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A Study of the Removal of Oily Soil by Rolling up in Detergency

Keizo Ogino and Wataru Agui

Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278

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The removal of simply constituted oily soil from a low-energy surface such as polypropylene (PP) has been examined in aqueous solutions of sodium dodecylbenzenesulfonate and its builders. Oleic acid, olive oil, lauryl alcohol, oleyl alcohol, and liquid paraffin were used as model oily soils. Rolling-up was observed in all the soils except oleyl alcohol and liquid paraffin. The rolling-up of the soil occurred in the contact angle range of $0° < \theta < 90°$ (θ is contact angle) when the soil was removed incompletely from PP. Apparent activation energies for rolling-up were derived, *i.e.*, 8 kcal/mol for oleic acid and 11.9 kcal/mol for olive oil. Complexes were formed for oleic acid, lauryl alcohol, and oleyl alcohol. The effects of the surfactant in various concentrations at various temperature, and with various builders were studied in view of the interfacial tension and the contact angle.

Although cleaning systems have in practice, complicated constitutions (*i.e.*, multicomponent soils in multiphase adhering to substrates which are immersed in a multicomponent cleaning both), it is known that there are three basic mechanisms by which liquid oily soil may be removed in detergent solutions: rolling-up, emulsification, and solubilization.[1,2]

Adam first pointed out that oily soil originally present as a thin layer coating the substrate is pushed into a sphere, together with the substrate, when immersed in a detergent solution; then, it can be removed from the substrate.[3] He also adopted Young's equation to relate the contact angle to the interfacial tension. Thereafter, many investigators reported microscopic studies of similar processes with various kinds of textile fibers and oily soils in the surfactant solutions.[4-7] Kling *et al.* showed some quantitative results on a process using nonpolar oily soil such as liquid paraffin.[8-10]

In the present paper, oleic acid (*cis*-9-octadecanoic acid), olive oil, lauryl alcohol(1-dodecanol), oleyl alcohol(*cis*-9-dodecen-1-ol), and liquid paraffin were used as model oily soils, and the removal of these oily materials from low-energy solid surfaces was studied.

Experimental

Materials. *Substrate*: Sheets of polypropylene (Mitsui Nobulene JHG) ($100 \times 40 \times 1.2$ mm) were prepared under a projecting pressure of 475/cm^2 at 250 °C and were pressed with a pressure of 200 kg/cm^2 at 180 °C. The sheets were then cut into specimens of $10 \times 10 \times 1.2$ mm: the surface was cleaned with a commercial detergent solution at 35 °C several times, rinsed with distilled water for 60 min, soaked in absolute ethanol for 5 min, dried in a vacuum for 3 h, and stored in a desiccator at room temperature before use.

Surfactant: The sodium dodecylbenzenesulfonate (NaDBS) was of an extra pure reagent grade, purchased from the Tokyo Kasei Co., and was purified by extraction with absolute ethanol.

Builders: The anhydrous sodium sulfate and sodium carbonate were of a guaranteed reagent grade, obtained from the Hikotaro Shudzui Co. and the Showa Chemical Co. respectively. The sodium tripolyphosphate was from the Mitsui Toatsu Chem. Co., it was the commercial grade.

Model Oily Soils: The oleic acid and lauryl alcohol were of a reagent grade from the Tokyo Kasei Co. The oleyl alcohol and liquid paraffin of an extra pure reagent grade were from the Wako Pure Chem. Co. The olive oil was commercially purchased from the Kozakai Seiyaku Co.

Apparatus and Procedure. An oily soil droplet of 1.5 µl was put on the surface of PP by means of a microsyringe connected with a micrometer. The sheet of PP was then set in a glass cell ($40 \times 25 \times 15$ mm). The glass cell was placed on the table of the Goniometer, M-2010, A-a, G-I type of the Erma Kogaku Co. Ltd., and then the detergent solution was poured slowly onto it. The contact angle of the droplet, its change, and the radius of the contact area between the droplet and the PP plate were measured in the solution, and the appearance of the droplet was photographed.

A polarizing microscope with crossed nicols (PFM type of the Nippon Kogaku Co. Ltd.) was used to observe the state of the droplets in the solution at 30 °C. The time required to remove oily soils from the PP by rolling-up was measured at 25, 30, 40, 50, and 55±1 °C. The interfacial tension of the system was measured by a Wilhelmy-type Surface Tensiometer, ST-1, of the Shimadzu Seisakusho Co. at 30 °C.

Results and Discussion

Observation of the Rolling-up Process. Figure 1 shows the behavior of oily soils adhering on PP in the

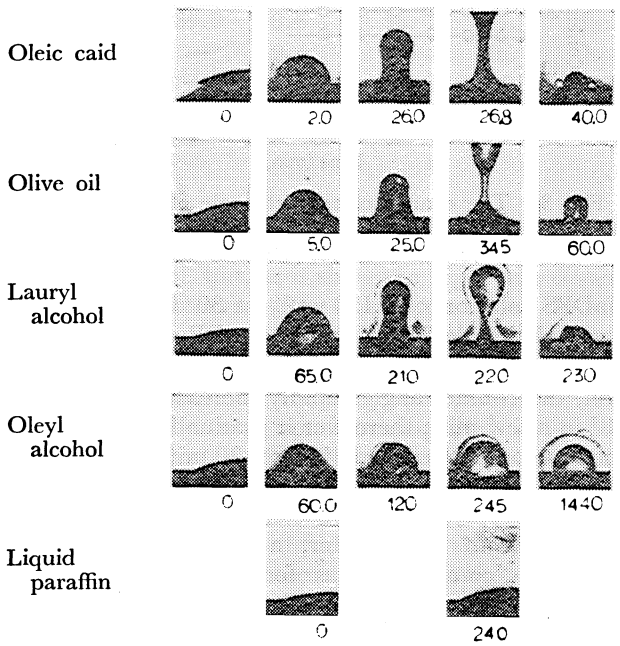

Fig. 1. Behavior of oily soils in 0.150% NaDBS solution at 30 °C. (Numbers show the time in minutes after immersion into the solution.)

Table 1. Removal of oily soils

Oily soil	Contact[a)] angle in air	Contact angle in water	In NaDBS 0.150% solution			
			Contact[b)] angle	Complex[c)] formation	Rolling up[d)]	Rolling up[e)] time
Oleic acid	27.5°	7.0°	81.7°	○	○	26.9
Olive oil	28.3°	5.0°	81.0°	×	○	34.5
Lauryl alcohol	17.0°	38.0°	67.0°	○	○	222.2
Oleyl alcohol	26.8°	6.9°	54.5°	○	×	—
Liquid paraffin	18.0°	0.0°	26.5°	×	×	—

a) Measured in air at room temperature. b) Angle quoted is final contact angle in the surfactant solution. c) ○: Complex formed visibly, ×: No complex formed visibly. d) ○: Rolling up occured, ×: No rolling up occured. e) The figures show the time (min), required to remove soils by rolling up.

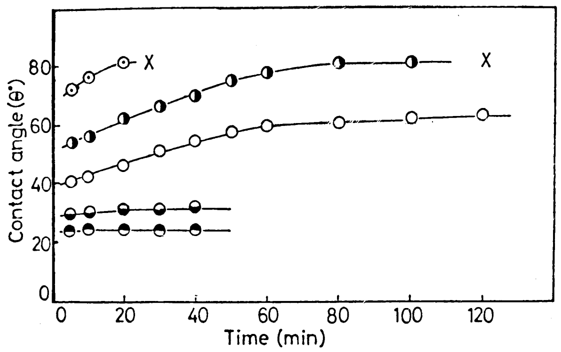

Fig. 2. The change of contact angle of oleic acid at varying concentration of NaDBS solution (30 °C). ⊙: 0.150%, ◑: 0.125%, ○: 0.100%, ◒: 0.050%, ◓: 0.025%, ×: shows Rolling up.

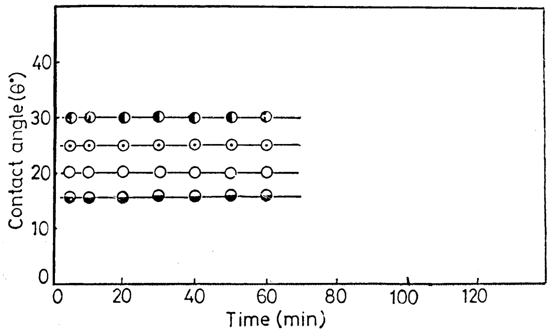

Fig. 3. The change of contact angle of liquid paraffin in NaDBS solution (at 30 °C). ◐: 0.200%, ⊙: 0.150%, ○: 0.100%, ◒: 0.050%.

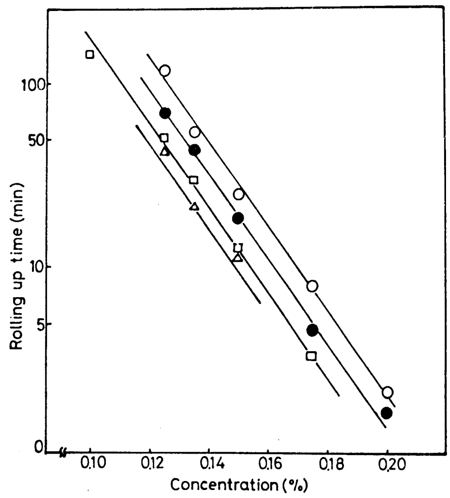

Fig. 4. The effect of NaDBS concentration of the time required for rolling up of oleic acid droplet. ○: 30 °C, ●: 40 °C, □: 50 °C, △: 55 °C.

NaDBS solution of 0.150 wt% at 30 °C. The contact angle of the oleic acid droplet on PP was 27.5° in air. As soon as the droplet came into the surfactant solution, the contact angle rapidly increased from 27.5° to 68° in a few min; thereafter it gradually increased with the time until it reached 81° after 20 min. Accordingly, the contact area between the droplet and PP decreased, and the droplet was constricted and floated away after about 26 min. Thereafter, a transparent layer, the so-called "complex," was formed at the remaining droplet/solution interface after about 40 min.

The olive oil droplet was removed incompletely from the PP surface after 34.5 min by the same process as that used for the oleic acid droplet, but in this case the complex was not formed. Lauryl alcohol behaved like oleic acid in the earlier stages, but the complex was formed on the surface of the droplet after 60 min and the droplet coated with the complex gradually grew and then was incompletely detached and floated away after 220 min. The oleyl alcohol droplet was kept for 50 h. The complex began to form after 150 min; it grew gradually with the time and covered the droplet, but no rolling-up occurred. A rigid complex seemed to form between oleyl alcohol and NaDBS. On liquid paraffin, little change was recognized within 50 min.

Figure 2 shows the dependence of the contact angle of oleic acid on PP on the time in the solutions of NaDBS at various concentrations. Similar relations were also obtained for olive oil, lauryl alcohol, and oleyl alcohol, but, as is shown in Fig. 3 no distinct change was recognized with the time for liquid paraffin in the solutions of NaDBS. Table 1 summarizes the results obtained above.

The contact angle of the soils in air decreased in this order: olive oil > oleic acid > oleyl alcohol > liquid paraffin > lauryl alcohol. These results agree approximately with Zisman's;[11)] that is, the contact angle of the same series of organic liquids on a low-energy surface decreases with the decrease both the molecular weight and the surface tension. However, when oily soils are placed in the NaDBS solution, the

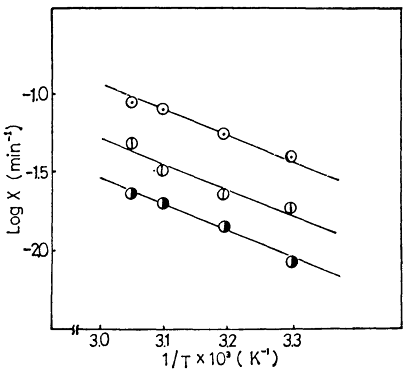

Fig. 5. Arrhenius plot for rolling up of oleic acid droplet in NaDBS solution.
⊙: 0.150%, ⦶: 0.135%, ◑: 0.125%.

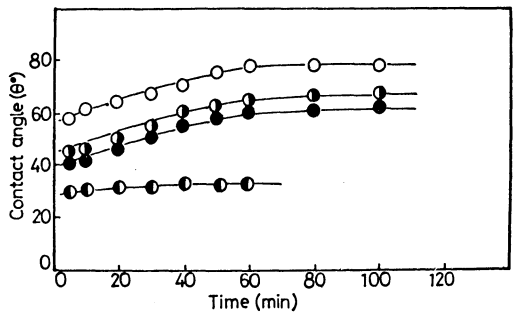

Fig. 6. The contact angle of oleic acid droplet in NaDBS–Na_2SO_4 solution (total solid 0.100%, at 30 °C). Surfactant: builder ratio, ●; 1 : 0, ○; 3 : 1, ◑; 1 : 1, ◐; 1 : 3.

contact angle of the oil/substrate interface gradually increases, and substantially the contact angle increases with the increase in the surfactant concentration. The rolling-up was observed in all the soils except oleyl alcohol and liquid paraffin; the time required for the rolling-up of soils from PP decreased in this order: lauryl alcohol>olive oil>oleic acid. Visible complexes were formed for oleic acid, lauryl alcohol, and oleyl alcohol at the surface of the droplets.

Effect of Concentration of NaDBS and Temperature. Figure 4 shows the effect of the concentration of the NaDBS solution on the time required for the rolling-up of an oleic acid droplet between 30 and 55 °C. It may be seen in Fig. 4 that the time required for the removal of the oleic acid droplet by rolling-up becomes shorter exponentially with the increase in the concentration at each temperature. A similar result was also obtained for olive oil.

In Fig. 5, the logarithms of the reciprocal rolling-up time (log X) are plotted as functions of the reciprocal absolute temperature($1/T$) for oleic acid. The relation gives a straight line. Consequently, the apparent activation energies for rolling-up are derived, *i.e.*, 8 kcal/mol for oleic acid and 11.9 kcal/mol for olive oil.

Effect of Neutral Builders. Figure 6 shows the time dependence of the contact angle of oleic acid against PP in the surfactant solutions containing

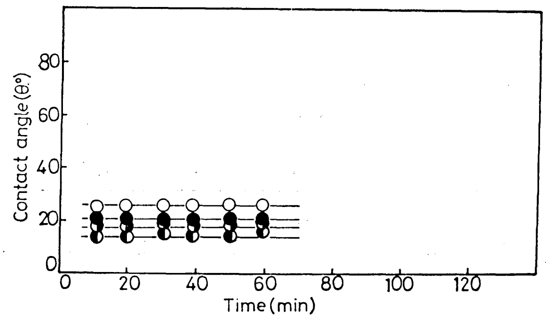

Fig. 7. The contact angle of liquid paraffin droplet in NaDBS–Na_2SO_4 solution (total solid 0.100%, at 30 °C). Surfactant : builder ratio, ●; 1 : 0, ○; 3 : 1, ◑; 1 : 1, ◐; 1 : 3.

Table 2. The time required for rolling up of oleic acid droplet in NaDBS–Na_2SO_4 solution at 30 °C (min)

Surf. : builder	Total concn (%)				
	0.100	0.125	0.150	0.175	0.200
1 : 0	—	120.2	26.9	7.9	2.2
3 : 1	—	92.0	14.5	6.3	2.4
1 : 1	—	—	88.3	70.6	17.4
1 : 3	—	—	—	—	—
0 : 1	—	—	—	—	—

Table 3. The time required for rolling up of olive oil droplet in NaDBS–Na_2SO_4 solution at 30 °C (min)

Surf. : builder	Total concn (%)				
	0.100	0.125	0.150	0.175	0.200
1 : 0	—	—	34.5	8.5	In.
3 : 1	39.0	8.6	In.	In.	In.
1 : 1	—	9.4	3.5	In.	In.
1 : 3	—	—	—	10.0	8.6
0 : 1	—	—	—	—	—

In: Instantaneous.

neutral builder sodium sulfate (0.100 wt%). Similar figures were also obtained for olive oil, lauryl alcohol, and oleyl alcohol, but, as is shown in Fig. 7, no distinct change was observed for liquid paraffin. It was found that, when the ratio of NaDBS to Na_2SO_4 was 3 to 1 by weight, the increase in the contact angle with the time became the largest at each oily soil. The effect of the total concentration of NaDBS and Na_2SO_4 on the rolling-up of the oily soils was further studied. The results are shown in Tables 2 and 3 for oleic acid and olive oil droplets respectively at 30 °C. As is evident from these results, the time required for rolling-up decreases most remarkably in the solution containing NaDBS and Na_2SO_4 at the ratio of 3 to 1, while the time required for the rolling-up of oleic acid was shorter than that of olive oil in the solution containing the neutral builder Na_2SO_4, but the result was the inverse in the surfactant solution

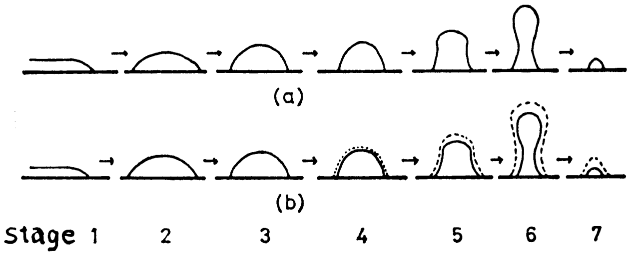

Fig. 8. Schematic diagram of the rolling up process of oily soils.
a) oleic acid or olive oil, b) lauryl alcohol.

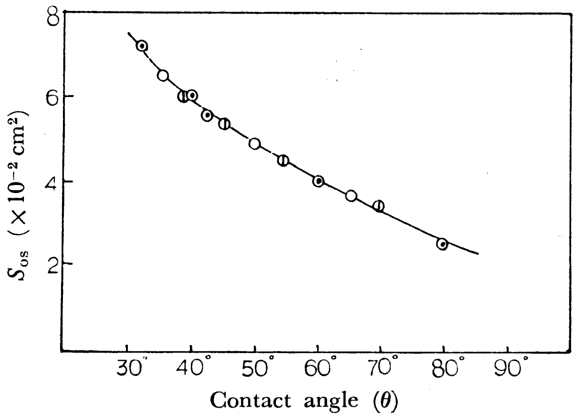

Fig. 9. The droplet/substrate interfacial area as a function of contact angle of the droplet on the substrate.
⊙: oleic acid, ⦶: olive oil, ○: lauryl alcohol.

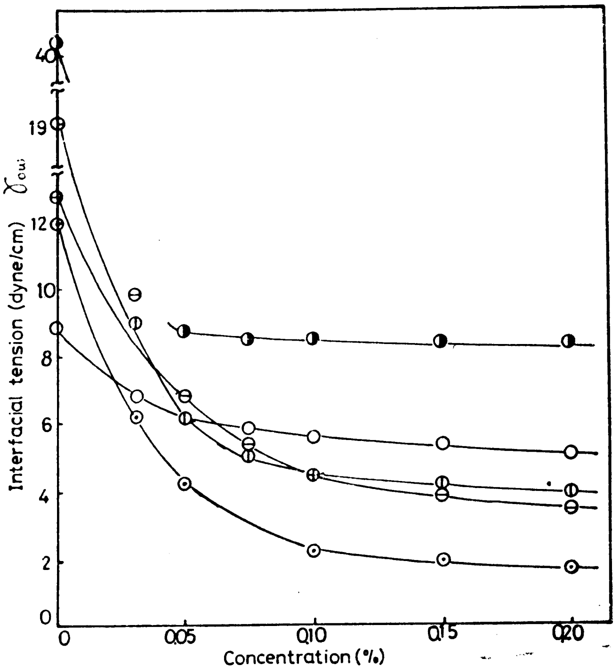

Fig. 10. The effect of NaDBS on the interfacial tension at oily soil/water interface at 30 °C.
⊙: oleic acid, ⦶: olive oil, ○: lauryl alcohol, ⊖: oleyl alcohol, ◑: liquid paraffin.

containing no builders.

Discussion of the Rolling-up Phenomenon. It is well known that the rolling-up of oily soils occurs at the contact angle (θ) of 180° on the substrates of various kinds of textile fibers.[4,6,9] However, as is shown in Fig. 1, on a low-energy surface such as PP sheet, rolling-up occurs at $0° < \theta < 90°$. The process of rolling-up for oleic acid, olive oil, and lauryl alcohol is illustrated schematically in Fig. 8 (a) and (b). In the initial stages [up to Stage 4 in Fig. 8 (a) or up to Stage 3 in Fig. 8(b)], the droplet/substrate contact area (S_{os}) is plotted against the contact angle of the droplet on the substrate in Fig. 9. From these results, the area of S_{os} seems to decrease with an increase in the contact angle of the droplet. The process in Fig. 8 is believed to be caused by the reduction of interfacial tension as a result of the adsorption of surfactant molecules to soil/water and substrate/water interfaces.[3,4,6]

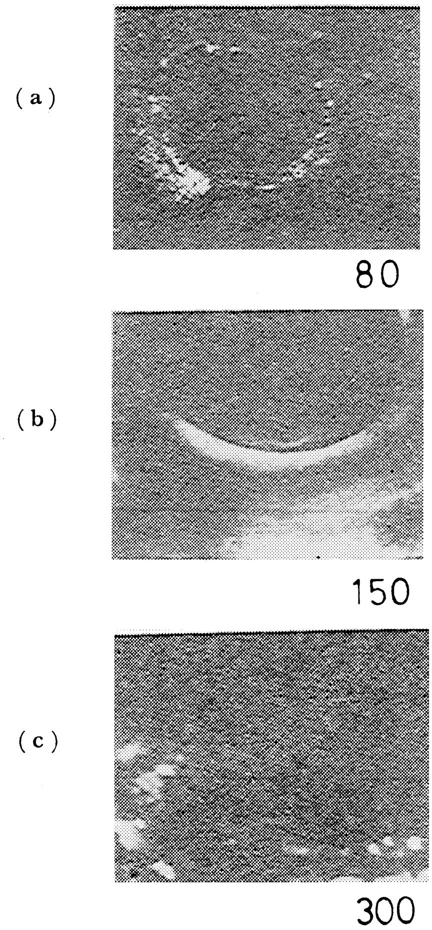

Fig. 11. The microscopic photograph of oily soils in 0.150% NaDBS solution with crossed nicols (number shows the time in minutes after immersion into the solution).
a) oleic acid, b) lauryl alcohol, c) oleyl alcohol.

The interfacial tension between oily soils and the NaDBS solution are shown in Fig. 10; the interfacial tension for polar oily soils decreases remarkably with an increase in the surfactant concentration. From the results, the surfactant can be expected to be adsorbed on the surface of polar oily soils.

It seems reasonable to assume that there are three substantial forces by which a liquid oily droplet may be removed by rolling-up in a detergent solution: the

Table 4. Removal of oily soils

	In 0.150% NaDBS solution		In NaDBS : Na_2SO_4=1 : 1 (total solid 0.200%) solution		In NaDBS : Alkaline builder= 1 : 1(total solid 0.200%) solution	
	Rolling up	Liquid crystal	Rolling up	Liquid crystal	Rolling up	Liquid crystal
Oleic acid	○	○	○	○	×	◎
Olive oil	○	×	◎	×	◎	×
Lauryl alcohol	○	○	×	○	×	◎
Oleyl alcohol	×	○	×	○	×	◎
Liquid paraffin	×	×	×	×	×	×

◎; Rolling up occurred instantly. ○; Rolling up occurred. ×; No rolling up occurred.
◎; Liquid crystal formed strongly. ○; Liquid crystal formed. ×; No liquid crystal formed.

(a)
(b)
(c)

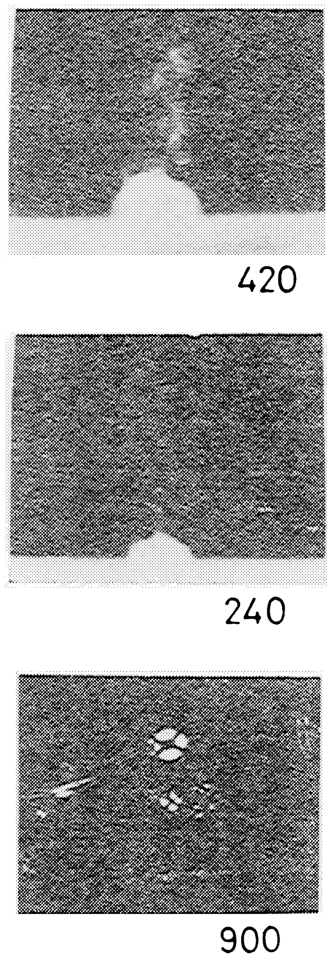

Fig. 12. The behavior of oily soil in the NaDBS containing alkaline builder.
a) oleic acid (NaDBS : STPP=1 : 1, total concn 0.200%, after 420 min).
b) lauryl alcohol (at the same condition of above, after 240 min).
c) myelinic figure for oleyl alcohol (NaDBS : Na_2CO_3=1 : 1, total concn 0.200%, after 900 min).

buoyancy of the oily soil, the cohesive force of the oil itself, and the adhesive force between oil and substrate. When these three forces are unbalanced and the buoyancy overcomes the other forces as a result of the adsorption and the desorption of surfactant molecules at the substrate/soil/solution interfaces under the hydrodynamic fluctuation or the convection of the solution, the incomplete detachment and floatation of the oily soil, the process from Stage 5 to Stage 7 in Fig. 8 will take place. We assume that the complex formation may also contribute to the rolling-up of lauryl alcohol [Fig. 8(b)].

Observation of Liquid Crystals. As is shown in Fig. 1, we observed complexes on the surface of soils, especially a distinct complex layer on lauryl and oleyl alcohol droplets. Figure 11 shows the appearance of complexes for oily soils in a 0.150 per cent NaDBS solution; we made the observation by means of the polarizing microscope with crossed nicols. Complexes from oleic acid (remaining droplet after rolling-up), lauryl alcohol, and oleyl alcohol show optical anisotropy around the original oily soil. Therefore, we assumed that these complexes might be regarded as ternary liquid crystalline phases composed of an oil–water–surfactant.[4,12]

We studied further the behavior of oily soils in the NaDBS solution containing builders. Table 4 summarizes the results. With respect to oleic acid, in the solution containing only NaDBS and NaDBS with Na_2SO_4, rolling-up occurred before the formation of the liquid-crystalline phase. As is shown in Fig. 12(a), though in the solution containing NaDBS and alkaline builders such as sodium tripolyphosphate(STPP) or sodium carbonate, no rolling-up occurred. Oleic acid is considered to react with the alkaline builder to form sodium oleate at the solution/soil interface; as a result, the oleic acid would be removed from the PP surface by a spontaneous emulsification.

Olive oil forms no liquid crystal; nevertheless, it is remarkably rolled up by the addition of builders to a surfactant. For higher alcohols, such as lauryl and oleyl alcohol, the time required to form a liquid crystal is shorter in the solution of NaDBS containing an alkaline builder than in the other solutions. As is shown in Fig. 12(b), lauryl alcohol was removed continuously in small droplets from PP in the solution of NaDBS containing STPP, while oleyl alcohol showed a myelinic appearance after about 900 min in the solution of NaDBS containing Na_2CO_3 [Fig. 12(c)]. With respect to liquid paraffin, no distinct change was recognized, not even in the solution of NaDBS containing builders.

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