Effects of Dry Grinding on Kaolin Minerals. I. Kaolinite

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Considerable work has been done on the effects of dry grinding on clay minerals and related minerals, particularly kaolinite[1]. The resolution of the grinding effects on kaolin minerals has proved helpful in the study of the structure of kaolin minerals. It is considered that understanding of the grinding process is useful for the study of weathering processes, soil fertility and the active solid.

It is well known that the grinding of kaolinite increases the base exchange capacity, but there is no consistent explanation of this increase. In the result of study concerning the dry grinding effect of kaolinite, there are two lines of thought, at least. One asserts that the dry grinding of kaolinite brings about only a reduction in particle size of kaolinite owing to cleavage and fracturing of the kaolinite crystal. The cleavage and fracturing of kaolinite crystal increases the specific surface and the broken bond. These facts lead to an increase in the base exchange capacity. The other insists that the dry grinding of kaolinite causes the formation of a zeolitic substance having a structure similar to that of the original kaolinite; that is, it distorts the lattice, and or decomposes kaolinite to alumina and silica gel. It is considered that wet grinding of kaolinite is effective in causing a change on the surface property but not in the structural change.

Studies heretofore of the grinding on kaolin minerals have been made mostly by ball-milling. Incidentally, it was found by Mackenzie and Milne that mechanical mortar is very effective in causing a change in structure of mica[2]. From this point of view, effects of several-hundred-hours mechanical-mortar dry grinding of kaolinite were studied by X-ray diffraction, thermal, electron microscopic and other methods in this study.

The purposes of this study are to obtain the fundamental information of the structure of kaolinite and the correct explanation of the grinding process of kaolinite, and to present the variation of the grinding effects of kaolin minerals with respect to the crystallinity.

Experimental

The following kaolinites were investigated: Kaolinite from Mesa Alta, N. M., U. S. A.; Kaolinite from Drybranch, Geor., U. S. A.. Both clays are the API Standard Clay Minerals. The structural characteristics of these original clays were discussed in the previous paper[3], and from

1) W. P. Kelly, W. H. Dore and S. M. Brown, *Soil Sci.*, **31**, 25 (1931).
W. P. Kelly and H. Jenny, ibid., **41**, 367 (1936).
C. E. Marshall, *J. Phys. Chem.*, **41**, 935 (1937).
M. L. Jackson and E. Truog, *Soil Sci. Soc. Am., Proc.*, **4**, 136 (1939).
B. T. Shaw, *J. Phys. Chem.*, **46**, 1032 (1942).
W. D. Laws and J. B. Page, *Soil Sci.*, **62**, 319 (1946).
C. W. Parkert, A. T. Perkins and R. D. Dragsdorf, *Trans. Kansas Acad. Sci.*, **51**, 386 (1950).
R. D. Dragsdorf, H. E. Kissinger and A. T. Perkins, *Soil Sci.*, **71**, 439 (1951).
S. J. Gregg, T. W. Parker and M. J. Stephens, *Clay Min. Bull.*, **2**, 34 (1953).
S. J. Gregg, K. J. Hill and T. W. Parker, *J. App. Chem.*, **4**, 631 (1954).
S. J. Gregg, T. W. Parker and M. J. Stephens, ibid., **4**, 666 (1954).

2) R. C. Mackenzie and A. A. Milne, *Clay Min. Bull.*, **2**, 57 (1953).
R. C. Mackenzie and A. A. Milne, *Min. Mag.*, **32**, 178 (1953).

3) H. Takahashi, This Bulletin, **31**, 275 (1958).

these results, it is found that Mesa Alta kaolinite is a triclinic in symmetry and so it has the highest degree of crystallinity of all kaolin minerals. The crystallinity of Drybranch kaolinite is somewhat lower than that of Mesa Alta kaolinite.

A 30 g. portion of the original kaolinite was charged and ground by a mechanical mortar (15.2 cm. in diameter and 8.4 cm. in depth). Specimens were taken out at intervals of 24 hour and examined by X-ray, thermal and electron microscopic method. In conjunction with the above measurements, base exchange capacity and density were measured.

X-ray diagrams were recorded by an X-ray diffractometer (Geigerflex). Experimental conditions are as follows: filtered Cu radiation (Cu$K\alpha$: 1.5418 Å) at 35 kV and 15 mA is used; scanning speed is 1° or 1/2° 2θ per minute; time constant is 4 seconds; receiving slit is 0.2 mm. or 0.1 mm.; angular aperture is 1° or 1/2°. The differential thermal analysis curves were obtained by the apparatus described by Sudo et al.[4]. Care was taken to pack a specimen into the sample block in a homogeneous manner and also keep the weight of the specimen constant. The mean heating rate is 12.5°C per minute. The density was measured by pycnometer in carbon tetrachloride. The base exchange capacity was measured by the following procedures. The specimen was treated with hydrochloric acid, thus convert it into "hydrogen-clay", and after being washed with water was titrated with sodium hydroxide solution. The base exchange capacity was expressed as the number of milli-equivalents of cation, per 100 g. of specimen, required to bring the pH to 7. Measurements of the density and the base exchange capacity were made after it had been dried at 110°C to avoid the influence of the adsorbed water. Electron micrographs were obtained by a Hitachi HU-10A type Electron Microscope.

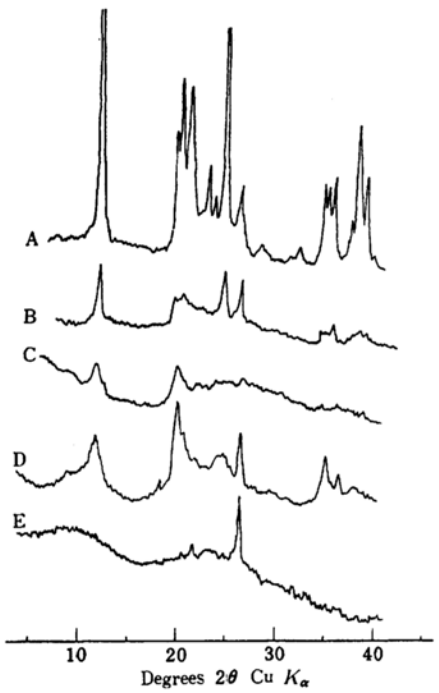

Fig. 1-a. X-ray diffractometer traces of ground kaolinite (Mesa Alta, N. M.).
A, original kaolinite
B, ground 168 hours
C, 168-hour-ground kaolinite treated with 0.1N NaOH
D, 168-hour-ground kaolinite treated with 0.1N HCl after 0.1N NaOH
E, ground 312 hours

4) T. Sudo, K. Nagasawa, M. Amafuji, M. Kimura, S. Honda and M. Tanemura, *J. Geol. Soc. Japan* (*Chishitsu-Gaku Zasshi*), 58, 679 (1952).

Results and Discussion

X-Ray Diffraction Studies. — X-ray diffractometer traces are shown in Figs. 1 and 2. Figs. 1-a and -b show the X-ray diffractometer traces at various stages of grinding of Mesa Alta kaolinite, and Figs. 2-a and -b show that of Drybranch kaolinite. The data obtained from the X-ray diagrams are shown in Tables I and II.

The following major differences, noted in the X-ray diagrams, were used as criteria to determine the structural characteristics:

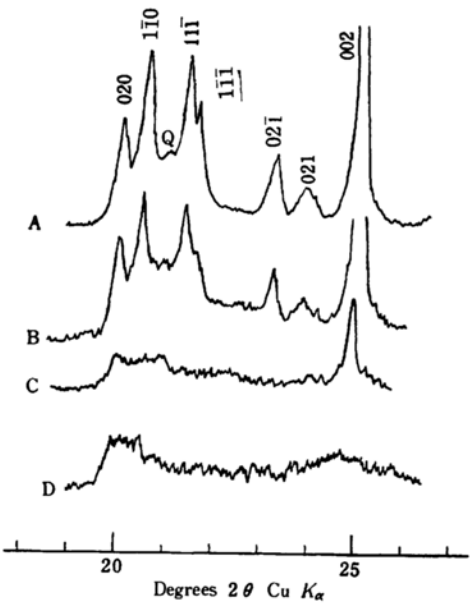

Fig. 1-b. Detailed X-ray diffractometer traces of ground kaolinite (Mesa Alta, N. M.).
A, original kaolinite
B, ground 48 hours
C, ground 96 hours
B, ground 168 hours

TABLE I

POWDER DATA OF GROUND KAOLINITE (MESA ALTA, N. M.) IN ANGSTROM UNITS

Brindley and Robinson			Original Kaolinite		Ground 48 hr.		Ground 96 hr.		Ground 168 hr.		Ground 168 hr. treated with 0.1N NaOH		Ground 168 hr. treated with 0.1N HCl after 0.1N NaOH		Ground 312 hr.	
d	*I*	*hkl*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
											10.0	Wbr	9.6	Wbr		
7.15	10+	001	7.14	VS	7.14	S	7.16	M	7.15	M	7.37	Mbr	7.5	Mbr	8.0	Mvbr
4.45	4	020	4.46	M	4.47	M	4.46	M	4.44	Mbr	4.44	Mbr	4.43	S		
4.35	6	$1\bar{1}0$	4.35	S	4.35	M	4.32	W								
4.17	6	$11\bar{1}$	4.18	S	4.18	M										
4.12	3	$1\bar{1}\bar{1}$	4.13	W	4.14	VW										
3.837	4	$02\bar{1}$	3.84	M	3.85	M										
3.734	2	021	3.73	W	3.75	W										
3.566	10+	002	3.57	VS	3.58	S	3.58	M	3.58	Wbr	3.2	Wvbr	3.62	Mbr	4.0	Mvbr
3.365	4	111	3.37	M	3.38	W										
3.138	2	$11\bar{2}$	3.14	W												
3.091	2	$1\bar{1}\bar{2}$	3.09	W												
2.748	2	022	2.75	W	2.75	W	2.75	VWbr								
2.553	8	$20\bar{1}, 1\bar{3}0, 130$	2.55	S	2.56	M	2.56	Wbr	2.57	VWbr	2.58	VWbr	2.55	M		
2.521	4	$13\bar{1}, 1\bar{1}2$	2.53	M	2.53	W	2.53	Wbr								
2.486	9	$1\bar{3}\bar{1}, 200, 112$	2.49	S	2.49	M	2.50	Wbr	2.50	VWbr	2.47	VWbr	2.46	M		
2.374	7	003	2.37	M	2.38	W	2.39	Wbr								
2.331	10	$20\bar{2}, 1\bar{3}1, 11\bar{3}$	2.33	VS	2.34	M	2.34	Wbr	2.34	VWbr			2.35	Wbr		
2.284	9	$1\bar{1}\bar{3}, 131$	2.29	S	2.29	M	2.29	Wbr	2.29	VWbr	2.30	VWbr				
2.243	1	$13\bar{2}, 040$	2.24	W												
2.182	3	$1\bar{3}\bar{2}, 220$	2.18	W	2.19	W	2.19	VWbr								
2.127	2	$02\bar{3}, 041$	2.13	W	2.13	VW										
2.057	1	$2\bar{2}\bar{2}$	2.06	W												

Key to Abbreviation: VS: very strong, S: strong, M: medium, W: weak, VW: very weak, br: broad, vbr: very broad.

TABLE II

POWDER DATA OF GROUND KAOLINITE (DRYBRANCH, GEOR.) IN ANGSTROM UNITS

Original Kaolinite		Ground 48 hr.		Ground 96 hr.		Ground 144 hr.		Ground 144 hr. treated 0.1N HCl after 0.1N NaOH		Ground 264 hr.		Ground 264 hr. treated with 0.1N NaOH		Ground 264 hr. treated with 0.1N HCl after 0.1N NaOH		Ground 384 hr.	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
										8.5	Mbr	9.2	VWvbr			8.5	VWvbr
7.15	VS	7.15	VS	7.16	S	7.20	M	7.22	VS	7.2	W						
4.45	S	4.45	M	4.45	W	4.44	Mbr	4.45	S	4.35	Wbr						
4.36	M	4.36	M	4.35	W	4.30	Wbr	4.20	W								
4.17	M	4.16	W														
3.86	W																
3.74	VW													3.8	Mbr	3.7	Wvbr
3.58	VS	3.57	VS	3.58	S	3.60	M	3.58	S	3.6	W	3.4	Mvbr	3.54	W	3.54	W
3.37	VW																
2.74	VW																
2.56	S	2.56	M	2.56	W	2.57	VWbr	2.57	M								
2.53	W	2.53	W	2.53	VW												
2.49	S	2.49	M	2.50	W	2.50	VWbr	2.50	W								
2.38	M	2.38	M	2.38	W	2.39	VWbr	2.38	M								
2.34	S	2.34	S	2.34	M	2.35	VWbr	2.34	W								
2.29	M	2.29	M	2.30	W												
2.24	VW																
2.18	W																

Key to Abbreviation: VS: very strong, S: strong, M: medium, W: weak, VW: very weak, br: broad, vbr: very broad.

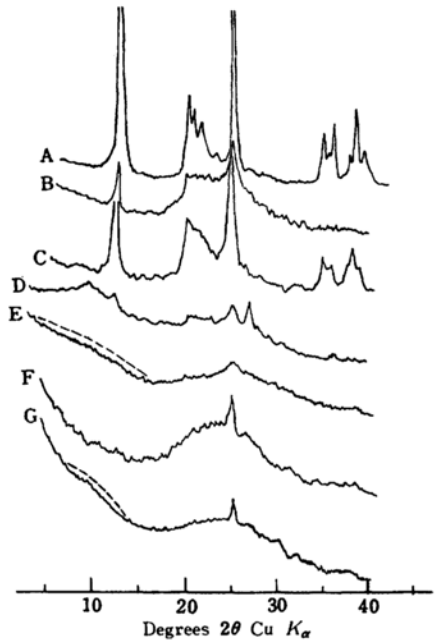

Fig. 2-a. X-ray diffractometer traces of ground kaolinite (Drybranch, Geor.).
A, original kaolinite
B, ground 144 hours
C, 144-hour-ground kaolinite treated with 0.1N HCl after 0.1N NaOH
D, ground 264 hours
E, 264-hour-ground kaolinite treated with 0.1N NaOH
F, 264-hour-ground kaolinite treated with 0.1N HCl after 0.1N NaOH
G, ground 384 hours

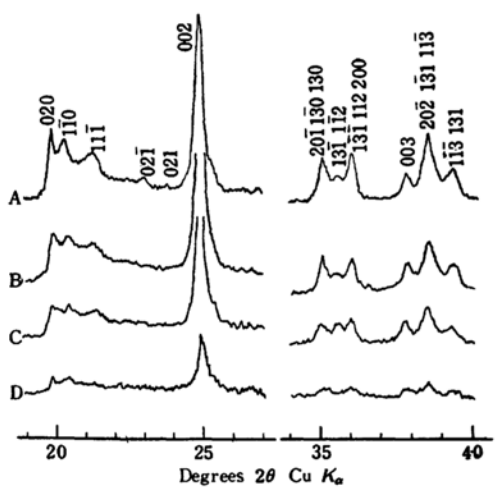

Fig. 2-b. Detailed X-ray diffractometer traces of ground kaolinite (Drybranch, Geor.).
A, original kaolinite
B, ground 48 hours
C, ground 96 hours
D, ground 144 hours

(1) Intensity and sharpness of the reflections.
(2) Number of reflections.
(3) Change in the basal spacing.
(4) Resolution between closely spaced reflections.
(5) Absence of certain reflections.
(6) Intensity of the background.

As shown in Fig. 1 and Table 1, the original sample of Mesa Alta kaolinite has the structural characteristics with the highest degree of crystallinity, since the $11\bar{1}$ and $1\bar{1}\bar{1}$ reflections are resolved each other and the $11\bar{2}$, $1\bar{1}\bar{2}$ and 022 reflections are present[5].

Important features of the initial stage of grinding are a decrease in the intensity of 00*l* reflections; however, the breadth of 00*l* reflections are considerably sharper than that of original kaolinite. In the 48-hour-ground specimen, it is found that the intensity of $02\bar{1}$ and 021 reflections decrease and $11\bar{2}$, $1\bar{1}\bar{2}$ and 022 reflections disappear, and that $11\bar{1}$ and $1\bar{1}\bar{1}$ reflections are nearly consistent. These facts show that the grinding causes some displacement of layers parallel with the *b*-axis in the structure of kaolinite. In the 96-hour-ground specimen, all reflections broaden, and the reflections of $1\bar{1}0$, $11\bar{1}$, $02\bar{1}$ and 021 disappear. These facts suggest that the crystalline part of the specimen has a pseudemonoclinic in symmetry similar to that of kaolin mineral of fireclay type, which indicates the displacement of layers by $nb_0/3$ along the *b*-axis[6]. After grinding for 168 hours, the structure of this specimen has the lowest degree of crystallinity among the kaolin minerals with the exception of halloysite which has a two-dimensional structure. That is, the assymmetric 02, 11 band and the broad band similar to that of 20, 13 band on the X-ray diagram of halloysite are observable. These facts mean that the structure of this specimen has a displacement of layers along the *a*-axis in addition to the displacement along the *b*-axis. In other words, it suggests that the two-dimensional kaolinite is formed by dry grinding. As shown in Fig. 1, after 312 hours, only two very broad bands are apparent.

With the grinding progresses, the background increases as the intensity of the reflections weaken. These facts lead to a non-crystalline substance is produced by

5) G. W. Brindley and K. Robinson, *Trans. Faraday Soc.*, **42B**, 198 (1946).
6) G. W. Brindley and K. Robinson, *Trans. Brit. Ceram. Soc.*, **46**, 49 (1947).

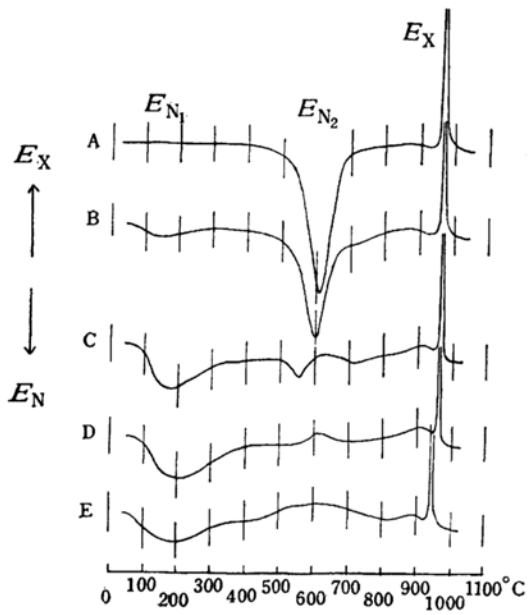

Fig. 3. Differential thermal analysis curves of ground kaolinite (Mesa Alta, N. M.).
A, original kaolinite
B, ground 48 hours
C, ground 96 hours
D, ground 168 hours
E, ground 312 hours

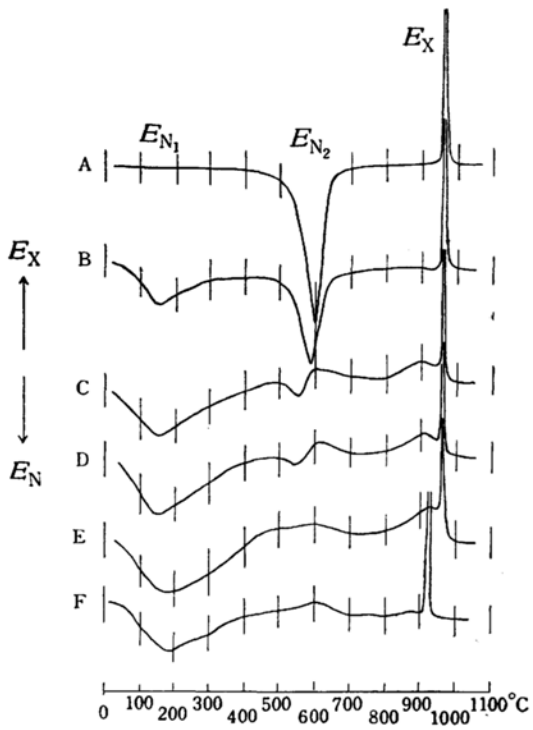

Fig. 4. Differential thermal analysis curves of ground kaolinite (Drybranch, Geor.).
A, original kaolinite
B, ground 48 hours
C, ground 96 hours
D, ground 144 hours
E, ground 264 hours
F, ground 384 hours

TABLE III
THERMAL DATA OF GROUND KAOLINITE (MESA ALTA, N. M.).
(ALL TEMPERATURES ARE DEGREES CENTIGRADE)

Grinding time (hr.)	E_{n1} Temp. at peak	E_{n1} Height of peak	E_{n1} Area of peak	E_{n2} Temp. at peak	E_{n2} Height of peak	E_{n2} Area of peak	E_x Temp. at peak	E_x Height of peak	E_x Area of peak	E_x Breadth (half value of breadth)
0	—	—	—	604°C	16	1080	966°C	39	220	5.1°
48	—155°C—	1	90	597	13	960	962	43	240	4.3
96	—170—	5	470	554	5	220	961	60	220	2.8
168	—175—	7	890	543	3	35	960	67	240	2.5
312	—180—	7	1110	—	—	—	937	58	260	3.5

TABLE IV THERMAL DATA OF GROUND KAOLINITE (DRYBRANCH, GEOR.).
(ALL TEMPERATURES ARE DEGREES CENTIGRADE)

Grinding time (hr.)	E_{n1} Temp. at peak	E_{n1} Height of peak	E_{n1} Area of peak	E_{n2} Temp. at peak	E_{n2} Height of peak	E_{n2} Area of peak	E_x Temp. at peak	E_x Height of peak	E_x Area of peak	E_x Breadth (half value of breadth)
0	—	—	—	592°C	20	1280	964°C	41	250	4.8°
48	—155°C—	6	670	582	15	750	963	45	270	4.0
46	—155—	10	1570	554	3	140	958	48	240	3.2
144	—160—	10	1960	548	2	70	957	56	250	3.1
264	—170—	10	1740	—	—	—	956	58	260	2.2
384	—190—	6	910	—	—	—	919	48	260	4.2

dry grinding. To ascertain this fact, the following treatment was made. That is, the 168-hour-ground specimen of Mesa Alta kaolinite was treated with a weak alkali solution. It forms a permutite-like substance. When it is immersed in a weak hydrochloric acid solution to dissolve the gel-like substance, the crystalline portion of the specimen is left. Fig. 1-D shows the X-ray diffractometer trace of the remaining crystalline portion; this diagram closely resembles that of halloysite. X-ray data and the following electron micrograph (Fig. 8-F) reveal that the structure of the kaolinite has changed into a two-dimensional structure.

In Drybranch kaolinite, as shown in Fig. 2 and Table II, it follows just the same process as Mesa Alta kaolinite in dry grinding. The difference is only that the structure of the original sample has a slightly lower degree of crystallinity than that of Mesa Alta kaolinite, so, the time it takes to become amorphous is somewhat shorter than that of Mesa Alta kaolinite.

Differential Thermal Analysis. — Differential thermal analysis curves and data of the grinding process of kaolinite are shown in Figs. 3 and 4 and Tables III and IV.

Measurements which were used are as follows:

(1) The peak temperature, height and area of the first endothermic reaction (E_{n1}) associated with the loss of the adsorbed water. The peak area was measured by planimeter from the base line of the thermal curve.

(2) The peak temperature, height and area of the second endothermic reaction (E_{n2}) associated with the loss of the lattice water.

(3) The peak temperature, height, area and breadth of the final exothermic reaction (E_x) corresponding to the mullite nucleation.

The endothermic reaction (E_{n1}) associated with the loss of adsorbed water, which is not present in the original sample, appears and its height and area increase; These phenomena mean that the substance produced by the dry grinding adsorbs more and more water vapor as grinding progresses. The peak temperature of this reaction gradually rises a little. This fact indicates that the water adsorbed by the ground substance is combined strongly as the grinding progresses.

In the second endothermic reaction (E_{n2}) associated with the loss of the lattice water, are observable a lowering in peak temperature, and a reduction in height and area. Finally this reaction disappears thoroughly. This corresponds with the gradual and complete disintegration of the kaolinite structure due to grinding. In the 96-hour-ground specimen of kaolinite, the X-ray diagram is similar to that of Kibushi-clay, but the height of this reaction is very small as compared with that of Kibushi-clay which is a kaolin mineral of fireclay type. This fact corresponds to the increase of the background of this specimen in its X-ray diagram, that is, a considerable amount of non-crystalline substance is produced by dry grinding.

In the exothermic reaction (E_x), there are some interesting phenomena. The peak temperature falls very slightly. But after 312 hour grinding the peak temperature lowers remarkably although the peak area is relatively unchanged. Except for the 312-hour-ground specimen on which grinding had progressed to an extreme degree, the peak height increases while the breadth decreases. As shown in the X-ray results, the perfectly ordered structure of kaolinite changes to a disordered structure as the grinding progresses. It is well known that the temperature range of the exothermic reaction (E_x) of kaolin with a higher degree of crystallinity is narrower than that of kaolin with a lower degree of crystallinity[7].

It is, therefore, difficult to draw a conclusion on the basis of the most important character of the exothermic reaction. Incidentally, it is known that the exothermic reaction corresponds to the transformation of kaolinite into mullite[8]. This transformation includes two elements of reaction, that is, nucleation of mullite and growth of mullite nuclei. Consequently, it is clear that kaolinite becomes liable to grow into mullite crystal from mullite nuclei produced by dry grinding.

To ascertain the character of the exothermic reaction of the ground specimen, the X-ray diffractometer traces of ground specimens obtained just after the exothermic reaction on the differential thermal analysis curves are recorded, which are given in Fig. 5.

As the grinding progresses, the presence of the reflection line of mullite becomes clear. That is to say, development of the

7) H. H. Murray, *Am. Mineral.*, **39**, 97 (1954).
8) W. D. Jones, *Min. Mag.*, **30**, 186 (1953).
G. W. Brindley and K. Hunter, ibid., **30**, 574 (1955).

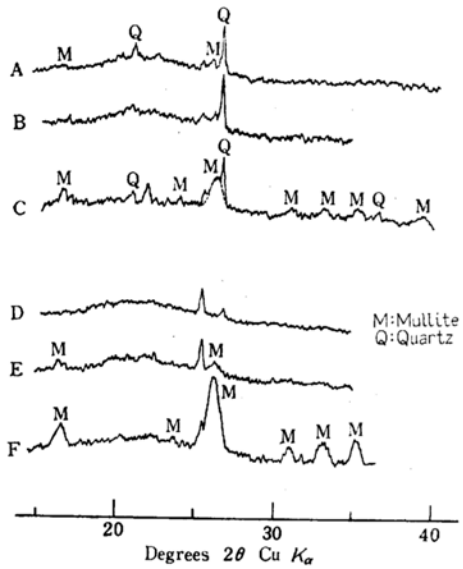

Fig. 5. X-ray diffractometer traces of ground kaolinite obtained just after the final exothermic reaction (E_x) on the differential thermal analysis curve.
A, original kaolinite (Mesa Alta, N. M.)
B, ground 168 hours
C, ground 312 hours
D, original kaolinite (Drybranch, Geor.)
E, ground 144 hours
F, ground 384 hours

mullite reflection corresponds to the increasing height of the exothermic peak as grinding progresses.

The features of the exothermic reaction of kaolinite are different from that of halloysite with a lower degree of crystallinity. Results of halloysite are reported in the following part III. From the comparison with the result of the grinding effects of halloysite, it is concluded that a non-crystalline substance produced by dry grinding of kaolinite, even in the 312-hour-ground specimen of Mesa Alta kaolinite or the 384-hour-ground specimen of Drybranch kaolinite, is an allophanic substance rather than the perfectly amorphous substance similar to the silica-alumina mixed gel.

Base Exchange Capacity and Density.— In Fig. 6 are shown the changes in the base exchange capacity at various periods of grinding.

As grinding progresses, the base exchange capacity at first increases. After reaching a maximum value, it gradually decreases until it attains a constant value. These features on the base exchange capacity curve show that the broken bonds of kaolinite increase at first owing to the

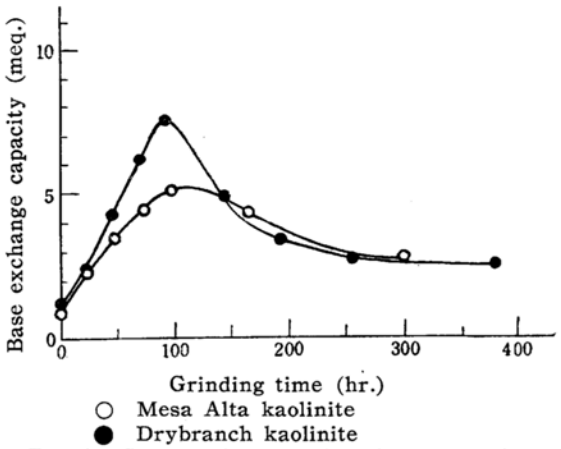

Fig. 6. Curves showing the changes of the base exchange capacity with the time of grinding.

cleavage and fracturing by dry grinding and that a non-crystalline substance gradually increases through dry grinding. These results support the thoughts of Laws and Page in the explanation of the increase on the base exchange capacity through dry grinding of kaolinite[1].

In Fig. 7 are shown the changes in the density at the various stages of grinding. As the grinding progresses, the density sharply decreases, but after reaching a certain point, it is maintained at a constant value. This constant value is nearly equal to the values of a silica-alumina-mixed gel or allophane which is a non-crystalline clay mineral. These facts show also that kaolinite changes to a non-crystalline or an amorphous substance by dry grinding.

The point of bend in the density curve and the maximum point in the base

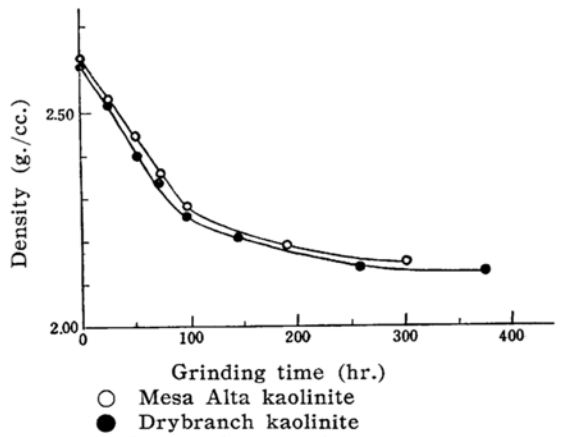

Fig. 7. Curves showing the changes of the density with the time of grinding.

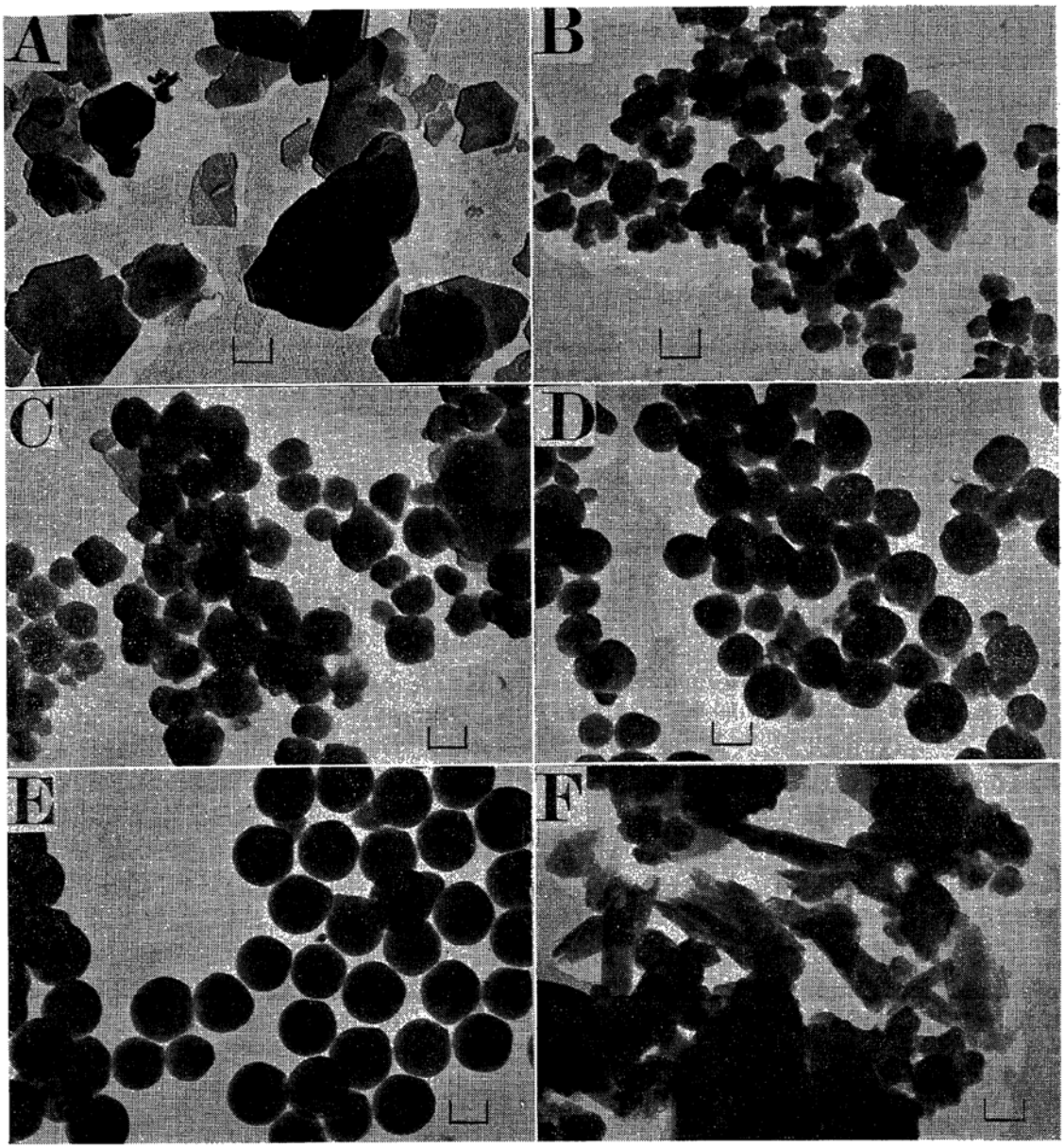

Fig. 8 Electron micrographs of ground kaolinite (Mesa Alta, N. M.).
The linear dimension on the micrograph represents 0.1 μ.

A, original kaolinite
B, ground 48 hours
C, ground 96 hours
D, ground 168 hours
E, ground 312 hours
F, 168-hour-ground kaolinite treated with 0.1N HCl after 0.1 N NaOH

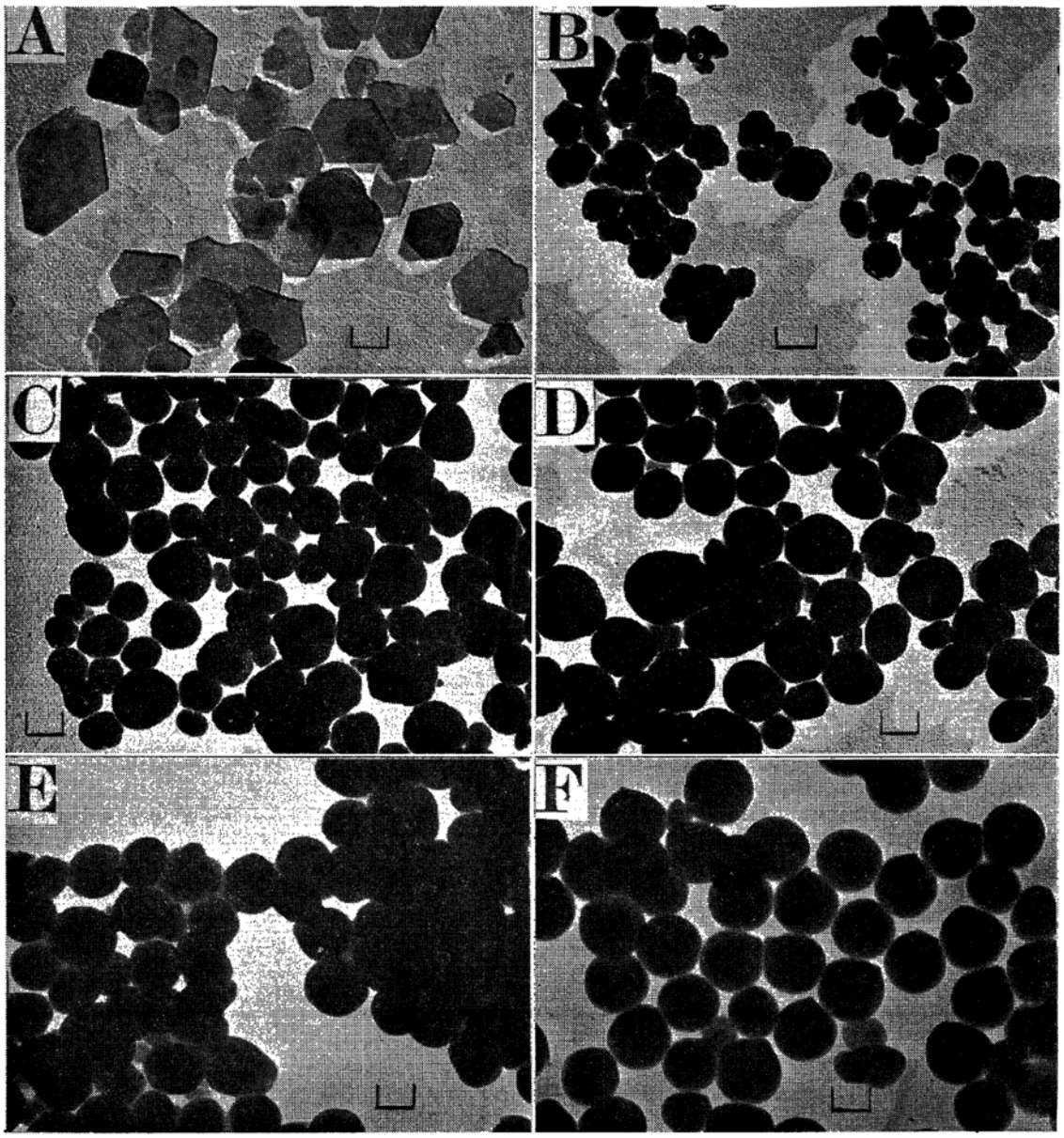

Fig. 9 Electron micrographs of ground kaolinite (Drybranch, Geor.). The linear dimension on the micrograph represents 0.1 μ.

A, original kaolinite
B, ground 48 hours
C, ground 96 hours
D, ground 144 hours
E, ground 264 hours
F, grornd 384 hours

exchange capacity curve are at nearly identical positions. In the light of the X-ray data, this stage seems to correspond to the point at which kaolinite changes into a zeolitic substance by dry grinding.

Electron Microscopic Studies. — Figs. 8 and 9 show electron micrographs of kaolinite after various periods of grinding. It is observable that, in the early stage of grinding, fine crystallites are produced by cleavage and fracturing of the kaolinite crystal. The fine crystallites reaggregate, and reaggregated particles become radial and the particle size increases, slowly changing into uniformly spherical particles. The specimen with a radial shape has a zeolitic structure and is made of both crystalline and non-crystalline portions. That is, in this specimen, the non-crystalline substance produced by dry grinding falls between the crystalline substance. The crystalline portion in the zeolitic substance is separated by the alkali and acid treatment from the original ground speimen. Fig. 8-F shows the electron micrograph of this crystalline portion. As is clear from these electron micrographs and X-ray data, the crystalline portion which makes a zeolitic substance has a considerably lower degree of crystallinity than that of the original kaolinite. As was presumed from the results of Kibushi-clay and halloysite to be described in the following parts, it seems that these radial particles grow irregularly as the grinding further progresses.

If the mean sizes of the fine particles which are produced through dry grinding and those of the particles which are produced through the reaggregation of such fine particles are plotted against the grinding time, the results are as shown in Fig. 10.

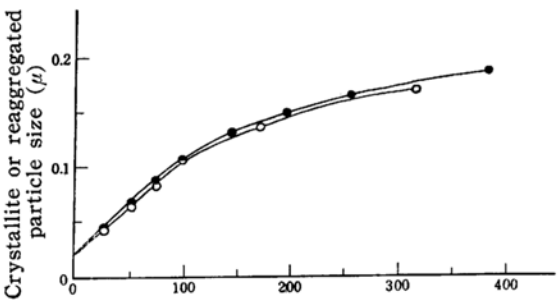

Fig. 10. Crystallite or reaggregated particle size of ground kaolinite plotted against the time of grinding.

The curve, if extrapolated to zero time, indicates almost the same value of about 200 Å for both kaolinites. Judging from this, it seems that the crystallites which separate from the original crystal during the early stage of grinding are about 200 Å in size. This value is consistent with the value in the "most dispersed state" of kaolinite in ball-milling obtained by Gregg et al., through the B. E. T. method[1].

Mechanism of Change in Kaolinite Structure with Dry Grinding. — When kaolinite is ground, kaolinite crystals cleave and fracture and then split into fine crystals that are considered unit crystallites. Such fine crystallites promptly reaggregate in groups of several. The assemblages of the original kaolinite crystallites produced through dry grinding disintegrate partially into allophane or gel-like substances. These substances and crystalline particles promptly reaggregate.

With grinding, the structure of the crystalline part of the reaggregated particle slowly becomes disordered kaolin and as an increase in the amorphous part, the reaggregated particles of the disordered kaolin and the amorphous substance become radial.

At a certain point in the grinding time corresponding to the maximum point on the base exchange capacity curve and the inflection point on the density curve, the particle becomes almost uniformly spherical. The structure of this spherical particle is considered to be zeolitic. This structure, with continued grinding, changes finally into a structure similar to the perfectly amorphous structure as silica-alumina mixed gel and its particle size increases irregularly.

The process of the structural change by dry grinding is the same in both Mesa Alta kaolinite and Drybranch kaolinite, except that the structural change of Drybranch kaolinite occurs slightly faster than that of Mesa Alta kaolinite. This means that the grinding effect on kaolinite is related to the structural perfectness of the original kaolinite. This fact has been ascertained by the study of the dry grinding effect of all kaolin minerals.

Summary

The effects of several-hundred-hour mechanical-mortar dry grinding of kaolinite were studied by X-ray, thermal,

electron microscopic and other methods. It has been found that there are two sorts of structural change in the process of dry grinding of kaolinite. One is the production of a non-crystalline substance attended by the disordering of the crystalline part, and the other is the reaggregation process. The process of the reduction in the particle size and the process of the production of the non-crystalline substance are connected to the process of the reaggregation. In a certain stage of the dry grinding, the reaggregates are spherical particles which have a zeolitic structure. As the grinding further progresses, the structure of the crystalline part in this radial particle becomes disordered due to the mechanical stress, and it changes into an amorphous substance at last. Consequently, the effect of dry grinding of kaolin mineral depends on the structural perfectness of aluminosilicate layers of the kaolin mineral, that is, the internal crystallinity of the kaolin mineral.

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