Effects of Titania Sol on the Mechanical Delamination of Talc

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The addition of titania sol to talc particles changed their aspect ratio to more than double during wet mechanical delamination in a ball mill. The role of titania sol was suspected to initiate the cleavage by adsorbing preferentially on the periphery of the talc particles. The optimum dose of titania sol was 0.1 wt %, which resulted in an aspect ratio about 90 with particle thickness ca. 0.1 μm.

Introduction

The role of talc in cosmetics [*1*] is to give better gliding properties and higher gloss. Delamination improves these functions. We already attempted to delaminate talc and established how to describe the geometrical properties of delaminated platelet particle [*2*]. However, we have not yet reached the satisfactory level of delamination to get the aspect ratio as high as 100 without damaging the original character of platelets.

One possibility to improve mechanical delamination is to use a special kind of grinding aid. The grinding aids have mainly been used for the purpose of improving the efficiency of grinding [*3–8*]. Such grinding aids also cause the change in the surface properties of materials by adsorption on the surface [*3–5,7*] and the mechanochemical effects [*6–8*].

Clay minerals often intercalate additives as in the case of titania sol into montmorillonite [*9*] and urea into kaolinite [*10*]. Intercalation can be classified into several types of reactions according to the mechanism [*11*]. The basal plane spacing increases as a result of the ion exchange of a guest particle into the interlayer spaces. Conventional grinding additives, however, do not delaminate the clay minerals [*10*].

The purpose of this study is to examine whether and to what extent the titania sol added during grinding promotes mechanical delamination of talc to obtain particles as thin as possible without excessive breakage of the platelets and whether the additive enters into the interlayer spaces. We also tried to find out the optimum condition for maximum aspect ratio.

Experimental Section

Materials. Clear titania sol was prepared by adding slowly 0.5 M titanium isopropoxide (Wako Pure Chemical) alcohol solution to stirred 0.1 M HCl alcohol solution. Suspensions of talc samples (Matsumura Sangyou, CROWN, nominal median diameter 20 μm) with 0.15 solid volume fraction in 0.01 M NH_4Cl aqueous solution were prepared. After the titania sol was added to the suspension, wet grinding was carried out immediately in a laboratory-size ball mill (Irie). The amount of titania sol was kept constant at 10 mg g^{-1} of talc, without the experimental for the adding amount of titania sol.

Characterization. The size of the grinding talc platelet was determined from the average Feret diameter, d_{xy}, i.e., those corresponding to the average diameter of the platelets, and from the average thickness, d_z, corresponding to the platelet thickness [*2*]. The adsorbed amount of titania sol on talc particles was determined by X-ray fluorescence for the samples washed with water. The state of adsorbed titania sol to talc particles was observed by electron microscopy equipped with energy-dispersive spectrometry (EDS) for elementary analysis. Apparent size distributions for the ground suspension samples were measured by a laser diffraction analysis instrument (Seishin-Kigyou, PRO-7000S).

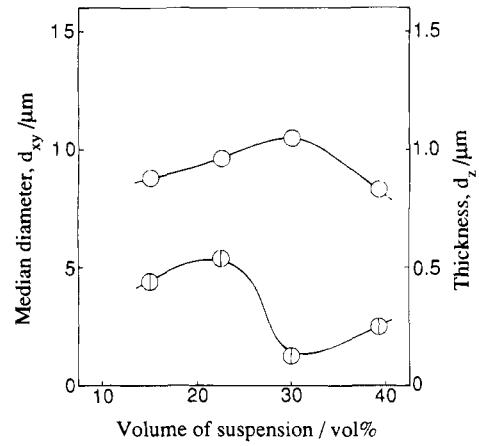

Figure 1. Variation of median diameter, d_{xy}, and thickness, d_z, with suspension volume: ○, d_{xy}; Φ, d_z.

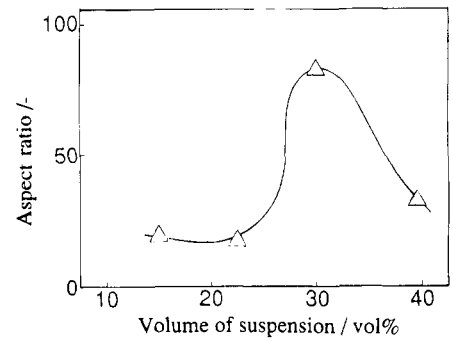

Figure 2. Variation of aspect ratio with suspension volume.

Results and Discussion

Delamination of Talc by Adding Titania Sol. The change in d_{xy} and d_z with the suspension volume for the vessel volume is shown in Figure 1, where added amount of titania sol relative to talc was kept constant. The corresponding change in the aspect ratio is shown in Figure 2. These figures show that there is an optimum volume percent of the suspension for the vessel volume, at 30 vol %, where the aspect ratio reached its maximum, being 83. In our previous study [*12*], it was found that grinding of talc without adding titania sol,

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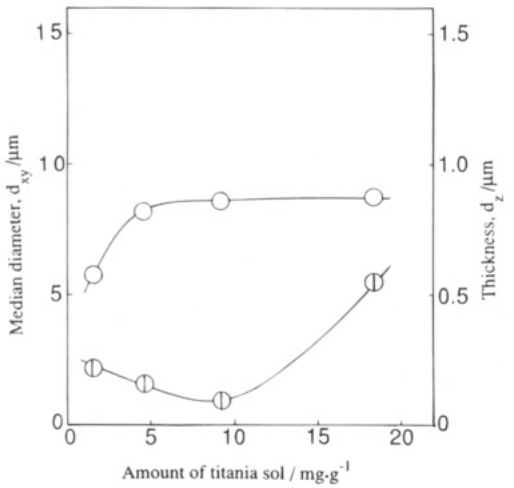

Figure 3. Variation of median diameter, d_{xy}, and thickness, d_z, with the added amount of titania sol: ○, d_{xy}; Φ, d_z.

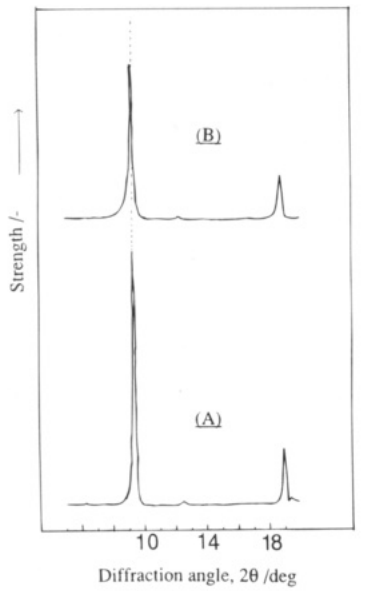

Figure 4. Representative X-ray diffraction profiles for the starting and the delaminated talc: A, without titania sol; B, with titania sol.

maximum aspect ratio was obtained at 25% suspension volume. The viscosity of suspension did not change significantly by adding titania sol.

Role of Titania Sol against Delamination of Talc. The change of d_{xy} and d_z with the amount of titania sol are shown in Figure 3. The volume of the talc suspension for the vessel volume without titania sol was kept constant at 30 vol %. The value of d_{xy} increased only at very low concentration and leveled off rapidly, while d_z showed a shallow minimum at 10 mg g^{-1} of talc, being optimum to give the maximum aspect ratio 92. X-ray diffraction profiles for the starting and the delaminated talc are shown in Figure 4. The diffraction peak from the basal plane was observed at 2θ equal 9.6° and 9.4°, respectively, for starting and delaminated samples, the latter obtained in the presence of titania sol 10 mg g^{-1}. The change in the spacing corresponds to ca. 0.2 Å or 2.2% of the basal plane spacing, 9.21 Å. The change could be significant, since the diffraction angle increased to the initial value when the specimen was heated at 200 °C in air for 2 h.

For the titania-pillared montmorillonite [*9*, *11*], it has been confirmed that the titania was fixed firmly to montmorillonite interlayer to make pillars. As a result, the basal plane spacing increased to 13.5−17 Å. This

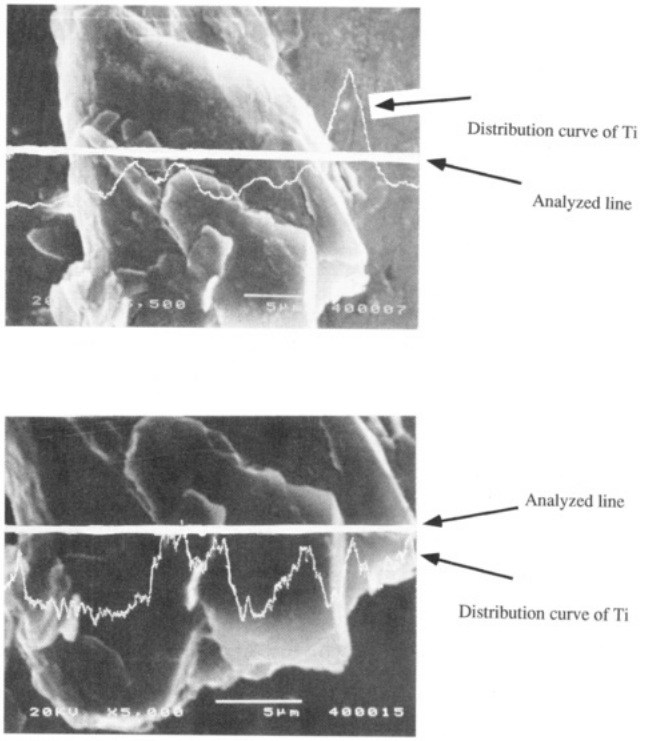

Figure 5. Scanning electron micrographs by electron probe microanalysis for two talc particles with titania sol.

kind of pillared structure was stable above 500 °C. In contrast, titania sol was not fixed in talc interlayer, talc does not have any cation exchange capacity, in contrast to montmorillonite [*9*]. As a matter of fact, the change in the diffraction peak was not observed before grinding. Furthermore, the diffraction angle did not vary with the amount of titania sol.

Adsorption of Titania on Talc. The slight increase in the interlayer spacing after delamination with titania sol might suggest the partial intrusion of the small particles adsorbed preferentially at the edge of the layer stacking, being subjected to desorption after heating at temperatures as low as 200 °C. To examine the state of titania sol, scanning electron microscopy was carried out with a simultaneous electron probe microanalysis (SEM-EPMA). By measuring from some different observed angles for a same talc platelet, the preferred concentration of Ti at the periphery by SEM-EPMA was supported and was not artifact. As shown in Figure 5, titania sol was found mainly on the periphery of the talc platelets, suggesting the preferential adsorption of titania sol at the edge of talc. This is attributed to the negative charge on the edge [*13*], since the charge of titania sol is positive [*9*] at pH lower than 7. The pH value of the suspension, from which the sample for Figure 5 had been taken, was below unity.

The relation between the amount of titania sol adsorption and the initial titania concentration is shown in Figure 6. Up to 10 mg g^{-1}, it was found that the entire quantity of titania was adsorbed by talc. When the initial concentration exceeded 10 mg g^{-1}, the adsorption began to level off. It seems not accidental that the optimum concentration of delamination was 10 mg g^{-1}, up to which the fraction adsorbed was 1.0.

While the amount of free titania sol in the supernatant could not be detected up to 10 mg g^{-1}, it was 3 mg g^{-1} at 18 mg g^{-1} of addition. The free titania sol, therefore plays some negative role for mechanical delamination by preventing the reduction of d_z, shown in Figure 3. The most significant role of the titania sol

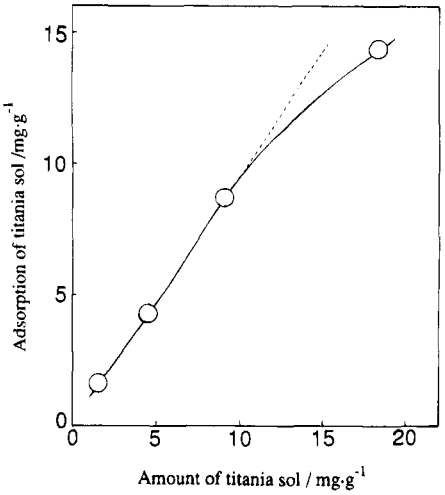

Figure 6. Relation between the amount of titania sol adsorption and the initial titania sol concentration.

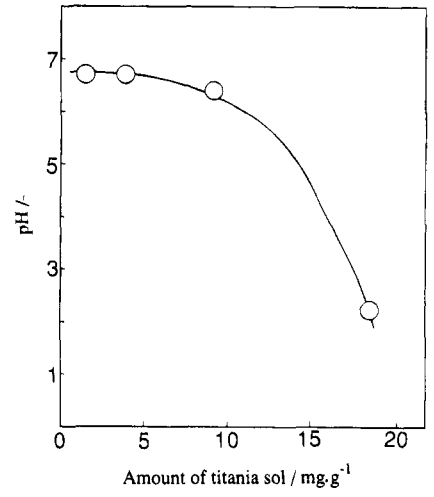

Figure 7. Variation of pH of ground suspension with the added amount of titania sol.

for mechanical delamination of talc is thus the adsorption at the edge. It is possible that the adsorbed titania sol opened the periphery of the closed interlayer, which might be the reason for the small increase in the interlayer spacing. It is also possible that the preferred adsorption at the edge of talc favored the dispersion of talc by preventing the edge-to-face flocculation [*14*].

The change of pH of suspension after grinding with the added amount of titania sol is shown in Figure 7. The pH remained constant up to 10 mg g^{-1}, while it decreased above 10 mg g^{-1}. From the isoelectric point of talc, which is below pH = 3 [*15*], the decrease of pH presumably caused preferentially the formation of the flocculated structure. For the dispersion states of the ground suspensions, the apparent average size, d_{50}, with the added amount of titania sol was measured and shown in Figure 8. The values of d_{50} with and without the ultrasonic wave dispersion (uwd) were different. The value of d_{50} without ultrasonic wave dispersion was 6 times larger than that with ultrasonic wave dispersion, when the apparent amount of titania sol was 18 mg g^{-1}. The large particle size without ultrasonic is attributed to flocculation of platelets to form cardhouse structure. Decreased delamination at titania concentration above 10 mg g^{-1} is presumably attributed to the flocculation mentioned above.

Conclusion

Addition of titania sol resulted in talc platelets with higher aspect ratio up to 93, in so far as no appreciable free titania was found in the medium. Titania adsorbed preferentially at the edge of the plates and did not enter deeper into the interlayer spaces.

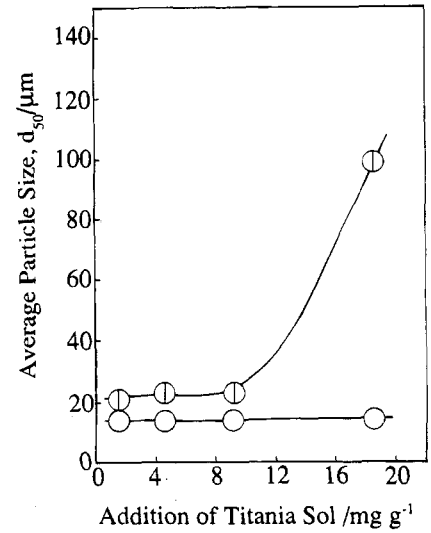

Figure 8. Variation of apparent average particle size, d_{50}, in ground suspension with and without ultrasonic wave dispersion (uwd), with the added amount of titania sol: ○, with uwd; Φ, without uwd.

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Received for review April 21, 1994
Revised manuscript received September 14, 1994
Accepted November 8, 1994[⊗]

IE940260N

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1995.