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The Crystal Structure and Tribology of a Novel Organic Crystalline Powder: the Mechanism of Lubricity

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A novel lubricant material, calcium *N*-lauroyl taurate ($C_{11}H_{23}CONH(CH_2)_2SO_3{\cdot}0.5Ca$, CaLT), has been synthesized and characterized. The powder of CaLT is a plate-shaped crystal with a lamellar structure. CaLT shows superior lubricity as a result of its unique internal and aggregate structure. When the CaLT powder is applied to an artificial skin, the frictional coefficient is favorably lower than that of other solid lubricants of similar type. The frictional coefficient of CaLT decreases rapidly at initial passage and becomes constant when CaLT is repeatedly rubbed onto an artificial skin. The high lubricity may result from disintegration of the powder aggregates, cleavage of the lamellar layers and deformation of the powder particles. This novel lubricant material, CaLT, will be a powerful ingredient of some cosmetic and/or personal-care products in the near future.

Consumer products, particularly personal-care products, are required to produce the favorable sensations through all five senses, i.e. sight, smell, taste, touch, and hearing. Powders providing the unique sensations and also the slippery property are quite useful when one formulates the personal-care products.[1] There are many kinds of physical properties which create a favorable feeling when touched, but the relationship between the physical properties and the feeling is not well understood. A little piece of empirical knowledge is that low frictional resistance is necessary to obtain a smooth feel sensation.

Some organic crystalline powders, i.e. some metal soaps such as zinc stearate (ZnST), N^{ε}-lauroyl-L-lysine (LL), and sodium-zinc salt of cethyl phosphate (NZCP), are suitable solid lubricants for cosmetics.[2–6] These molecules containing long alkyl chains assemble to form lamellar crystals. The interaction between lamellar layers is van der Waals attraction and is weaker than that between molecules inside the lamellar layer. So, the crystalline powder is easily cloven at the plane between lamellar layers and gives a good lubricity. When such metal soap is added to powdery cosmetics, the fluidity and/or molding are improved.[2] But unfortunately, it induces sticky feeling rather than soft one when applied to human skin. LL and NZCP, as the first solid lubricants providing the soft feelings, are frequently used as filler pigments or surface modification agents in the cosmetic industries.[4–6]

In a search for more excellent lubricant materials than those currently in use, we have synthesized a novel lubricant powder, calcium *N*-lauroyl taurate (CaLT, Fig. 1). The crystal structure of CaLT was analyzed by X-ray diffraction (XRD) technique and atomic force microscopy (AFM).[7] In this research, the superior lubricity of CaLT and its lubricant mechanism have been investigated.

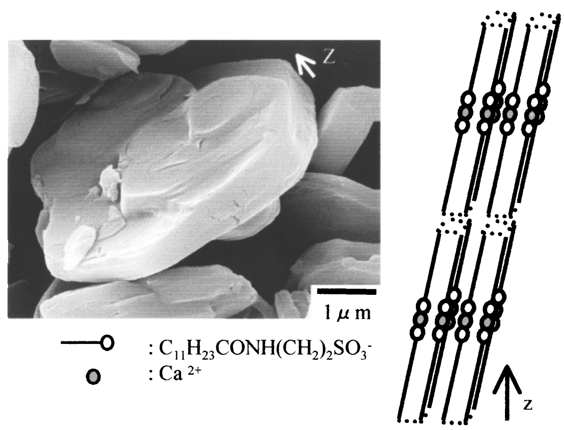

Fig. 1. A SEM image and a crystal structure of CaLT crystalline particles.

Experimental

Materials. CaLT and NZCP (average diameter of 10 μm) were synthesized by methods described in the literature.[6,7] Mica (Yamaguchi-mica Co., Y2300, average diameter of 5 μm), talc (Yamaguchi-mica Co., KK500s, average diameter of 10 μm), boron nitride (Toray Industries, Inc., T-BN-C, average diameter of 10 μm), LL (Ajinomoto Co., Inc., amihope LL, average diameter of 10 μm), and ZnST (Seido Chemical Co., average diameter of 1 μm) were purchased as commercial products, and were used without further purification.

Instruments and Analysis. XRD was performed using a Rigaku Co. RINT 2500 V with Cu $K\alpha$ as the X-ray source (1.54 Å) at 25 °C. An AFM image in contact mode was obtained using a Digital Instruments NanoScope II scanning probe microscope.

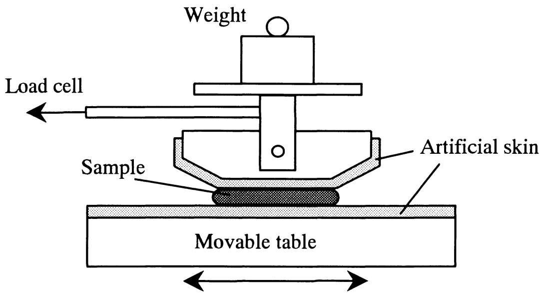

Fig. 2. A measuring device of frictional coefficients.

The particle size was measured using a Horiba LA-920 laser scattering particle distribution analyzer for the powder sample dispersed in ethanol. The angle of repose was measured using a Seishin Multi Tester MT-1000.

Frictional coefficients were measured by a method described in the literature[6,7] using a Heidon 14DR surface property tester at room temperature (Fig. 2). Frictional coefficients were measured by rubbing the powder (200 mg) under a weight of 200 g with 9 cm^2 of a black artificial skin. The sliding distance was 0.1 m; the number of repeated rubbing was 10; the sliding velocity range was $1.2{\cdot}10^{-4}$–$9.9{\cdot}10^{-2}$ m s^{-1}, respectively. The artificial skin had a surface roughness, R_a, of approximately 30 µm (urethane, Okamoto OK sheet).

Results and Discussion

Physical Properties and Crystal Structure of CaLT. CaLT is a white powder with a high fluidity (angle of repose = 53°). The average particle size is 8 µm, with a plate-like shape (Fig. 1). CaLT is insoluble in water, and decomposes above 300 °C in air.

The crystal structure of CaLT was studied by using XRD technique. Strong diffraction peaks that are assigned to the (100), (200), (300), (400), and (500) crystal faces were observed at 2.3, 4.6, 6.9, 9.2, and 11.5°. The XRD pattern indicates that the crystal has a lamellar structure with a long spacing of 37.6 Å. In addition, some weak diffraction peaks were observed in the region of 20–30°. If these peaks are attributed to diffractions by short axis faces, the spacing should be 3–5 Å. Figure 3 shows an AFM image of the CaLT surface, revealing an ordered pattern with a spacing distance of 3–5 Å. The pattern is consistent with alkyl chains ordered in a lamellar structure of metal soaps.[8] The results of XRD and AFM indicate that CaLT is a lamellar molecular crystal with laminated layers of linear molecules (Fig. 1).

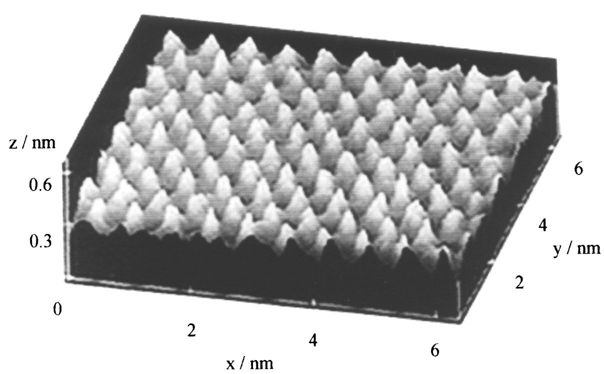

Fig. 3. An AFM image of CaLT surface.

Lubricity of CaLT. When CaLT was applied to an artificial skin, the frictional coefficient, 0.27, was lower than that of other solid lubricants used frequently in personal-care products (Fig. 4). The frictional coefficient was irrespective of the weight between 100 to 1000 g. Moreover, stick-slip phenomena, i.e. periodic changes of the frictional resistance, were not observed when CaLT was applied to an artificial skin under a low sliding velocity ($1.2{\cdot}10^{-4}$ m s^{-1}), while such stick-slips appeared when inorganic powders were applied as shown in Fig. 5. The "stick" is due to the high static friction between two surfaces, and the "slip" due to the low kinetic friction during the slipping motion.[9] The smooth profile of the friction on the surface covered with CaLT indicates that the difference between the static and kinetic friction for CaLT is smaller than that for the inorganic compounds.

The stick-slip phenomena are generally observed when the differential coefficient of the frictional coefficient on the slid-

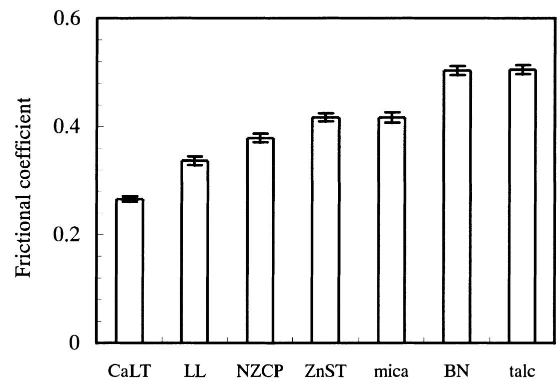

Fig. 4. Frictional coefficients of CaLT and other powder lubricants (sliding velocity = $3.3{\cdot}10^{-2}$ m s^{-1}, number of repeat passage = 7).

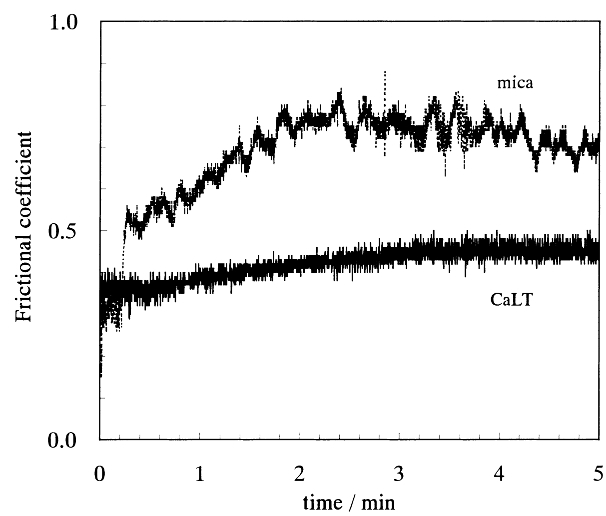

Fig. 5. A time-course of frictional coefficients on application process of CaLT and mica (sliding velocity = $1.2{\cdot}10^{-4}$ m s^{-1}).

ing velocity is largely negative. Figure 6 shows the relationship between frictional coefficient and sliding velocity for CaLT and mica. The frictional coefficient decreases with increasing the sliding velocity both for CaLT and mica, but their profiles are different from each other. The frictional coefficient of CaLT decreases with increasing sliding velocity at below ~0.01 m s^{-1}, and becomes constant at 0.01–0.1 m s^{-1}. On the other hand, that of mica decreases with increasing sliding velocity in every region. The small change of the frictional coefficient for CaLT should contribute to inhibition of the stick-slip phenomena.

Figure 7 shows the relationship between frictional coefficient and number of repeat passages for CaLT and mica. The frictional coefficient of CaLT decreases rapidly at initial passage and becomes constant at 0.25–0.3. On the other hand, the frictional coefficient of inorganic powder decreases gradually and becomes constant at 0.4–0.45.

We can clearly realize the soft and smooth feeling of CaLT when applied to our skin. Such favorable feeling may result from the low and smooth friction profile and the rapid decrease of the frictional coefficient mentioned above. The details of sensuous evaluations will be published in the future.

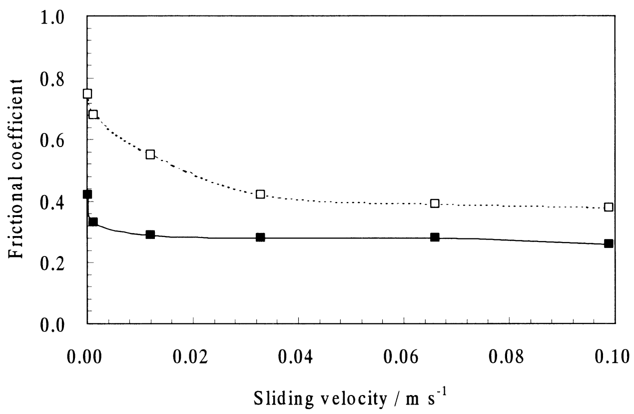

Fig. 6. Relationship between frictional coefficient and sliding velocity. ■; CaLT, □; mica.

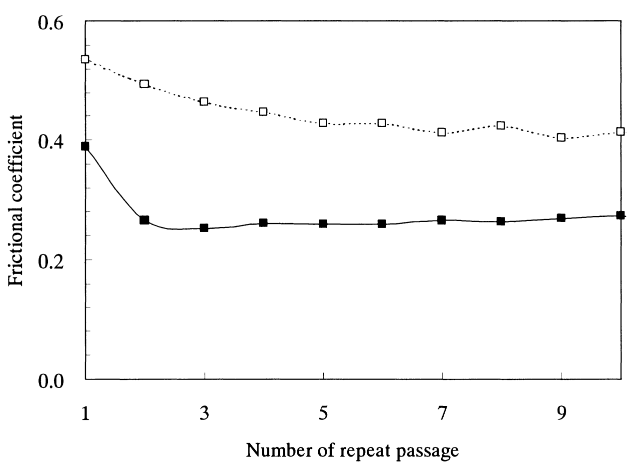

Fig. 7. Relationship between frictional coefficient and number of repeat passage. ■; CaLT, □; mica.

Mechanism of the Lubricity. Lamellar compounds are generally known to show low frictional resistance due to cleavage of lamellar layers.[3] We predict, however, that the lubricity originates not only from the cleavage property but also from other factors such as disintegration of the powder aggregates and deformation of the powder particles. Figures 8 and 9 show that CaLT is actually deformed to become a thin layer when applied to an artificial skin. The substrate has originally a larger roughness, R_a, than the order of microns. The thin layer

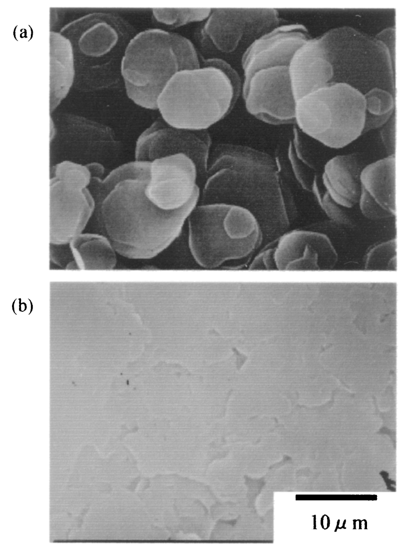

Fig. 8. SEM images of powder-coated artificial skins before (a) and after rubbing (b).

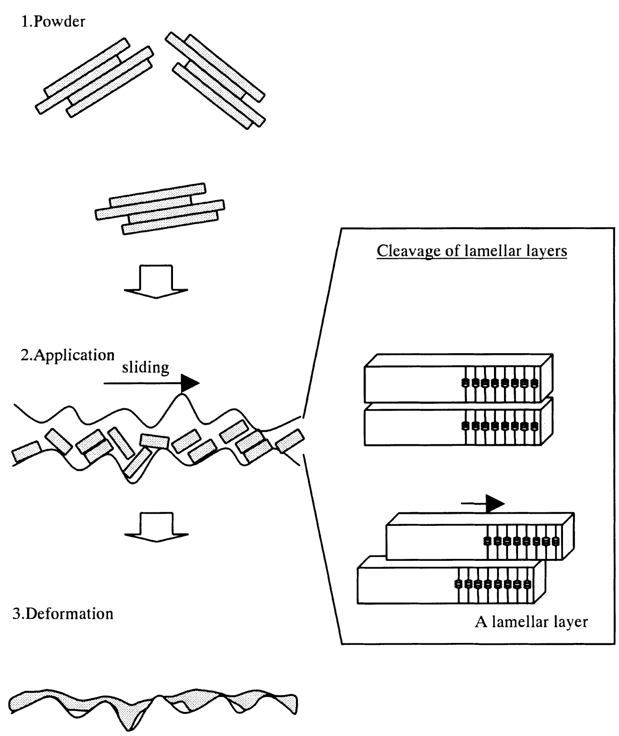

Fig. 9. Schematic illustration to show the mechanism of the lubricity of lamellar compounds.

Table 1. Physical Properties of Organic Crystalline Powders

Organic crystal	Decomposition temp/°C	Intermolecular interaction			Frictional coefficient	Ref.
		van der Waals	Electrostatic	Hydrogen bonding		
CaLT	> 300	○	○	○	0.27	this work
LL	230	○		○	0.35	4
NZCP	200	○	○		0.39	6
ZnST	120	○	○		0.43	11

covers the rough surface of the artificial skin and may lower the frictional coefficient.

The deformation seems to take place due to cleavage of lamellar layers by repeated rubbing. The XRD results indicate that the lamellar structure still remains after the above deformation. Moreover, an ordered pattern as shown in Fig. 3 was also observed by AFM. Although the powder is cloven at the plane between lamellar layers and deformed to a thin layer, the structure inside the lamellar layers is preserved due to the strong intermolecular interactions, as mentioned later.

The frictional coefficients indicate that CaLT is a better lubricant than other organic crystalline powders, i.e. ZnST, NZCP and LL (Fig. 4). We hypothesize that the low frictional nature of CaLT is resulted from the regularity of its crystal structure. It is clear that the CaLT molecules assemble each other by van der Waals interactions between alkyl chains and electrostatic interactions between Ca^{2+} ions and sulfonate groups (Fig. 1). Furthermore, as indicated by an IR spectrum showing N–H (3311 cm^{-1}) and C=O (1639 cm^{-1}) stretching bands, the taurate moieties bind strongly through hydrogen bonding.[10] These strong intermolecular interactions should induce highly regular lamellar layers, a smooth lamellar surface and high lubricity. In fact, the decomposition temperature of CaLT is above 300 °C, higher than that for other organic crystalline powders, e.g. 120 °C for ZnST and 230 °C for LL (Table 1).[4,12] The higher decomposition temperature could be attributed to stronger intermolecular interactions than those occurring in other crystalline materials.

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