—	3.84	—	0.0317	0.0288	0.306	1.56	—	4.00	—
Ka-7 IV	0.0433	0.0961	1.16	1.89	—	5.63	—	0.105	0.366	3.76	4.97	—	12.2	—
Ka-7 V	0.0134	0.0192	0.0645	0.225	—	—	—	0.0194	0.0462	0.197	1.10	—	—	—

* 32%.

The plastic viscosity data of the 6.5 pH suspensions, as well as the yield point and apparent viscosity data for both the pH series, show relationships similar to Fig. 1.
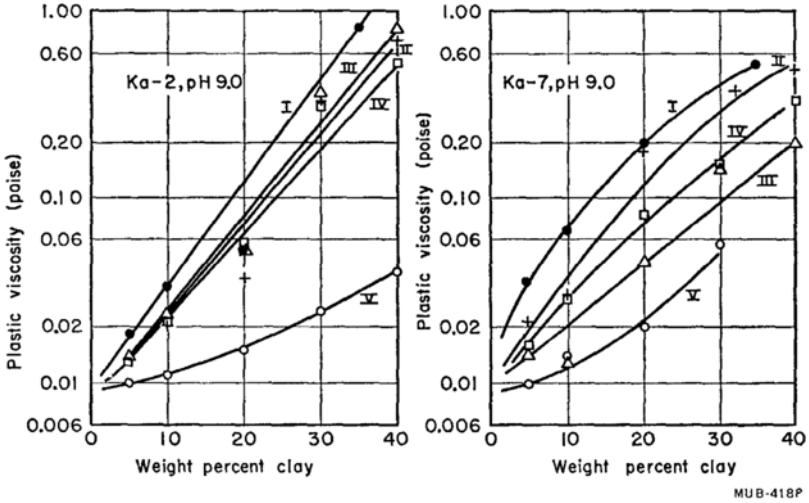

FIG. 1. Semilogarithmic plots showing the effect of the five processing steps on plastic viscosity as a function of clay concentration for 9.0 pH slurries of the two kaolins.

Key: ● Treatment I; + Treatment II; △ Treatment III; □ Treatment IV; O Treatment V.

Microstructure Examination of 6.5 pH and 9.0 pH suspensions containing 0.1 per cent clay (by weight) with transmitted light revealed considerable dispersion of the particles. A number of aggregates, however, were observed. Plate 1 presents micrographs of the pH 9 suspensions of Ka-2 III and Ka-7 III. The specimens were prepared by placing a few drops of suspension between a cover glass and microscope slide, which were held apart by a few 80μ grains. In both of these cases, as well as with the other specimens, the suspended particles varied greatly in size, with the larger particles having a diameter of some 50–100 times that of the smaller particles. Furthermore, the Ka-2 specimens had particles larger than the Ka-7 specimens. The suspended particles remained in constant motion (Brownian type), usually vibrating around a stationary point in the suspension. The larger particles vibrated only slightly. The mottled appearance of the background of the micrographs is due to the vibration of the smaller particles, which are not well defined due to the length of time required to expose the film properly (3 to 5 sec).

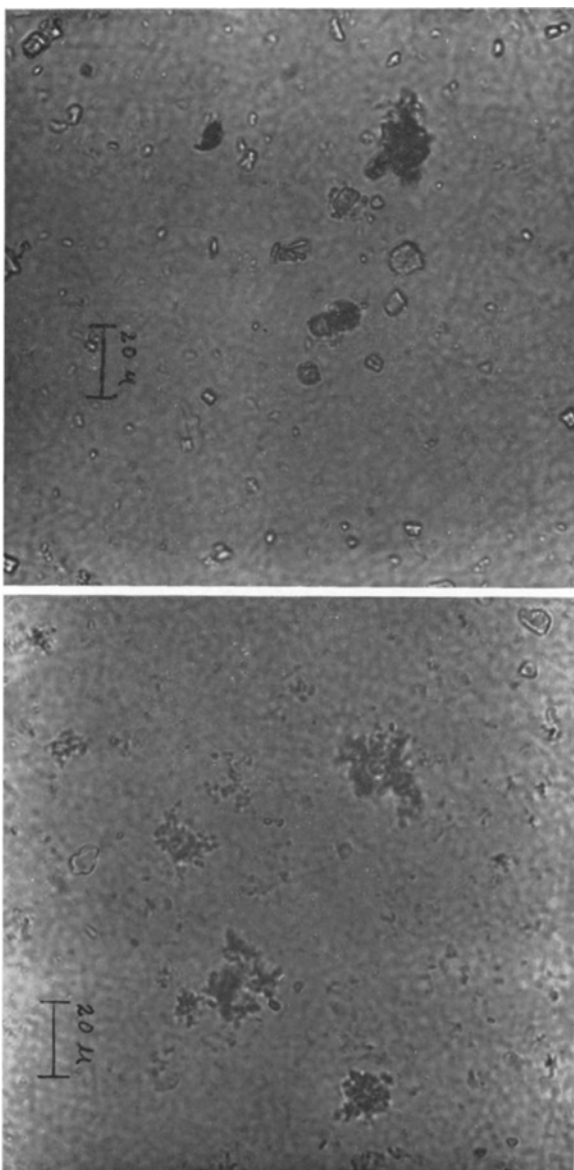Plates 2 shows electron micrographs of the clay solids of Ka-2 I and

PLATE 1. Transmitted light photomicrographs of 9.0 pH, 0.1 weight % clay suspensions. Ka-2 III (above) and Ka-7 III (below). The dark blotch areas are agglomerates, while the mottled background appearance was produced by vibration of the smaller particles.
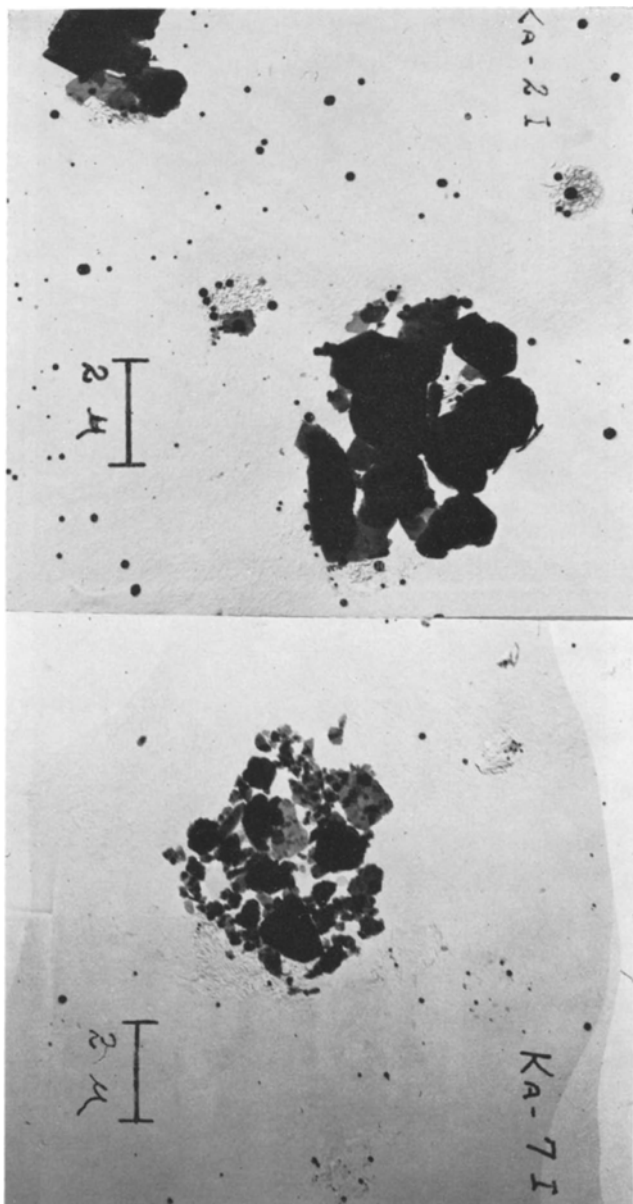
PLATE 2. Electron micrographs showing differences in particle-size distribution between Ka-2 I (above) and Ka-7 I (below).

Ka-7 I. The specimens were prepared from the pH 9.0, 0.1 per cent clay suspensions using a technique consisting of spraying, freezing, and drying by sublimation. They further illustrate the greater crystallinity and larger particle size of Kaolin 2.

DISCUSSION

The rheological behavior, in this case specifically the coefficient of viscosity, of a clay suspension is sensitive to the structure of the suspension. In a general way, this sensitivity can be expressed in terms of a modified Einstein's equation as presented by Langston and Pask (1958) in equation (1):

$$\eta = \eta_0 \left[+ k(\gamma_h + \gamma_c) \, \theta_{\text{solid}} \right] \tag{1}$$

in which γ_h, an effective hydrodynamic volume factor; γ_c, a particle interference factor; and k, a shape factor, are functions of θ_{solid}, the weight fraction of the solid, and the particle-size distribution in some complex way. The γ_h factor is an overall term that converts the θ_{solid} factor into the corresponding volume fraction of the effective dispersed phase; it increases with any hydration, gelation, adsorption of water, or entrapment of water in any structure that may form due to interaction between the solid-phase particles. The γ_c factor is a term that takes into account any interactions between and within the portions of the more rigid phase of the system and thus becomes more important at higher concentrations and with an increase in the number of particles for a given weight or volume of a solid. The data (Table 3) showing the relationship between viscosity and concentration can be interpreted in a general way on the basis of these principles.

Since the consistency measurements were made on clays that were, after all treatments, washed with a NaCl solution to remove excess treating chemicals, then washed to remove the excess chloride ions, and finally adjusted to either pH 6.5 or 9.0, it can be assumed that they were essentially Na-clays. The relatively minor rheological differences between the two pH series support this assumption, although the plastic viscosities and yield points, as expected, are lower at pH 9.0 for otherwise equivalent suspensions. The observed changes in plastic viscosity for either clay for a given clay concentration must then be due to structural changes in the suspension that have resulted from the various treatments to which the clays were subjected.

The specific effects of all of the various treatments on the clays themselves have not been evaluated. The principal indications of changes have been provided by the X-ray diffraction analyses. Besides the kaolinite lines, some lines for expandable three-layer lattice minerals are present. These minerals are different in the two specimens; those in Kaolin-7 were more susceptible to the chemical treatments. The Ka-7 III specimen indicated that the " iron oxide removal " treatment did attack and probably removed the expandable fraction. DTA runs support this conclusion in that the kaolinite thermal peaks

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of Ka-7 III are larger and sharper than those of the Ka-7 I and Ka-7 II specimens. The lack of a significant change in the total iron content suggests that the remaining phases have essentially the same fraction of iron content as the removed phase.

Of further interest is the appearance of diffuse diffraction in the 10 to 12 Å region on the Ka-2 V specimen heated to 600°C; it may indicate the presence of disordered three-layer material, which would account for the higher total silica content in this specimen.

The removal of impurity three-layer minerals in the discarded fine fraction in the preparation of the Ka-2 V and Ka-7 V specimens suggests that they were removed as individual fine particles or as aggregates. The aggregates were of lower density caused by the association of water with the solids either as a hydrosphere about individual particles, as interlayer water or as interstitial water in agglomerates. It is thus evident that Stokes' law calculations could be misleading for systems whose microstructure is not known under the existing test conditions. The Ka-2 V and Ka-7 V fractions showed the lowest plastic viscosities and yield points of their respective series for corresponding weight suspensions but were not equivalent; the former had lower values presumably because of larger (and, consequently, a smaller number of) particles with smaller shape factors, as seen in Plate 2.

The change in plastic viscosity with increasing clay concentration follows a different pattern for the two kaolins, which can be attributed largely to the nature and amount of three-layer lattice minerals present. The Ka-7 suspensions generally show a higher viscosity at the lower clay concentrations and a lower viscosity at the higher concentrations (compared to the Ka-2 suspensions). Also, the greater sensitivity of Ka-7 to chemical treatment is reflected in the viscosity data. The reduction in plastic viscosity after the carbonaceous removal treatment is expected on the basis that the presence of such material would generally be expected to aid in the formation of agglomerates or of a gel-like structure. The compositional changes caused by subsequent chemical treatments, as discussed previously, are also shown by the viscosity results. The Ka-2 III and Ka-2 IV suspensions exhibit only minor changes in plastic viscosity from that of Ka-2 II. The Ka-7 III and Ka-7 IV suspensions, however, show significant changes. The " iron oxide removal " treatment apparently attacks the three-layer lattice mineral, with a resulting decrease of aggregate structures as suggested by the correspondingly large decrease in viscosity. The " allophane removal " treatment apparently removed amorphous cementing material between kaolinite crystallites, resulting in a larger number of smaller particles with larger shape factors and consequently higher viscosities. The lower viscosities of Ka-7 I– Ka-7 IV suspensions (compared to the Ka-2 specimens) at the higher concentrations can be attributed to particles and structures that can be more easily distorted and sheared, as might be expected from the presence of an appreciable fraction of three-layer lattice mineral and of thinner, smaller and more numerous clay particles.

CONCLUSIONS

The rheological behavior of kaolinite suspensions free of three-layer lattice minerals is similar; differences are primarily due to differences in the size distribution and shape factor of the kaolinite particles. The presence of impurities of the gel and the expanding layer lattice mineral types causes large changes in rheological behavior by especially affecting the effective hydrodynamic volume factor. Some of these phases are more sensitive to any chemical treatments to which they may be subjected, which, in turn, results in changes in rheological behavior.

A more quantitative analysis would require a detailed study of the structure existing in the suspension for a given set of conditions for which adequate techniques have not yet been developed. A further complicating factor is that, in most cases, the structure in the suspension is dynamic and undergoes continual changes with the nature of the shear pattern.

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