Effects of Dry Grinding on Talc

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In the previous papers, the effects of dry grinding on kaolin minerals were studied, and the mechanism of the structural change caused by dry grinding was presented[1]. That is, there are two ways of change in structure. One is the production of a non-crystalline material attended with disordering of a crystalline portion, and the other is the reaggregation process. Finally, the kaolin mineral changes into a completely amorphous substance through a formation of a zeolitic substance. The mechanism of the dry grinding on kaolin minerals must be common somewhat to any substances with layered structure. In the ball-milling of graphite, too, a remarkable disordering in structure was observed by Bacon[2]. However, the effects of grinding for substances with the layered structure have not been studied very much heretofore, with the exceptions of kaolinite and mica[3]. The mechanism of dry grinding on kaolin minerals is somewhat common to that of other clay and related minerals, for example, such as montmorillonite, mica, attapulgite, pyrophyllite, serpentine and chrysotile. The results of the grinding

1) H. Takahashi, "Proc. Sixth Natl. Conference on Clay and Clay Minerals", Natl. Res. Council-Natl. Acad. Sci., (in press); H. Takahashi, This Bulletin, **32**, 235, 245, 252 (1959).

2) G. E. Bacon, *Acta Cryst.*, **5**, 392 (1952).

3) M. L. Jackson and E. Truog, *Soil Sci. Soc. Am., Proc.*, **4**, 136 (1939); R. C. Mackenzie and A. A. Milne, *Min. Mag.*, **32**, 178 (1953); R. C. Mackenzie and A. A. Milne, *Clay Min. Bull.*, **2**, 57 (1953).

effects on these clay and related minerals are reported in the following papers. Talc is an end-member of clay mineral with three-layered structure. In this study, the effects of a mechanical-mortar dry grinding on talc are discussed in the structural change, and compared with those of kaolin minerals.

Experimental

The sample used in this study is talc from Kanjun, China. The dry grinding was done in the same manner as for kaolin minerals. That is, 30 g. of original sample was charged and ground by a mechanical-mortar (15.2 cm. in dia. and 8.4 cm. in depth). Experimental specimens were taken out at intervals of 48 hours and examined by X-ray diffraction, differential thermal and electron microscopic methods. The density was also measured.

X-ray powder diagrams were recorded by an X-ray diffractometer (Geigerflex). Experimental conditions are as follows. Filtered Cu radiation (Cu $K\alpha$: 1.5418Å), at 35 kV and 15 mA is used, scanning speed is 1° or 1/4° 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° were used. The differential thermal analysis curves were recorded by the apparatus described by Sudo et al.[4]. Care was taken to pack a specimen into the sample block in the homogeneous manner and also to keep the weight of specimen constant. The mean heating rate is 12.5°C per minute. The density was measured by pycnometer in carbon tetrachloride. It was done after it had been dried at 110°C in order to avoid the effect of the adsorbed water. Electron micrographs were obtained by the Hitachi HU-10A type Electron Microscope.

Results and Discussion

X-Ray Diffraction Studies.—X-ray diffractometer traces and data are given in Fig. 1 and Table I. In this table, the interplaner spacing and the relative intensity measured from the X-ray trace are shown and the values described in ASTM Card are given for reference.

Generally, as the grinding progresses, even though the X-ray diagram is similar to that of the original sample, a decrease in the intensity of reflections except for some reflections and an increase in the background are observable. The intensity of reflections belonging to the basal reflections come to decrease sharply as compared with that of the original sample during the early stage of grinding. Another distinct feature observable in the X-ray

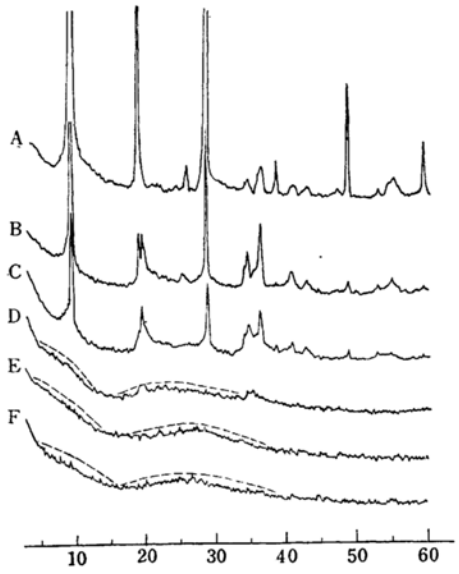

Fig. 1. X-ray diffractometer traces of ground specimens of talc.
A, original talc
B, ground 96 hours
C, ground 192 hours
D, ground 240 hours
E, ground 384 hours
F, ground 528 hours

diagram is that the reflection of 4.60Å spacing comes to be remarkably distinctive as the reflection of 4.69Å spacing weakens due to the progress of grinding. The profile of this reflection becomes an assymmetric broad band which is similar to the (02,11) band found in the X-ray diagram of halloysite. It seems that this reflection is related to the structure of talc and has (020) index rather than a spurious line[5]. The above-mentioned two characteristics with respect to the intensities of reflection line and background observed in the early stage of grinding become more and more distinct as the grinding progresses up to 192 hours. After 192 hours in grinding, the change of the interplaner spacing is not so remarkable. When the grinding progresses further, the X-ray diagram changes remarkably in contrast with that observed thus far. In the 240-hour-ground specimen, the X-ray diagram scarcely has any distinct reflection, but only two very diffuse bands. It is clear that a non-crystalline substance is produced by dry grinding. In the process of the grinding of talc, a remarkable change

4) T. Sudo et al., *J. Geol. Soc. Japan*, (*Chishitsu-Gaku-Zasshi*), 58, 679 (1952).

5) D. M. C. MacEwan, "X-Ray Identification and Crystal Structures of Clay Minerals", Mineralogical Society (London), Edited by G. W. Brindley, p. 311 (1951).

TABLE I
POWDER DATA OF GROUND TALC

A.S.T.M. Index (No. II-1238)		Original Talc		Ground 96 hr.		Ground 192 hr.		Ground 240 hr.		Ground 384 hr.		Ground 528 hr.	
$d(kX)$	I	d(Å)	I	d	I	d	I	d	I	d	I	d	I
9.4	8	9.4	VS	9.3	VS	9.3	MS	9.8	W vbr	9.8	VW vbr	9.8	VW vbr
4.69	4	4.69	S	4.70	M	4.69	W						
		4.60	VW	4.59	M	4.58	M br	4.55	VW				
3.88	1b												
3.37	3	3.45	MW	3.50	W			3.8	W vbr	3.3	W vbr	3.4	W vbr
3.11	10	3.12	VS	3.11	MS	3.12	M						
2.70	1	2.63	W	2.63	MW	2.64	VW						
2.59	2	2.60	W	2.60	MW	2.60	MW	2.60	VW				
2.47	5	2.48	MW	2.49	MS	2.49	M br						
2.32	1	2.34	MW	2.34	VW	2.34	VW						
2.20	3	2.21	W br	2.21	W br	2.22	W br						
2.09	2	2.11	W br	2.11	W br	2.12	W br						
1.92	0.5	1.927	W										
1.86	3	1.870	MS	1.870	W	1.873	W						
1.725	2	1.731	W	1.73	W	1.73	VW br						
1.67	4	1.665	MW br	1.67	MW br	1.68	VW br						
1.652	1—2												
1.632	1b												
1.55	3	1.560	M	1.56	W br	1.56	VW br						

Key to abbreviatin: VS: very strong, S: strong, MS: medium strong, MW: medium weak, W: weak, VW: very weak, br: broad, vbr: very broad.

occurs in the structure at the period between 192 hours and 240 hours under the experimental condition of this experiment. In the 384-hour-ground specimen, the X-ray diagram is nearly similar to that of the 240-hour-ground specimen. As the grinding progresses, the maximum points of diffuse bands in the X-ray diagram gradually become more and more indistinct, and the intensity of the background at the small angle part of a scattering angle increases progressively.

That a zeolitic substance is formed in the dry grinding of kaolin minerals can be supported on the basis of the X-ray diagram of the ground specimen treated with a weak alkali- and acid-solution as described in the previous papers[1]. These procedures were used for some ground specimens of talc. A part of these X-ray traces are shown in Fig. 2.

From a comparison of these X-ray traces with those of the original ground specimen, the following conclusions are drawn. In the alkali-treated specimen of 192-hour-ground talc, only a slight increase in the intensity of background is observable in the X-ray diagram, as compared with that of the original ground specimen. The X-ray pattern of the acid-treated specimen after being treated with the above weak alkaline solution is almost similar to that of

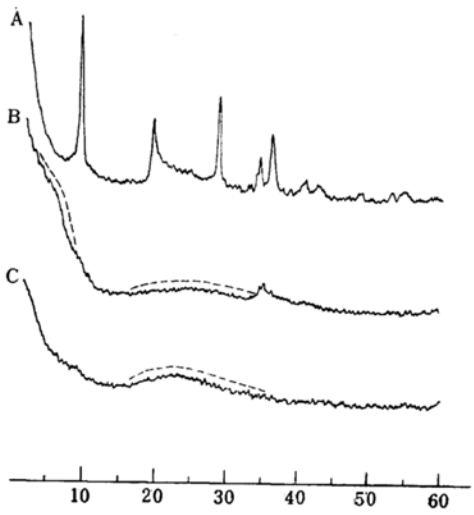

Fig. 2. X-ray diffractometer traces of alkali- and acid-treated specimens of ground talc.
A, 192-hour-ground talc treated with 0.1 N HCl after treated with 0.1 N NaOH
B, 240-hour-ground talc treated with 0.1 N NaOH
C, 240-hour-ground talc treated with 0.1 N HCl after treated with 0.1 N NaOH

TABLE II
THERMAL DATA OF GROUND TALC
(ALL TEMPERATURES ARE DEGREES CENTIGRADE)

Grinding time (hr.)	E_{n1}		E_x		E_{n2}	
	Temp. at peak (°C)	Height of peak	Temp. at peak (°C)	Height of peak	Temp. at peak (°C)	Height of peak
0	—	—	—	—	990	13
48	—138—	6	807	9	980	8
96	—135—	9	805	20	970	6
192	—140—	14	807	50<	968	4
240	—150—	13	807	8	945	2
528	—140—	15	825	1	—	—

the original ground specimen, however, the pattern becomes somewhat distinct owing to a dissolution of an amorphous substance produced by dry grinding. In the X-ray diagram of the weak alkali-treated 240-hour-ground specimen, two very diffuse bands are noticeable as is clear by comparison of Fig. 1-D and Fig. 2-B. The positions of the maximum points of these bands are about 14.7Å and 3.5Å in the interplaner spacings. In addition to these diffuse bands, a very remarkable scattering is also observable in the region of a scattering angle as low as six degrees. To dissolve the amorphous substance produced by dry grinding, acid treatement was given. The X-ray diagram of the residual part has a broad band with a maximum of 3.86Å in spacing. The background decreases below that before acid treatment. This fact indicates that in the 192-hour-ground specimen, the disordering in the talc structure is observable but the production of an amorphous substance is yet remarkable. In this stage, a zeolitic substance is not to be formed. In the 240-hour-ground specimen, the crystalline substance is not present. This fact is ascertained by the X-ray diagram of a residual substance treated with alkali and acid. Therefore, it is considered that the structure of this specimen is not perfectly amorphous, but it is related somewhat to the original structure though the original talc structure disintegrates due to dry grinding. In the light of the X-ray data, the structure of the 384-hour-ground specimen is considerably similar to that of the 240-hour-ground specimen. In the 528-hour-ground specimen, the amorphous substance dissoluble by the alkali-acid treatment considerably increases. This means an increase of the amorphous substance by dry grinding.

Consequently, it is concluded that in the dry grinding of talc, the disordering of structure is remarkable up to a certain stage of grinding, and past this stage, the specimen changes wholly into a non-crystalline substance and then gradually changes into a completely amorphous substance. Therefore, the formation of a zeolitic substance is not remarkable as compared with that of kaolin mineral.

Differential Thermal Analysis. — Differential thermal analysis curves of the specimens in the various periods of grinding are shown in Fig. 3, and thermal data measured from these curves are given in Table II.

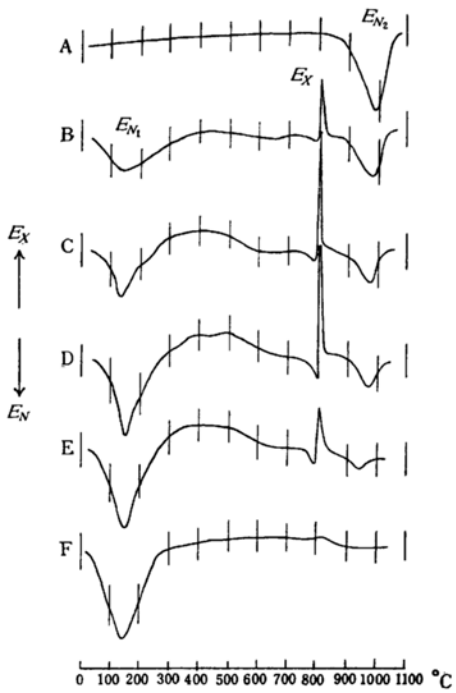

Fig. 3. Differential thermal analysis curves of ground talc.
A, original talc
B, ground 48 hours
C, ground 96 hours
D, ground 192 hours
E, ground 240 hours
F, ground 528 hours

The original sample has only an endothermic reaction (E_{n2}) associated with the loss of lattice water. The peak temperature of the endothermic reaction is 990°C, which is nearly equal to the value given in literature[6]. In the 96-hour-ground specimen, the first endothermic reaction (E_{n1}) associated with the loss of adsorbed water is apparent. This fact means that a non-crystalline substance is produced by dry grinding. As that of a kaolin mineral, a lowering in the peak temperature and a decrease in the height are observable in the second endothermic reaction (E_{n2}). It seems that these characteristics are related to the partial disintegration of the original structure. In the differential thermal analysis curve of this specimen, another important characteristic is observable. That is, a sharp exothermic reaction (E_x) is apparent at about 800°C, and there is the presence of a slight but distinct endothermic reaction immediately before this reaction. In the 192-hour-ground specimen, all features observed in the differential thermal analysis curves of the 48- and 96-hour-ground specimens become all the more distinct. An increase in the height of the first endothermic reaction, a remarkable increase in the intensity of the exothermic reaction, a lowering in the peak temperature and a decrease in the height of the second endothermic reaction are observable. Moreover the endothermic reaction just before the exothermic reaction becomes more distinct. The first endothermic reaction of ground specimens up to 192 hours is considered to be caused by a non-crystalline substance produced by grinding rather than by the water which gets into the inter-layers of talc as an inter-layer water, because the basal spacing of these specimens does not change much. In the 240-hour-ground specimen, the height of the exothermic reaction sharply decreases and the height of the second endothermic reaction decreases remarkably as compared with those of the 192-hour-ground specimen. In a many-hour-ground specimen, for example, the 528-hour-ground specimen, the reaction which is present in the original specimen is absent. Only the first endothermic reaction associated with the loss of the adsorbed water, and the weak and broad exothermic reaction at 825°C are observable. Then the endothermic reaction just before the exothermic reaction has already disappeared.

On the differential thermal analysis curves of the ground specimens, an important and interesting phenomenon is observable. That is, a new phase different from the original structure is apparent in the course of dry grinding. To ascertain this new phase, the X-ray traces of the 192-hour-ground specimen taken out just before and after the exothermic reaction on the differential thermal analysis curve are compared. A difference is observable in that only a reflection of 2.885Å spacing is apparent. From the facts that all reflections of the original 192-hour-ground specimen remain in the X-ray diagram of the specimen taken out just after the exothermic reaction and that a new reflection appears, it is supposed that the exothermic reaction on the differential thermal analysis curve is not based on the structural change of original talc. And from the fact that this exothermic reaction disappears again in many-hour-ground specimens, it is supposed that this exothermic reaction is not also based on the structural change of a perfectly amorphous substance produced by dry grinding. Therefore, it is clear that this exothermic reaction is based on crystallization from the new phase formed by dry grinding which is not the talc structure and is not a perfectly amorphous structure. This sort of structural change is not found at all in the case of kaolin minerals. The appearance of a new phase

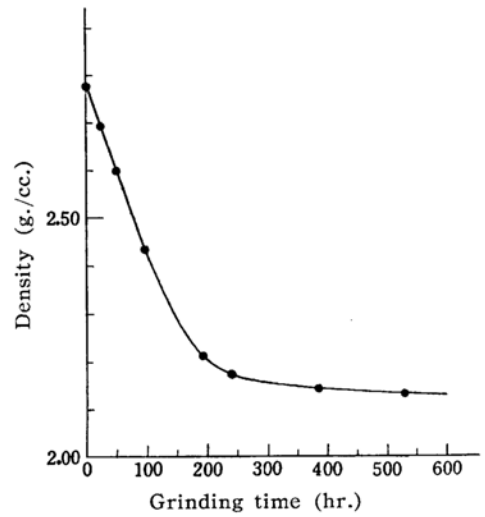

Fig. 4. Curve showing the change of the density with the time of grinding.

6) M. M. Taboadela and V. A. Ferrandis, "Differential Thermal Investigation of Clays", Mineralogical Society (London), Edited by R. C. Mackenzie (1957). p. 176.

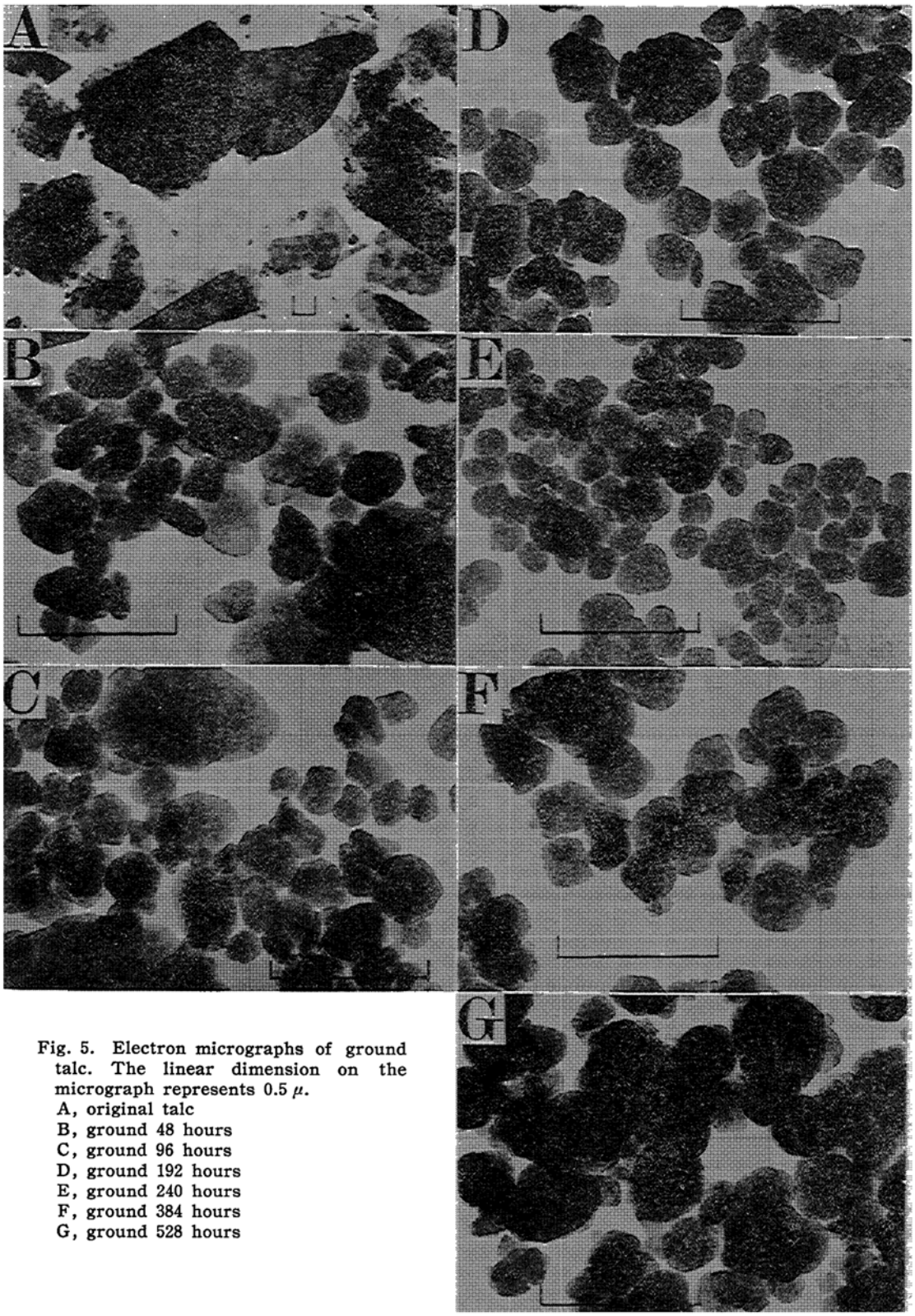

Fig. 5. Electron micrographs of ground talc. The linear dimension on the micrograph represents 0.5 μ.
A, original talc
B, ground 48 hours
C, ground 96 hours
D, ground 192 hours
E, ground 240 hours
F, ground 384 hours
G, ground 528 hours

by dry grinding is an important characteristic of talc.

Density.—A curve showing the change of the density in the process of the dry grinding on talc is shown in Fig. 4.

The density sharply decreases up to about 200 hours in the grinding, but thereafter it reaches a nearly constant value. This constant value is nearly equal to that of a gel-like substance. The point of the bend in the density curve is existent between the points of 192 hours and 240 hours. In the light of the X-ray and thermal data, this point corresponds to the point where the structure of talc changes wholly into a new structure by dry grinding. In talc, grinding takes a longer time for the density to reach the constant value than that of kaolin minerals. This means that talc suffers the effects of dry grinding less than kaolin minerals do, for the structure of talc is stronger than that of kaolin minerals.

Electron Microscopic Studies. — Fig. 5 shows the electron micrographs in the process of grinding on talc.

The original sample is an irregular and platty particle with a sharp edge, and the particle has several microns in size. In the 48-hour-ground specimen, it is observed that the particles are fine as compared with those of the original particle, while considerably large particles are also observable. It seems that the fine particles do not aggregate unlike the fine particles in the grinding process of kaolin minerals, and the edge of this particle is not sharp. The shape of the considerably large particle is spherical. As the grinding progresses, number of large particles decreases and that of fine particles increases, but the size of the fine particles remains almost unchanged. This means that the reaggregation process is not very remarkable in this case. In the 240-hour-ground specimen, the shape of the particle is almost uniformly spherical as compared with that of the 192-hour-ground specimen but it is not so spherical as the shape of particles found in the process of dry grinding of kaolin minerals. The mean value of the particle size of this specimen is about 0.1 micron. Past this stage in grinding, the particle size increases as compared with that of the 240-hour-ground specimen. As the grinding further progresses, an irregular growth of the particle is observable. This corresponds to the fact that the completely amorphous substance has been produced by grinding.

Summary

The several-hundred-hour mechanical-mortar dry grinding on talc was examined by X-ray diffraction method, differential thermal analysis, electron microscopy and density measurements, and they were compared with those of kaolin minerals. In the dry grinding on talc, some characteristics in the structural changes by dry grinding were found. As the grinding progresses, the original crystals cleave and fracture and then split into fine crystals. Disordering in structure of these fine crystals is observable before the talc structure disintegrates completely. In talc, a new substance is produced by dry grinding, which is somewhat related to but different from the original talc structure. The appearance of this new phase is most remarkable in the stage of grinding where the crystalline pattern of talc entirely disappears in the X-ray diagram. This new phase has a non-crystalline structure, but the strurcture is not completely amorphous. It crystallizes into a new crystal at about 800°C. As the grinding progresses, the structure of this new phase gradually disintegrates to a completely amorphous structure similar to that of a silica-magnesia mixed gel. The formation of a zeolitic structure is not so remarkable; also, even if this structure is formed, the period of its stage is very short. It is an important characteristic that talc wholly changes into a new non-crystalline substance by dry grinding. It is generally supposed that talc does not easily suffer the effects of dry grinding because the structure is stronger than that of kaolin minerals.

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