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The Changes in the Secondary Properties of Zinc Oxide in the Process of Mechanical Treatment

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The changes in the secondary properties of zinc oxide upon mechanical treatment were studied. In the process of the mechanical treatment of zinc oxide, the Blaine specific surface area, the sedimentation volume, and the particle size distribution changed periodically with the treatment time. Such periodical changes are characteristic of the state of association of the particles, and can be interpreted as the changes in the total energy content of the solid.

In the previous paper,[1] we reported an analysis of the primary structural change in zinc oxide upon mechanical treatment, an analysis made by using an X-ray diffraction method, electron-microscopy, and BET specific surface area and density measurements. The following effects were observed:

1) a diversification of the crystallinity of the particles;

2) a structural disordering on the surface and in the interior, and

3) a color change.

The manners of these primary structural changes show a gradual increase, a gradual decrease, or a change in linearity with respect to the treatment time. These mechanical effects are more remarkable in a sample prepared at a higher temperature than in one prepared at a lower one. Thus, such changes depend upon the nature of the materials before treatment, that is, on the conditions of the preparation. In addition to these changes, the growth of the secondary particles due to an aggregation or agglomeration of the fine-grained particles was observed.

Therefore, this paper will deal with such phenomena as the aggregation, agglomeration, and flocculation of the unit particles of zinc oxide. The changes in the secondary properties of the aggregates and the degree of dispersion for the particles in liquid will be studied in connection with the Blaine specific surface area, the sedimentation volume, and the particle size distribution.

Experimental

All the specimens of zinc oxide used in this work were the same as have been described in the previous paper.[1] That is, zinc oxide which had been prepared by the pyrolysis of zinc oxalate (extra pure quality) in the air at various temperatures for five hours was dry-ground by a ball mill.

The samples examined will be identified by both the pyrolysis temperature of the original zinc oxide and the grinding interval. For example, the samples will be indicated as ZnO(400)-24, *etc.*

The specific surface area of the secondary particles was measured by the air-permeability method using the Blaine apparatus[2] and was calculated by Kozenry-Carman's formula.[3] The relation between the specific surface area, S_w, and the time measured, t, is expressed as follows:

$$S_w = \sqrt{\frac{\varepsilon^3}{(1-\varepsilon)^2}} \cdot K_B \cdot \frac{1}{\rho} \cdot \sqrt{\frac{t}{\eta}} \tag{1}$$

where ε is the porosity of the sample powder layer; K_B, the apparatus constant as decided from the reference material; ρ, the density of the sample, and η, the viscosity of the air. In all experiments, the porosity, ε, was 0.5.

The sedimentation volume was measured in benzene and water at 25°C. Three grams of zinc oxide, after being dried, were introduced into a graduated glass tube, about 35 cc in capacity, with a ground-glass stopper; then *ca.* a 20-cc portion of liquid was poured in. The tightly-stoppered tube was then shaken and allowed to stand. Zinc oxide powder settled on the bottom of the tube in a few hours; however, it usually took several days to attain the definite volume. The sedimentation volume was measured when such an equilibrium had been attained. In this experiment, no dispersing agent was used.

The particle size distribution was measured by using the Andreasen pipette method at 25°C.[4] In the pipette, a suspension of 2 g of zinc oxide and 600 cc of water, with 0.1 wt% of sodium pyrophosphate added as a dispersing agent, was introduced; then the zinc oxide powder was allowed to fall. At various intervals, each fraction of the dropping sample was taken out, dried, and weighed. Assuming the particle to be spherical, its size was calculated by Stokes' formula:

$$d = \sqrt{\frac{18\eta V}{(\rho_1 - \rho_2)g}}, \tag{2}$$

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[1] H. Takahashi and K. Tsutsumi, This Bulletin, **40**, 7 (1967).

[2] R. L. Blaine, *A. S. T. M. Bull.*, **108**, 17 (1941).

[3] R. C. Carman, *J. Soc. Chem. Ind. (London)*, **57**, 225 (1938).

[4] A. H. M. Andreasen, *Kolloidchem. Beih.*, **27**, 349 (1927).

where d is the particle size; ρ_1, the density of the sample; ρ_2, the density of the dispersing medium (water); g, the acceleration of gravity; η, the viscosity of the dispersing medium (water), and V, the dropping velocity of the sample.

Results and Discussion

The specific surface area of the zinc oxide obtained by the Blaine method is plotted against the times of mechanical treatment in Fig. 1. These values and tendencies are considerably different from those obtained by the BET method.[1] As the mechanical treatment progresses, the following periodical changes are observed; a significant decrease in the initial stage, an increase in the following stage, and then a gradual reduction. This tendency is seen in both ZnO(1000) and ZnO(400), regardless of the difference in the temperatures at which the original samples were prepared. This suggests that the specific surface area measured by the Blaine method is affected not so much by the microstructural changes as by a change in the state of the association of the particles.

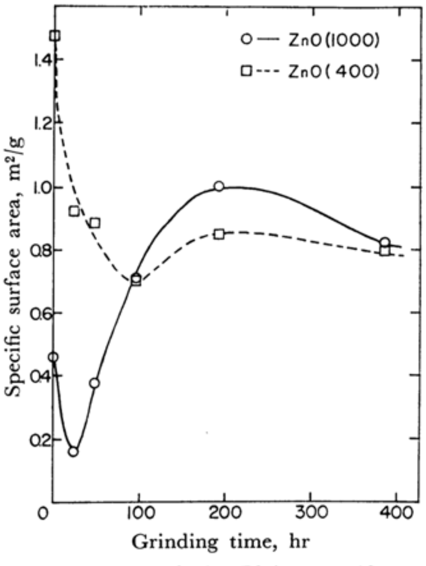

Fig. 1. Change of the Blaine specific surface area of zinc oxide in the process of mechanical treatment.

Accordingly, there seems to be two kinds of states of association. One is a short-range phenomenon, which is presented by crystallites or unit particles, while the other is a long-range one presented by secondary particles formed by short-range aggregates. The latter is predominant in the specific surface area obtained by the Blaine method and leads it to a periodical change. Such a periodicity in the specific surface area against the time of mechanical treatment was also observed by Naeser *et al.* in the case of the BET specific surface area of NaCl.[5]

The particle sizes of the samples measured by the BET method are as small as 0.05 to 0.1 μ.[1] Thus, it may not be possible to determine accurately the Blaine specific surface area of such a fine powder.[6] However, these values should be useful in suggesting the state of association of secondary particles.

The sedimentation volume of the crystalline powder in a liquid is known to vary depending on the size or shape of the particles as well as on the nature of the dispersion medium. It reflects the size distribution and the flocculated or deflocculated state of the particles. Thus, the sedimentation volume can be a measure of the degree of association and dispersion for the particles in the liquid. The sedimentation volume of zinc oxide particles in benzene is shown in Fig. 2. In a polar-nonpolar system such as the zinc oxide-benzene system considered in the present study, the significant effect of water has previously been known.[7-9] In this experiment, the sample was evacuated at 150°C under 10^{-3} mmHg for 20 hr. Benzene (extra pure quality) was dehydrated with phosphorus pentoxide. The total water content in this system was measured by means of a Karl-Fischer reagent; it was under 0.007 wt%. Therefore, it seems that water has only a minor effect

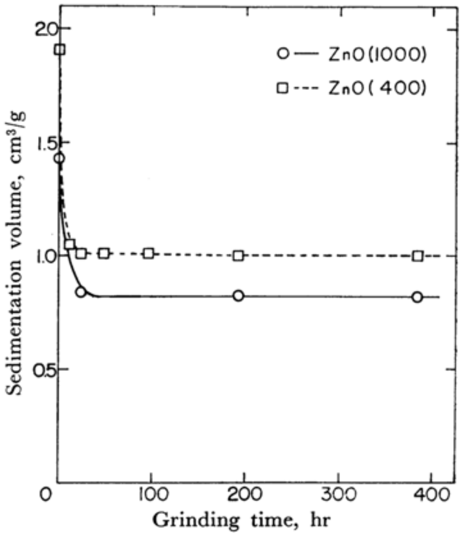

Fig. 2. Change of the sedimentation volume of zinc oxide in benzene in the process of mechanical treatment.

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[5] G. Naeser, W. Scholz and A. Fiedler, *Kolloid-Z.*, **188**, 147 (1963).

[6] M. Arakawa and E. Suito, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **63**, 556 (1960).

[7] W. D. Harkins and D. M. Gans, *J. Phys. Chem.*, **36**, 86 (1932).

[8] C. R. Bloomquist and R. S. Shutt, *Ind. Eng. Chem.*, **32**, 287 (1940).

[9] S. Ross and H. F. Schaeffer, *J. Phys. Chem.*, **58**, 865 (1954).

on the value of the sedimentation volume. As is clearly shown in Fig. 2, in the initial stage of treatment, the sedimentation volume rapidly decreases, but subsequently it becomes constant in both ZnO(1000) and ZnO(400). It is especially noticeable that the sedimentation volume becomes constant in spite of the remarkable decrease in the size of the unit particles in the case of ZnO-(1000).1) As zinc oxide is lyophobic to benzene, its aggregate, which had been formed through the water molecules physically or chemically adsorbed on the particle surface, was broken up into unit particles by evacuation; each fine particle settled in a new stable flocculated state in benzene.

The sedimentation volume in water is shown in Fig. 3. The sedimentation volume of the original specimen in water is less than that in benzene, since zinc oxide is polar. The fact that the volume of ZnO(400)-0 is larger than that of ZnO(1000)-0 results from the difference in the crystal growth between the two specimens; namely the former probably packs poorly as a result of the irregularity of its particle shape.10) In the cases of both ZnO(1000) and ZnO(400), the sedimentation volume in water changes periodically with respect to the treatment time. The mode of these changes shows that the particles of zinc oxide flocculate and then deflocculate repeatedly. It is clear that the structure and the nature of the surface of zinc oxide particles sensitively vary according to the mechanical treatment.

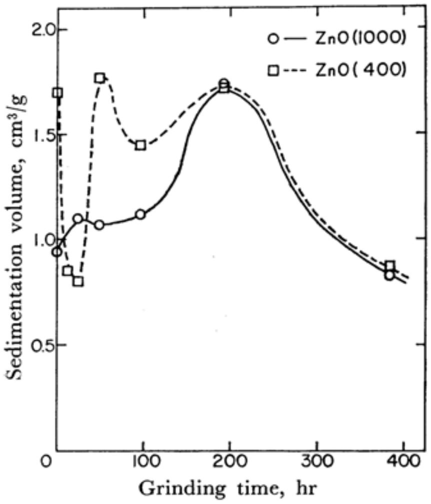

Fig. 3. Change of the sedimentation volume of zinc oxide in water in the process of mechanical treatment.

Figure 4 shows the cumulative curve of the particle size (weight base). In the initial stage of treatment, a reduction in the size distribution of large particles and an increase in the size distribution of small particles are observable. These phenomena lead to the simultaneous occurrence of the flocculation of the small particles and the deflocculation of the large particles of zinc oxide at all times during the mechanical treatment.

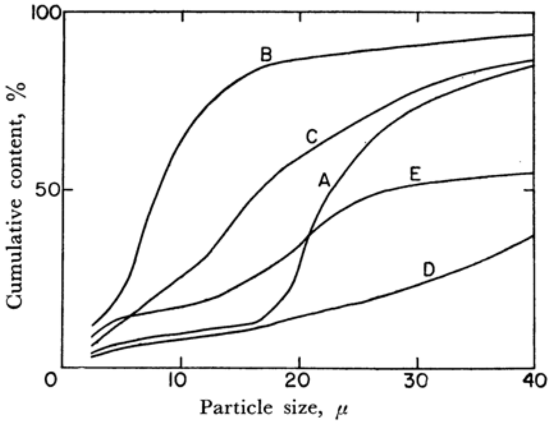

Fig. 4. Cumulative curve of the particle size (weight base) at various stages of mechanical treatment.

A	ZnO(1000)-0
B	ZnO(1000)-48
C	ZnO(1000)-84
D	ZnO(400)-0
E	ZnO(400)-384

This can be seen clearly from the change in the median diameter of the particles (weight base) during the mechanical treatment, a change shown in Fig. 5.

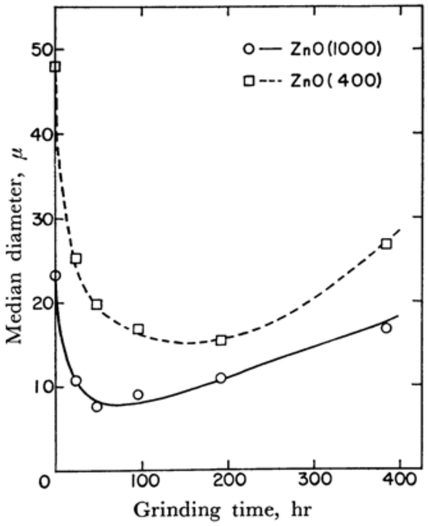

Fig. 5. Change of the mediane diameter of zinc oxide in the process of mechanical treatment.

In order to compare the secondary particle with the primary particle, the change in the particle size as measured by the various methods discussed

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10) E. Köhler, V. Hofmann, E. Scharrer and K. Frühanf, *Ber. Dtsch. Keram. Ges.,* **37**, 493 (1960).

TABLE 1. CHANGE IN THE PARTICLE SIZE OF ZINC OXIDE IN THE PROCESS OF MECHANICAL TREATMENT

Species		D(X-Ray)	d_g(E. M.)	d_{sp}(BET)	d_{sp}(Blaine)	d_e(Median)
ZnO (1000)-	0	∞	0.8 —2.4 μ	1.06 μ	2.36 μ	23.3 μ
	24	2050 Å	0.6 —0.8	0.28	7.30	10.7
	48	1060	0.3 —0.4	0.20	2.86	7.6
	96	745	0.15—0.25	0.17	1.51	9.2
	192	634	0.05	0.12	1.08	10.9
	384	505	0.04	0.072	1.30	16.8
ZnO (400)-	0	756	0.06—0.1	0.065	0.73	48.0
	24	740	0.06—0.1	0.084	1.16	25.2
	48	703	0.06—0.08	0.088	1.21	19.8
	96	669	0.05—0·07	0.091	1.53	16.8
	192	645	0.05—0.07	0.099	1.27	15.4
	384	612	0.05—0.06	0.093	1.34	26.8

in the previous paper1) and in the present one is shown in Table 1.

Consequently, from the measurements of the Blaine specific surface area, the sedimentation volume, and the particle size distribution, the following informations are obtained on the state of association of the particles of zinc oxide powder crystal during mechanical treatment:

1) there is a periodicity in the aggregation, flocculation, and dispersion of the particles, and

2) there is a possibility of the simultaneous occurence of the aggregation, flocculation, and dispersion of the particles.

3) Results 1) and 2) demonstrate the property of secondary particles.

4) There are two kinds of states of association.

i) The short-range state of association is formed by the crystallites or the unit particles. The bond between particles seems to be nearly chemical, that is, the hydrogen bonding of the water molecule chemically adsorbed on the particle, and also the sintering of the particles upon local heating. The bonding force of such chemical bonds is so strong that nitrogen gas cannot be adsorbed in the intervals.

ii) The long-range state of association is formed by the unit particles or the secondary particles described in i). Its bonding force is weak, so the association state changes in a liquid medium.

The periodicity in the change of the secondary properties with respect to the treatment time may be interpreted as follows. Solid materials, when mechanical energy is added to them, are able to retain it as internal energy,[*1] and also are able to release it as thermal energy.11) Therefore, the total energy content of the solid changes periodically with respect to the treatment time. The energy released as thermal energy can contribute to arranging the lattice point regularly.5,12) Moreover, the activated surface which has excess surface energy strengthens the interaction between the particles, and thus the surface area is apt to be lowered. Besides, a change in the energy content, namely, a change in the potential field, seems to have an influence on the chemical activity of the powder.

Summary

The secondary properties of zinc oxide powder crystal, when mechanical energy is added, change in the following ways. The changes in the Blaine specific surface area, the sedimentation volume in benzene and water, and the particle size distribution show a similar tendency regardless of differences in the temperature at which the original material is prepared. These effects depend upon the conditions of the mechanical treatment of the zinc oxide. The modes of these changes are periodical with respect to the treatment time; this results from the periodical change in the total energy content of the zinc oxide.

The authors wish to express their hearty thanks to Professor Hideo Akamatu for his kind advice and encouragement.

[*1] The internal energy includes the strain energy caused by the structural defect and the electric energy caused by the charge unbalance.

11) M. K. Hüttig, *Z. anal. Chem.*, **86**, 95 (1931).

12) A. L. Titschener and M. B. Bever, "Progress in Metal Physics," No. 7, Butterworth Scientific Publ., London (1958), p. 247.