Studies of the Removal of Oily Soil by Rolling-up in Detergency. II. On Binary Soil Systems Consisting of Oleic Acid and Liquid Paraffin

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The rolling-up mechanism of oily soil from the surface of a polypropylene (PP) sheet in an aqueous solution of sodium dodecylbenzenesulfonate (LAS) was studied by the observation of the contact angle (θ). A binary system consisting of *cis*-9-octadecenoic acid (oleic acid)–liquid paraffin (Nujol) was used as an example of oily soil. The time required for the removal of the oily soil mixture from the PP sheet by rolling-up became shorter with the increase in the liquid paraffin content of the mixture. The oily soil with binary components was more easily removed from the substrate than a single-component oily soil.

Although the mechanism of the practical cleaning of oily soil is extremely complicated, it is well known that the cleaning consists of three basic processes that may occur simultaneously or in succession: rolling-up, solubilization, and emulsification.[1)]

The process of rolling-up may be explained as follows. As soon as the soil-substrate system of air is purged and the solution/soil/substrate interfaces become stable, the contact angle at the soil/substrate interface begins to increase and attains the intrinsic equilibrium state. At the same time, the force acting between the oily soil and the substrate decreases; when the contact angle reaches 180°, the oily soil is completely removed from the substrate.

Smith *et al.*[2)] have reported a change in the contact angle of an oily soil/substrate system in detergent solutions of various concentrations in the course of time, using mineral oil as the oily soil and fiber as the substrate. On the other hand, Stevenson[3)] found that polar oil was far more easily removed from fiber than was mineral oil and that the addition of polar substances to mineral oil greatly facilitated the removal. However, their studies were only presented qualitatively by photographs; the inter-relations of the changes among the components of the soil, the concentration of the detergent in the solution, and other factors were not described.

In the previous report, we studied the removal of single-component oily soil from a low-energy surface.[4)] In this study, the rolling-up process of oily soil on a polypropylene surface in a detergent solution was examined in terms of the change in the contact angle with time, using mixtures of polar and non-polar soils in certain proportions (by weight), and the interaction between the oily soil and surfactant was speculated upon.

Experimental

Materials. *Substrate*: A polypropylene (PP) sheet from Mitsui Noblene J. H. G. was used as the substrate. The preparation of the specimen from the obtained sheet was described in the previous report.[4)] The sheet was cut into specimens of $10\times10\times1.2$ mm, and the surface was cleaned several times with a commercial detergent solution at 35 °C, rinsed with distilled water for 60 min, soaked into absolute ethanol for 5 min, dried in a vacuum for 3 h, and stored in a dessicator at room temperature till use.

Surface-active Agents: The sodium dodecylbenzenesulfonate (LAS) was of commercial grade from the Wako Chemical Co., Ltd.

Oily Soil: Oily soil of a binary system was prepared by mixing oleic acid (reagent grade from Tokyo Kasei Co.) and liquid paraffin (reagent grade from Wako Pure Chemical Co., Ltd.) in the ratios of 1:0, 3:1, 1:1, 1:3, and 0:1 (by weight).

Apparatus. The contact angle and its change with the time were measured by means of a Goniometer (Erma Kogaku Co., Ltd., M 2010, A-a, G-type), while the surface tension of the oily soil was measured by means of a Wilhelmy-type Surface Tensionmeter ST-1 (Shimadzu Seisakusho).

Procedure. A volume of 1.5×10^{-3} ml of the oily soil was dropped on a PP sheet by means of a microsyringe connected with a micrometer. Then the sheet with a drop of the soil on it was set in a glass cell ($40\times25\times15$ mm). The glass cell was placed on the table of the Goniometer, and then the surfactant solution was poured slowly onto it. The change in the contact angle with the time and the time required for the removal of the oily soil from the surface by rolling-up were measured as in the previous report.[4)]

Results and Discussion

Wetting of the Polypropylene Sheet with Organic Liquids. Figure 1 shows the contact angle and the surface tension of the binary oily soil on a PP sheet in the air. Both the contact angle and the surface tension decreased with an increase in the proportion of liquid paraffin in the soil and reached the highest value at 100 per cent oleic acid. This result is consistent with that of Zisman[5)] that the contact angle of organic liquid on a low-energy

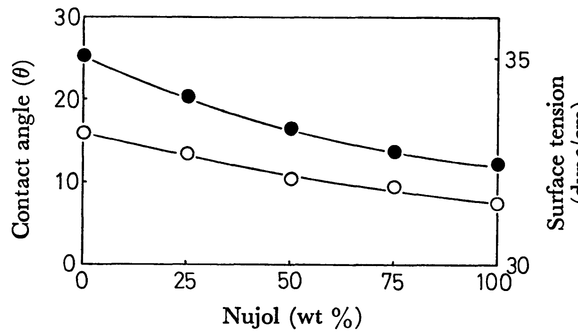

Fig. 1. Contact angle on PP sheets and surface tension of oleic acid–liquid paraffin binary systems in air (at 30 °C).
●: Contact angle,
○: Surface tension.

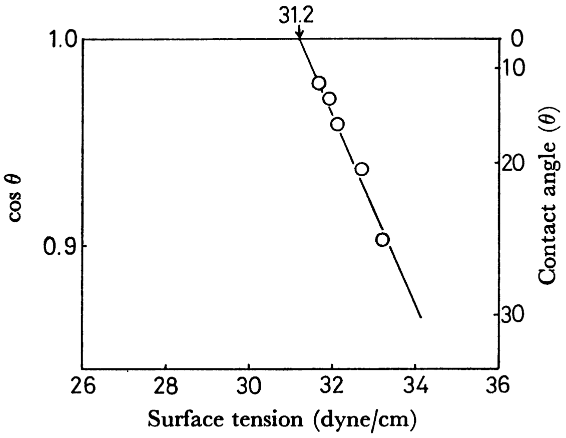

Fig. 2. Surface tension *vs.* cosine of the contact angle of the same mixed liquids as Fig. 1 on polypropylene.

surface tends to decrease with a decrease in the surface tension for a homologous series of liquids.

From the results shown in Fig. 1, the relation between the contact angle and the surface tension was derived; it is plotted in Fig. 2, which indicates a linear relationship between the two properties; the critical surface tension of PP, γ_C, is 31.2 dyne/cm, a calculated from the relationship extrapolated to cos $\theta=1$.

Change in the Appearance of Oily Soil in a Detergent Solution. The change in the appearance of oily soil which had been dropped onto the PP sheet was observed in accordance with the time-course of the change in the contact angle in LAS solutions of various concentrations. The results for the binary oily soil systems are shown in Figs. 3, 4, and 5. Similar results have been obtained for the single-component systems of oleic acid or liquid paraffin, as has been described in the previous paper.[4] The change in the appearance of oily soils of various compositions in LAS solutions is illustrated in Fig. 6.

As may be seen in Figs. 3, 4, and 5, the contact angle changed with the time in oleic acid–liquid paraffin binary systems; the cause of this change is considered

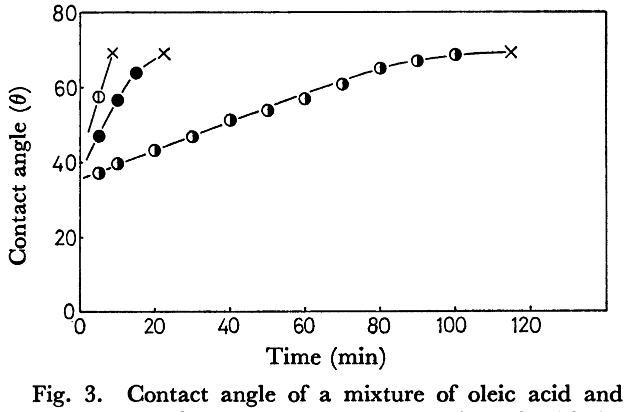

Fig. 3. Contact angle of a mixture of oleic acid and liquid parafin (3: 1) in aqueous solution of LAS (at 30 °C).
⦶: 0.125 (wt% of LAS),
●: 0.115 (wt% of LAS),
◑: 0.100 (wt% of LAS),
×: rolling-up.

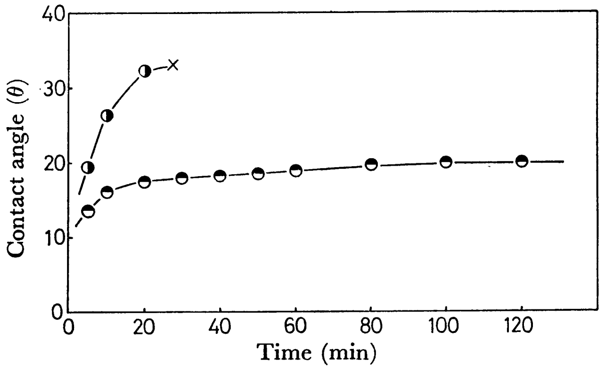

Fig. 4. Contact angle of a mixture of oleic acid and liquid paraffin (1: 1) in aqueous solution of LAS (at 30 °C).
◑: 0.100 (wt% of LAS),
◓: 0.075 (wt% of LAS),
×: rolling-up.

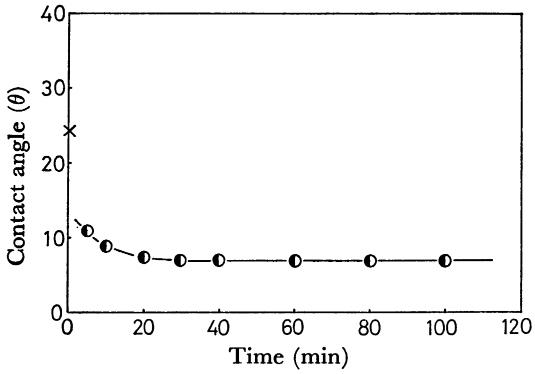

Fig. 5. Contact angle of a mixture of oleic acid and liquid paraffin (1: 3) in aqueous solution of LAS (at 30 °C).
×: Rolling-up (0.100 wt% of LAS),
◐: 0.065 (0.100 wt% LAS).

to be the adsorption of a surface-active agent on the oily soil surface. When the droplet of oleic acid on the substrate was brought into the surfactant solution, the contact angle rapidly increased and rolled back, as was shown in the previous paper.[4] After about 20 min in the 0.150 per cent LAS solution, the droplet was constricted and floated away.

For a mixture of oleic acid and liquid paraffin in the proportion of 3: 1, the addition of a 0.115 per cent LAS solution causes the roll back of the droplet, much as with oleic acid alone; necking begins after about 22 min of rolling-up, but a portion of the soil remains intact on the PP sheet after the removal of the droplet (Figs. 3 and 6). In contrast to the soil of oleic acid alone, the binary soil of oleic acid and liquid paraffin rolls up in a more dilute solution of LAS; for example, the time required for rolling-up was 114.9 min in 0.100 per cent, 22.3 min in 0.115 per cent, and 8.7 min in 0.125 per cent solutions of LAS.

Similarly, the rolling-up phenomena were observed for the mixtures of oleic acid and liquid paraffin in the ratios of 1: 1 (Figs. 4 and 6) and 1: 3 (Figs. 5 and 6). Both mixed soils were removed incompletely from the PP surface; the time for the removal was 27.6 min for the former and about 30 s for the latter in an LAS

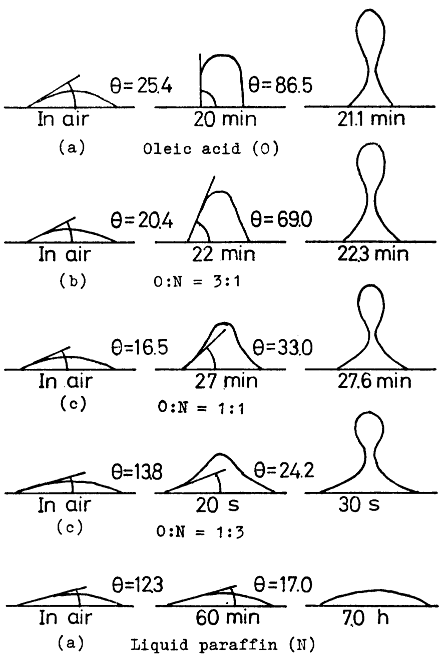

Fig. 6. Rolling-up process in aqueous solution of LAS.
(a): 0.150 (wt% of LAS),
(b): 0.115 (wt% of LAS),
(c): 0.100 (wt% of LAS).

Table 1. Removal of oily soils

Oily soils	In air (at 30 °C)		In aq. solution of LAS (at 30 °C)		
	Contact angle (θ)	Surface tension (dyne/cm)	Contact angle (θ)	Rolling up[a]	Rolling up time (min)
Oleic acid (O)	25.4	33.2	86.5	○	21.1[b]
O:N=3:1	20.4	32.7	69.0	○	22.3[c]
O:N=1:1	16.5	32.1	33.0	○	27.6[d]
O:N=1:3	13.8	31.9	24.2	○	0.5[d]
Liquid paraffin (N)	12.3	31.5	17.0	×	—[b]

a) ○: Rolling up, ×: No rolling up. b) Measured in 0.150 percent level of LAS solution. c) Measured in 0.115 percent level of LAS solution. d) Measured in 0.100 percent level of LAS solution.

solution at a 0.100 per cent concentration.

As presented in the previous study and in Fig. 6, non-polar liquid paraffin was the only material which showed no appreciable changes in the contact angle in the detergent solutions.

In Table 1, the values of the contact angle and the time required to remove the mixed oily soil from the PP sheet by rolling-up in an LAS solution are shown. It is apparent from these results that the rolling-up phenomenon occurs for the mixed oily soil, but not for the liquid paraffin alone. On the other hand, both the value of the final contact angle of the oily soil to the PP sheet in a LAS solution and the time required to remove oily soil by rolling-up decrease with an increase in the proportion of liquid paraffin in the soil. Besides, it is confirmed that the addition of paraffin to oleic acid facilitates the rolling-up of the droplets.

For the mixture of oleic acid-liquid paraffin placed as an oily soil on a low-energy surface such as polypropylene, the rolling-up occurs at the contact angle of $0° < \theta < 90°$. It is noteworthy that, on a high-energy surface, rolling-up occurs only when $\theta = 180°$.[6]

From Fig. 6, the adsorbed concentration of LAS molecules at the solution/oily soil interface seems to be larger than that at the solution–substrate interface. On the other hand, in the mixed oily soil systems, the contact angle in a LAS solution decreases, while the contact area does not decrease, with the increase in the proportion of liquid paraffin. These differences between the soils of the binary components and oleic acid alone are presumed to be due to the difference in the orientation of the oleic acid and liquid paraffin molecules.

The intermolecular force in the bulk of liquid oily soil is strongly exerted by the polar molecules, and the intervention of non-polar molecules with the polar molecules causes a decrease in the intermolecular forces. As a result, the reduction of the cohesive force of the molecules in the oily soil gives rise to rolling-up in spite of the small contact angle in the LAS solution. It was clarified in the previous paper[4] that polar oils interact with a surfactant more strongly than non-polar substances. This must be the reason for the easier rolling-up of the polar soils.

When a drop of oily soil placed onto a substrate was immersed into a solution of the surface-active agent, the contact angle increased and approached equilibrium, and the oily soil underwent necking and rolling-up depends on three forces: the cohesive force of the oily soil itself, the buoyancy, and the adhesive force between the substrate and the oily soil. For instance, a droplet of oleic acid rolls up because the horizontal tension nearly disappears at a contact angle, θ of 86.5° (nearly 90°).[4] It is presumed that the balance of the above three forces is shifted in a solution of a surface-active agent by the adsorption and desorption of LAS molecules at the oil/solution/substrate triple interfaces.

From these results, it may be speculated that, in all oily-soil systems of multiple components except those of paraffin alone, one of the three forces which exert influence on the oily soil, buoyancy, exceeds the other two forces; the reduction of cohesive force between the molecules in the soil is considered to be the inherent reason for the rolling-up process. Also, on a low-energy surface such as polypropylene, oily soil including polar components tends to roll up. The presence of polar components in the soil is one of the factor controlling the rolling-up.

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