EFFECT OF DRY GRINDING ON KAOLIN MINERALS

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ABSTRACT

The effect of dry grinding of kaolin minerals by a mechanical mortar was examined by x-ray, thermal, and electron microscopic methods. Base exchange capacity and apparent density were also measured. In the early stage of grinding, kaolin crystals cleave and fracture and then split into fine crystals which are considered unit crystallites. Such crystallites gradually change to a disordered kaolin and partially decompose into a noncrystalline substance as grinding progresses. The crystalline and the noncrystalline substances promptly reaggregate and these reaggregated particles have a radial shape. After further grinding, the structure of the reaggregated particle seems to be zeolitic. Finally, the kaolin mineral thoroughly changes to a completely amorphous substance similar to a silica–alumina mixed gel. Consequently, the effect of dry grinding of kaolin is related to the degree of crystallinity of the original kaolin mineral.

INTRODUCTION

Considerable work has been done on the effect of grinding on kaolinite, and it has proved helpful in the study of the structure of kaolin minerals. It is considered that understanding of the grinding effect is useful for the study of weathering processes, soil fertility, and the active solid.

There are two lines of thought concerning the effect of dry-grinding of kaolinite. One asserts that the dry grinding of kaolinite brings about only a reduction in particle size owing to cleavage and fracturing of the kaolinite crystal (Kelley, Dore and Brown, 1931; Kelley and Jenny, 1936; Shaw, 1942). The other insists that dry grinding of kaolinite causes formation of a zeolitic substance having a structure similar to that of the original kaolinite (Laws and Page, 1946; Parkert, Perkins and Dragsdorf, 1950; Dragsdorf, Kissinger and Perkins, 1951), or distorts the lattice (Marshall, 1937; Jackson and Truog, 1939; Gregg, Parker and Stephens, 1953; Gregg, Hill and Parker, 1954).

Previous studies of the grinding of kaolin minerals have been made mostly by ball-milling. Incidentally, Mackenzie and Milne (1953, 1953a) found that grinding by a mechanical mortar is very effective in causing a change in structure of mica.

In the present study the effects of several hundred hours of dry grinding on kaolin minerals by a mechanical mortar were examined by x-ray, thermal, electron microscopic, and other methods.

EXPERIMENTAL

Kaolinite from Mesa Alta, N. M., and halloysite from Tintic, Utah, were investigated. Both clays are API Standard Clay Minerals.

Thirty-gram samples of the original kaolin minerals were ground by a mechanical mortar (15.2 cm in diam. and 8.4 cm in depth). Specimens were taken out at intervals of 24 hr and examined by x-ray, thermal, and electron microscopic methods. In conjunction with the above measurements, base exchange capacity and apparent density were measured.

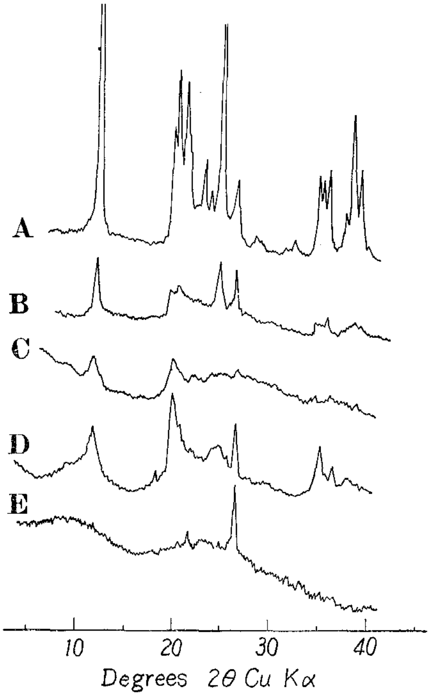

FIGURE 1.—x-Ray diffractometer traces of ground kaolinite. A, Original kaolinite. B, Kaolinite ground 168 hr. C, Kaolinite ground 168 hr, treated with 0.1 N NaOH. D, Kaolinite ground 168 hr, treated with 0.1 N HCl after 0.1 N NaOH. E, Kaolinite ground 312 hr.

x-Ray powder reflections were recorded by an x-ray diffractometer. Experimental conditions are as follows: Filtered Cu radiation (CuK_α: 1.5418 Å), 35 kV, 15 mA, scanning speed 1 degree and $\frac{1}{4}$ degree 2θ per min., time constant 4 sec, receiving slit 0.2 mm and 0.1 mm, angular aperture 1 degree and $\frac{1}{2}$ degree.

Differential thermal analysis curves were recorded by the apparatus described by Sudo and others (1952). Great care was taken to pack the sample into the sample block in the same manner for each run and also to keep the weight of samples constant. The mean heating rate was 12.5°C per min.

The apparent density was measured using carbon tetrachloride. The base exchange capacity was measured by the following procedures. The specimen was treated with hydrochloric acid, thus converting it into hydrogen-clay, and after being washed repeatedly with water the clay was titrated with sodium hydroxide solution. The base exchange capacity was taken as the number of milliequivalents, per 100 g of specimen, required to bring the pH to 7.

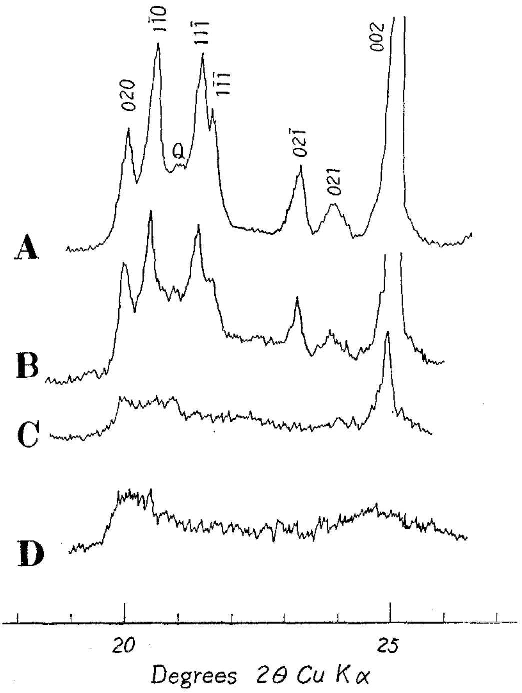

FIGURE 2.—Detailed x-ray diffractometer traces of ground kaolinite. A, Original kaolinite. B, Kaolinite ground 48 hrs. C, Kaolinite ground 96 hrs. D, Kaolinite ground 144 hrs.

Electron micrographs and electron diffraction patterns were obtained by a Hitachi HU–10A type electron microscope.

X-Ray Diffraction Studies

X-ray diffractometer traces made at various stages in the grinding of kaolinite are shown in Figs. 1 and 2, and the data are also shown in Table 1.

When kaolinite is ground, it gradually assumes a more-and-more disordered structure; that is, the background increases as the intensity of the

TABLE 1.—POWDER DATA FOR GROUND KAOLINITE, IN ÅNGSTRÖM UNITS

Brindley and Robinson (1946)			Original Kaolinite		Ground 48 hr		Ground 96 hr		Ground 168 hr		Ground 168 hr Treated with 0.1 N NaOH		Ground 168 hr Treated with 0.1 N HCl after 0.1 N NaOH		Ground 312 hr	
d	I	*hkl*	*d*	I	*d*	I	*d*	I	*d*	I	*d*	I	*d*	I	*d*	I
											10.0	W br	9.6	W br		
7.15	10+	001	7.14	VS	7.14	S	7.16	M	7.15	M	7.37	M br	7.5	M br	8.0	M vbr
4.45	4	020	4.46	M	4.47	M	4.46	M	4.44	M br	4.44	M br	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	S	3.58	M	3.2	W vbr	3.62	M br	4.0	M vbr
3.365	4	111	3.37	M	3.38	W										
3.138	3	$11\bar{2}$	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	VW br								
2.553	8	$20\bar{1}$, $1\bar{3}0$, 130	2.55	S	2.56	M	2.56	W br	2.57	VW br	2.58	VW br	2.55	M		
2.521	4	$13\bar{1}$, $1\bar{1}2$	2.53	M	2.53	W	2.53	W br								
2.486	9	$1\bar{3}\bar{1}$, 200, 112	2.49	S	2.49	M	2.50	W br	2.50	VW br	2.47	VW br	2.46	M		
2.374	7	003	2.37	M	2.38	W	2.39	W br								
2.331	10	$20\bar{2}$, $1\bar{3}1$, $11\bar{3}$	2.33	VS	2.34	M	2.34	W br	2.34	VW br			2.35	W br		
2.284	9	$1\bar{1}\bar{3}$, 131	2.29	S	2.29	M	2.29	W br	2.29	VW br	2.30	VW br				
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	VW br								
2.127	2	$02\bar{3}$, 041	2.13	W	2.13	VW										
2.057	1	$22\bar{2}$	2.06	W												

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

reflections weakens. After 48 hr of grinding, only a slight difference in its intensity is observable as compared with the original kaolinite. After 96 hr, however, the intensity of 001 reflections is very weak. In Fig. 2C, no reflection is observable other than the 020, 110 and 002 lines. After 168 hr, only the 02,11 band and a very broad 002 band are observable. As shown in Fig. 1, after 312 hr, only two very broad bands are apparent.

When a 168 hr specimen, considered to have a zeolitic structure, is 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. Figure 1D shows the x-ray traces of the remaining crystalline portion; this diagram closely resembles that of halloysite. The x-ray data and electron micrograph (Fig. 9F) reveal that the structure of the kaolinite has changed into a two-dimensional structure.

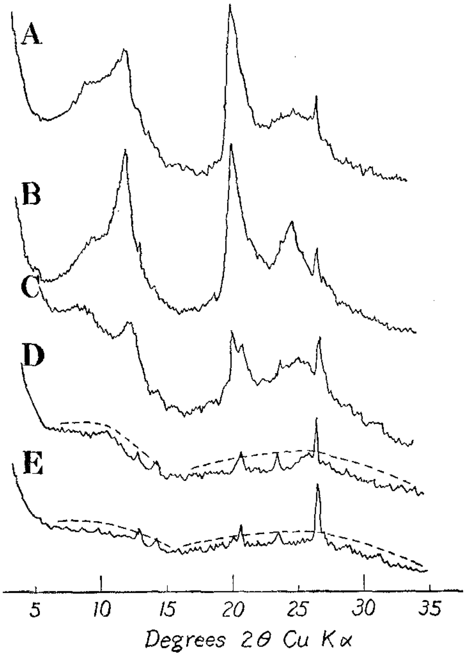

FIGURE 3.—X-ray diffractometer traces of ground halloysite. A, Original halloysite. B, Halloysite ground 48 hr. C, Halloysite ground 96 hr. D, Halloysite ground 144 hr. E, Halloysite ground 240 hr.

Halloysite follows the same process as kaolinite in dry grinding. The difference is that its structure becomes disordered more rapidly and the time it takes to become amorphous is far shorter than in the case of kaolinite.

X-ray diffraction traces and data are shown in Fig. 3 and Table 2. The

240 hr specimen of halloysite has a gel-like structure and the clay dissolves completely during the above-mentioned alkali and acid treatments.

TABLE 2.—POWDER DATA FOR GROUND HALLOYSITE, IN ÅNGSTRÖM UNITS

Original Halloysite		Ground 48 hr		Ground 96 hr		Ground 144 hr		Ground 240 hr	
d	I	*d*	I	*d*	I	*d*	I	*d*	I
10.1	M	10.0	M	10.0	M br	8.2	M vbr	8.1	W vbr
7.37	S	7.36	S	7.3	M br				
4.44	VS	4.44	VS	4.44	M				
3.66	M br	3.61	M	3.54	M br	3.6	M vbr	3.5	M vbr
2.56	M br	2.56	M br	2.56	W br				
1.68	M br	1.68	W br						
1.48	M br	1.48	M br	1.48	W br				

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

Thus it can be seen from the x-ray diagram that kaolin comes to have a disordered structure through dry grinding. It partially changes into an amorphous-like substance, and finally into a perfectly amorphous substance.

Differential Thermal Studies

Thermal curves and data of the grinding process of kaolinite and halloysite are shown in Figs. 4 and 5 and Tables 3 and 4.

Figure 4 sums up the thermal results for kaolinite : An endothermic peak associated with the loss of interlayer water or adsorbed water (En_1), which is not present in the original specimen, appears and its size and area increase ; this phenomenon means that the substance produced by the grinding adsorbs more and more water vapor as the grinding progresses.

In the second endothermic peak associated with the loss of the lattice water (En_2) are observable a lowering in peak temperature and a reduction in size and area. Finally the second endothermic reaction disappears. This corresponds with the gradual and complete disintegration of the kaolinite structure due to grinding.

The peak temperature of the exothermic reaction (Ex) falls very slightly. After 312 hr, this peak temperature lowers remarkably although the peak area is relatively unchanged. Except for the 312 hr specimen, on which grinding had progressed to an extreme degree, the peak height increases while the breadth decreases. This phenomenon is interesting because the exothermic reaction is known to correspond with the transformation of kaolin into mullite. This transformation includes two elements of reaction, that is, nucleation of mullite and growth of the mullite nuclei. Kaolinite becomes liable to grow into mullite crystals from mullite nuclei produced by grinding.

Figure 6 shows the x-ray diffraction traces of specimens obtained just before or after the exothermic reaction on the D.T.A. curve. As grinding progresses, the presence of the reflection line of mullite becomes clear. That is to say, development of the mullite reflection corresponds to the increasing size of the exothermic peak as grinding progresses.

The D.T.A. curve for halloysite, except for its exothermic reaction, resembles the curve for kaolinite; viz., the height and area of the first endothermic reaction increase. A small difference is that its endothermic reaction at about 250°C is pronounced as compared with that of kaolinite. Probably, such a difference is due to a different manner of hydration. The second endothermic reaction for halloysite closely resembles that for kaolinite, though it disappears in a considerably shorter time than that of kaolinite.

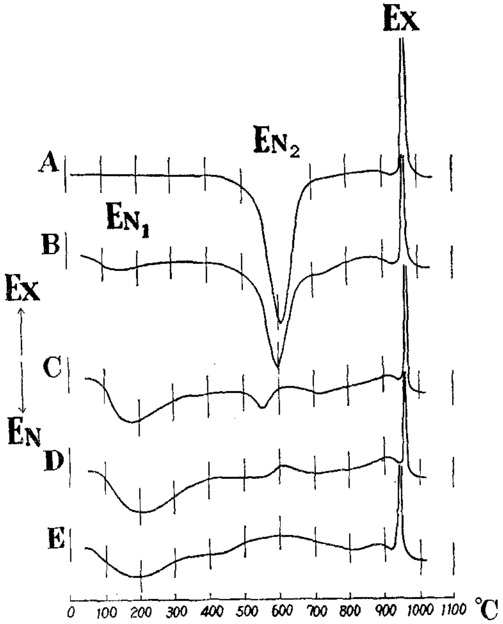

Figure 4.—Differential thermal analysis curves of ground kaolinite. A, Original kaolinite. B, Kaolinite ground 48 hr. C, Kaolinite ground 96 hr. D, Kaolinite ground 168 hrs. E, Kaolinite ground 312 hr.

The exothermic reaction of halloysite behaves differently from that of kaolinite. At first its temperature tends to be somewhat low, but as grinding progresses, its temperature rises considerably. Its peak size increases at first, but soon decreases markedly. The peak size, as the peak temperature becomes higher, increases again. The peak breadth, too, becomes narrow at first, but soon increases and decreases again. To determine whether there is a difference between their exothermic reactions, x-ray diagrams were taken of several specimens just before and after the exothermic reaction on the D.T.A. curve. These traces are shown in Fig. 6D–G. As grinding progresses, the growth of mullite crystals becomes more pronounced on heating, but the presence of mullite is unobservable just before the exothermic reaction.

It is difficult to draw a conclusion from the character of the exothermic reaction as to the grinding effect on the halloysite used in the experiments, but it may be interpreted as follows :

The halloysite used in the experiments is considered to have a lower degree of crystallinity than the kaolinite, and the noncrystalline substance produced by grinding has a structure which is not similar to that of the original halloysite. It probably is a gel-like substance. For this reason the aluminosilicate, which is reduced to the kaolin unit layer as grinding progresses, may disintegrate almost completely to silica–alumina mixed gel or a mixture of alumina gel and silica gel. The transformation of kaolin into mullite is closely related to the original kaolin structure. In this case, however, the original kaolin structure disintegrates to a remarkable extent, and the transformation requires much more energy than that of kaolinite. Thus it is considered that the reaction produces a high temperature. In the case of kaolinite, the substance produced by grinding may be allophanic rather than gel-like.

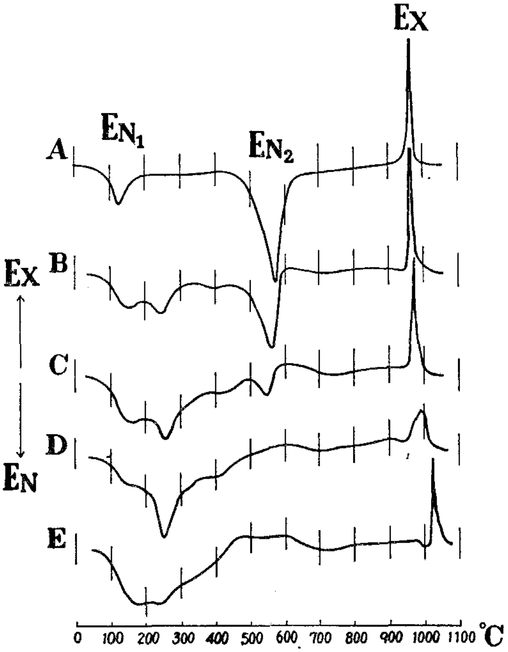

Figure 5.—Differential thermal analysis curves of ground halloysite. A, Original halloysite. B, Halloysite ground 48 hr. C, Halloysite ground 96 hr. D, Halloysite ground 144 hr. E, Halloysite ground 240 hr.

TABLE 3. THERMAL DATA FOR GROUND KAOLINITE
(ALL TEMPERATURES IN DEGREES CENTIGRADE)

Grinding Time (hr)	En_1			En_2			Ex			
	Temp. at Peak	Size of Peak	Area of Peak	Temp. at Peak	Size of Peak	Area of Peak	Temp. at Peak	Size of Peak	Area of Peak	Breadth (Half Value of Breadth)
0	—	—	—	604°	16	1080	966°	39	220	5.1°
48	-155°-	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 4.—THERMAL DATA FOR GROUND HALLOYSITE
(ALL TEMPERATURES IN DEGREES CENTIGRADE)

Grinding Time (hr)	En_1			En_2			Ex			
	Temp. at Peak	Size of Peak	Area of Peak	Temp. at Peak	Size of Peak	Area of Peak	Temp. at Peak	Size of Peak	Area of Peak	Breadth (Half value of Breadth)
0	130°	4	170	571°	12	680	969°	16	170	9.4°
48	-155- -240-	5 6	350	562	10	480	966	30	200	3.6
96	-165- -260-	5 9	790	548	3	100	967	19	150	7.5
144	-250-	11	1120	—	—	—	994	5	140	39.2
240	-170- -260-	8	1340	—	—	—	1023	15	130	7.3

Base Exchange Capacity and Apparent Density

In Figs. 7 and 8 are shown the base exchange capacities and densities in the various stages of grinding. As grinding progresses, base exchange capacity at first increases. After reaching a maximum value, it gradually decreases until it attains a constant value.

As grinding proceeds, the density sharply decreases, but after reaching a certain point, it is maintained at a constant value.

The point of the bend in the density curve and the maximum point in the base 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 the kaolin structure changes to perfect zeolitic structure.

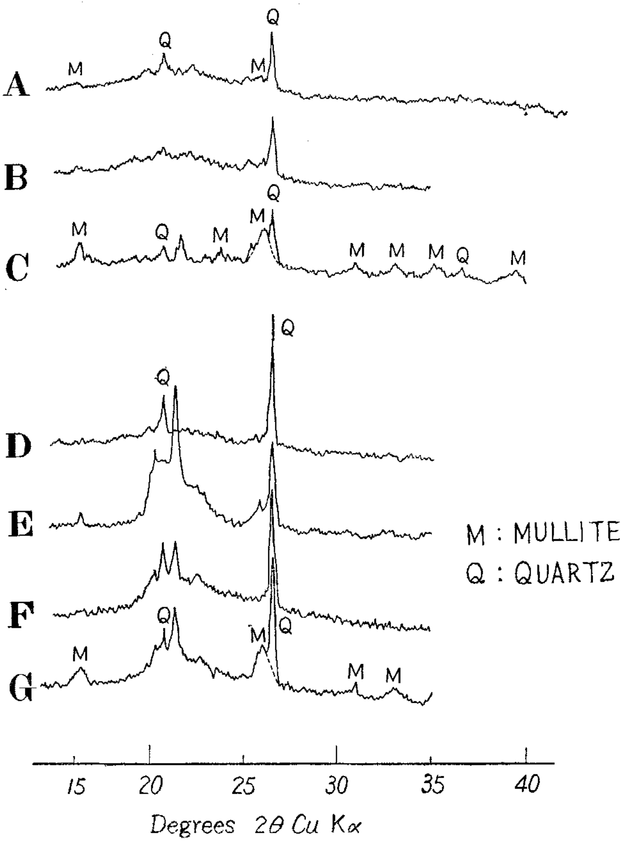

FIGURE 6.—x-Ray diffractometer traces of ground kaolin minerals obtained just before or after the final exothermic reaction (Ex) on the differential thermal analysis curve. A, Original kaolinite obtained just after Ex. B, 168 hr ground kaolinite obtained just after Ex. C, 312 hr ground kaolinite obtained just after Ex. D, Original halloysite obtained just after Ex. E, 144-hrs-ground halloysite obtained just after Ex. F, 240 hr ground halloysite obtained just before Ex. G, 240 hr ground halloysite obtained just after Ex.

Electron Microscopic Studies

Figures 9 and 10 show electron micrographs of the kaolin minerals 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 kaolin crystal. The fine crystallites then reaggregate and their particle size increases, slowly changing into uniformly spherical particles. With halloysite, however, as the grinding proceeds, the particles grow irregularly.

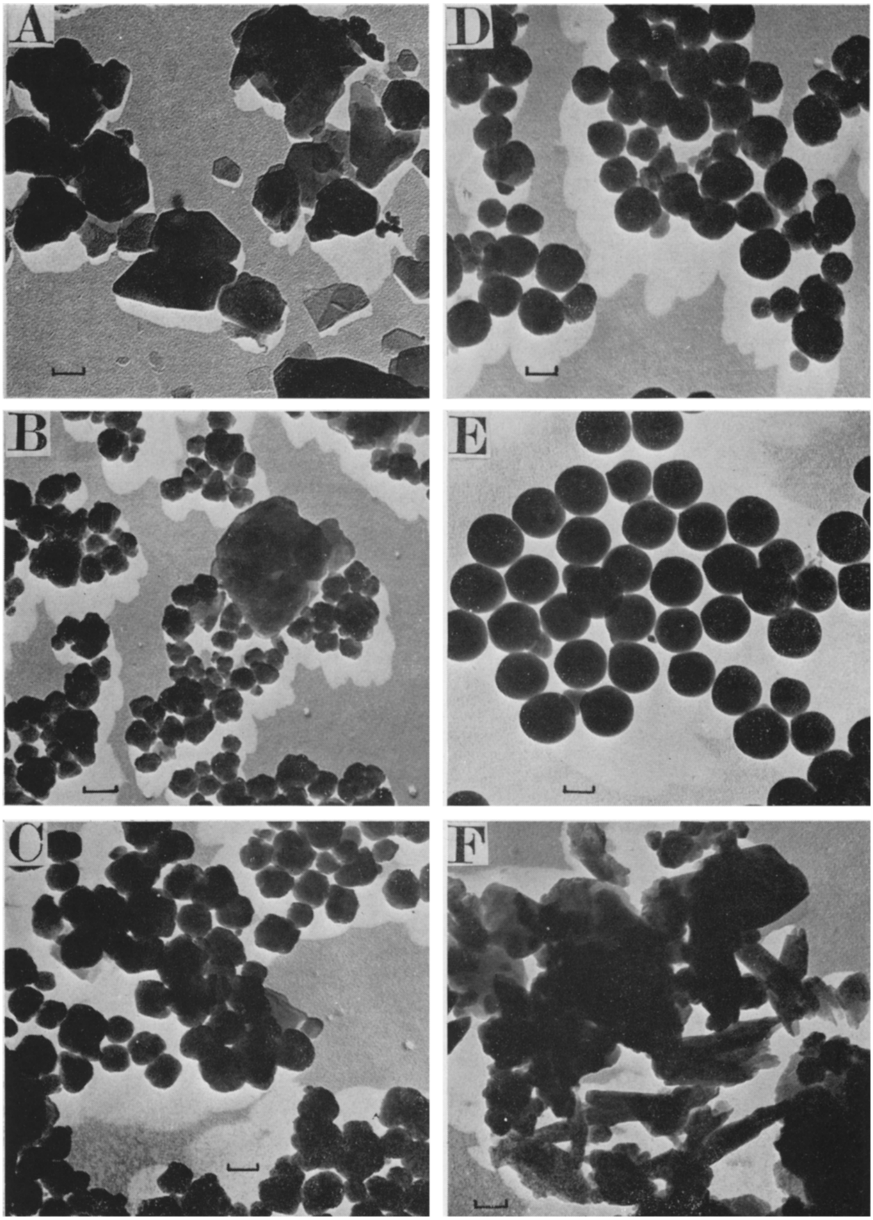

FIGURE 9.—Electron micrographs of ground kaolinite. The linear dimension shown in the electron micrographs represents 0.1μ. A, Original kaolinite. B, Kaolinite ground 48 hr. C, Kaolinite ground 96 hr. D, Kaolinite ground 168 hr. E, Kaolinite ground 312 hr. F, Kaolinite ground 168 hr, treated with 0.1 HCl after 0.1 N NaOH.

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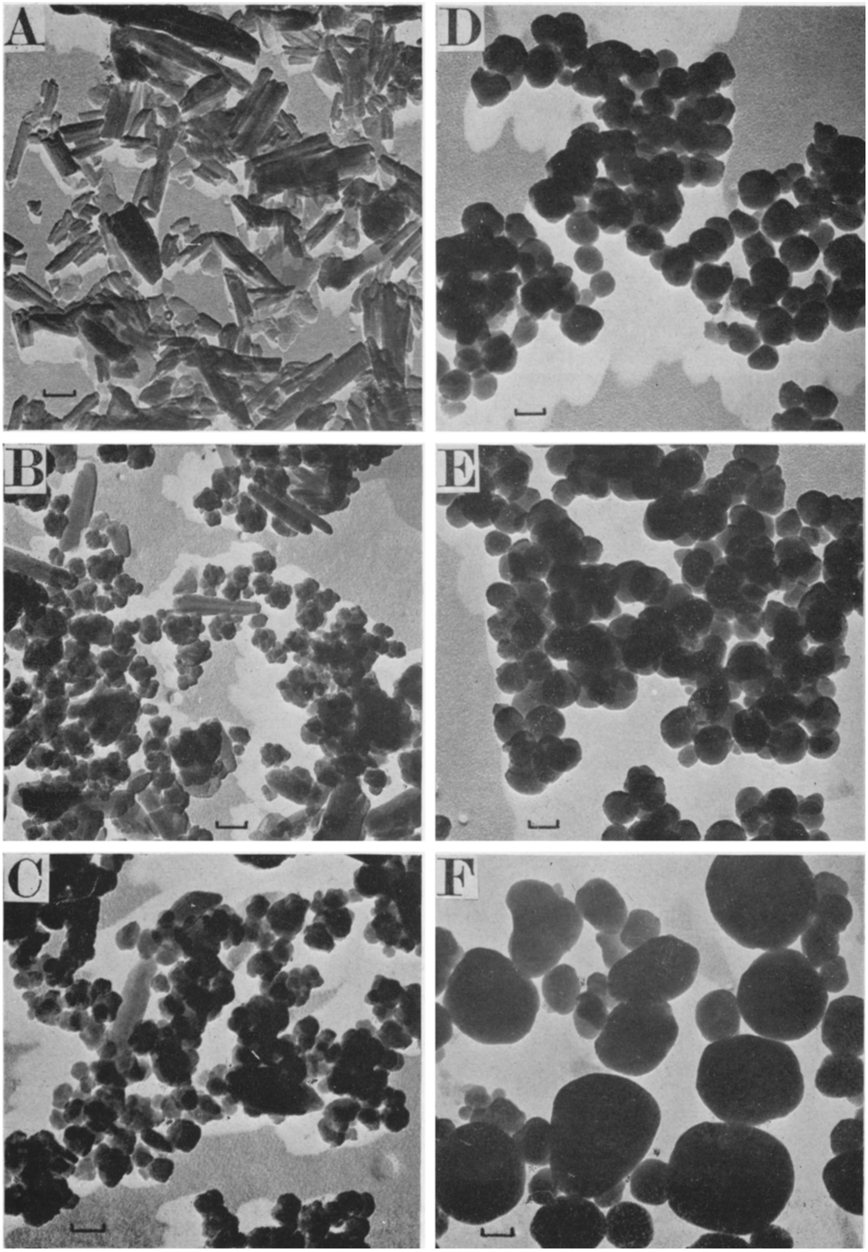

Figure 10.—Electron micrographs of ground halloysite. The linear dimension shown in the electron micrographs represents 0.1μ. A, Original halloysite. B, Halloysite ground 48 hr. C, Halloysite ground 72 hr. D, Halloysite ground 96 hr. E, Halloysite ground 144 hr. F, Halloysite ground 240 hr.

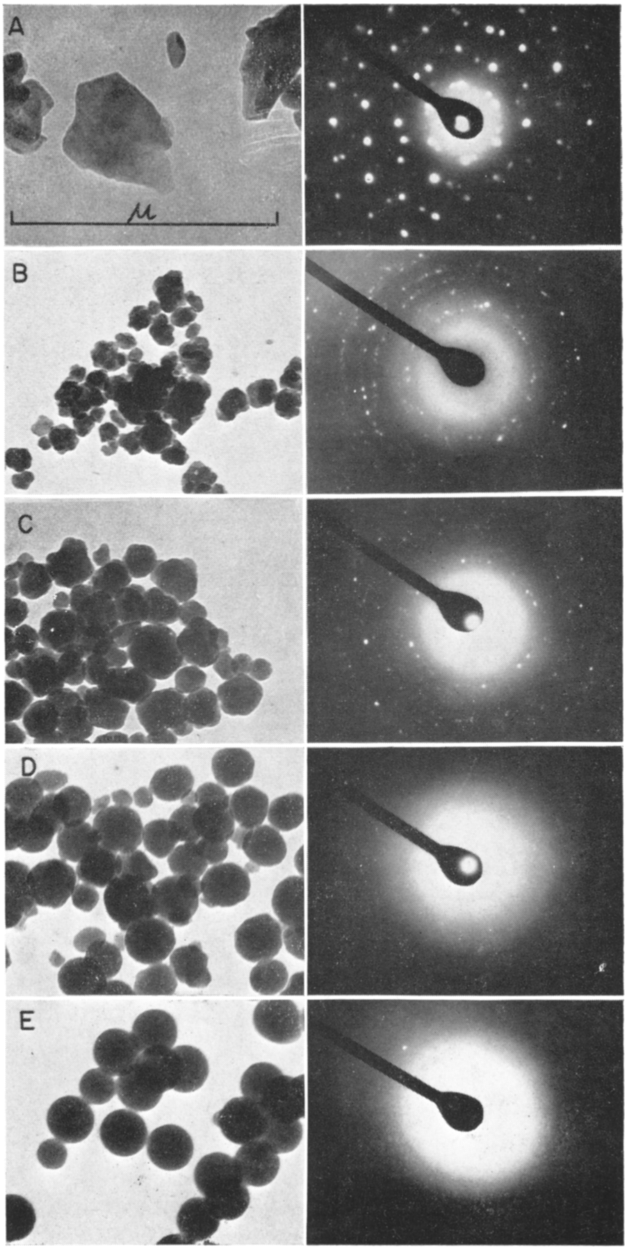

Figure 12.—Selected-area electron diffraction patterns of ground kaolinite. A, Original sample, B, 48 hr, 3, 96 hrs, D, 168 hr, E, 312 hr.

If the sizes of the fine particles which are produced through grinding and the particles which are produced through the reaggregation of such particles are plotted against the grinding time, the results are as shown in Fig. 11. The curve, if extrapolated to zero time, indicates almost the same value of about 200Å for both kaolinite and halloysite. Thus it seems that the crystallites which separate from the original crystal during the early stage of grinding are about 200Å in size. This value agrees with the value of the "most dispersed state" of kaolinite in ball-milling obtained by Gregg, Parker and Stephens (1954) through the B.E.T. method.

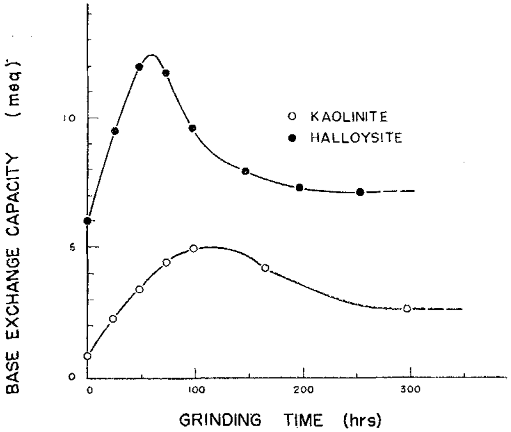

Figure 7.—Curves showing variation of base-exchange capacity with time of grinding.

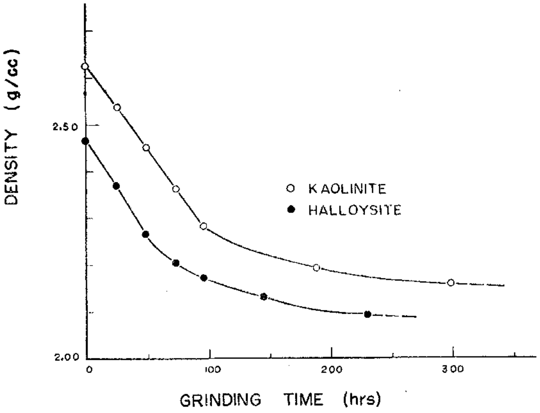

Figure 8.—Curves showing variation of apparent density with time of grinding.

Figure 12 shows electron diffraction photographs of the kaolinite specimen after various periods of grinding.

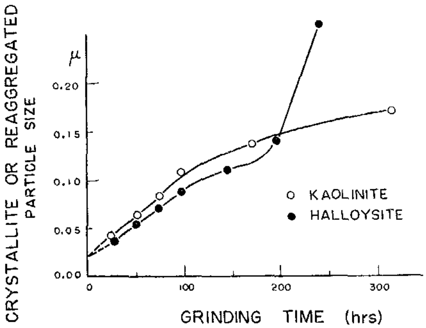

Figure 11.—Curves showing variation of crystallite or reaggregated particle size with time of grinding.

MECHANISM OF CHANGE IN KAOLIN STRUCTURE DUE TO DRY GRINDING

If kaolin minerals are ground, the crystals cleave and fracture and then split into fine crystals that are considered unit crystallites and that promptly reaggregate. The assemblages of the original kaolin crystallites produced through 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. With increase in time of grinding and in quantity of amorphous material, the reaggregated particles of disordered kaolin and amorphous substance become disk-shaped.

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 of alumina–silica mixed gel and its particle size increases irregularly.

The change of structure due to dry grinding is the same in both kaolinite and halloysite, except that less grinding is required for halloysite. Therefore the effect of grinding on kaolin minerals is related to the structural perfection of the original kaolin mineral. This fact has been ascertained by the study of the all-over grinding effect of kaolin mineral.

ACKNOWLEDGMENTS

The author wishes to express his hearty thanks to Professor H. Akamatu for his interest and encouragement. Thanks are due to Professor T. Sudo and Professor R. E. Grim for their valuable suggestions and discussion. The author desires to express his gratitude for the generous help of Professor J. A. Pask and Dr A. Swineford.

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