

# ✂ Examination of the Parameters Governing Oily Soil Removal from Synthetic Substrates

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## ABSTRACT

The rate of removal of mineral oil soils from model polyester substrates by the roll-up mechanism shows a marked dependence on nonionic surfactant concentration even above the critical micelle concentration (cmc). Similarly, although the solid/water interfacial tension is observed to be constant, the equilibrium oil/water interfacial tension in these systems consistently decreases as the nonionic surfactant concentration is increased. The dependence of removal time and oil/water interfacial tension on surfactant concentration above the cmc is most pronounced for nonionic surfactants having relatively high cmc. At a given concentration, surfactants exhibiting the lowest equilibrium oil/water interfacial tension generally provide the most effective soil removal, suggesting that the reported dependence of removal time on surfactant concentration is related to the commensurate lowering of the oil/water interfacial tension. Nonyl phenol ethoxylates perform exceptionally well with mineral oil on polyester substrates because of the combination of a low oil/water interfacial tension and high solid/water adhesion tension. Regardless of surfactant structure, mineral oil on Teflon FEP maintains a high contact angle in the water because the solid/oil interfacial tension is less than the solid/water interfacial tension. Oil removal in such systems occurs only by an inefficient necking and drawing process. Oleyl alcohol displays a high contact angle in the water on both Teflon FEP and Mylar substrates for reasons similar to that of mineral oil on Teflon FEP. Partial oil removal occurs from both substrates in selected built systems, presumably because a low oil/water interfacial tension promotes necking and drawing. Given sufficient time, unremoved oils develop a liquid crystalline phase which results in slow oil removal via dispersion. Triolein soils also possess a relatively low solid/oil interfacial tension and similarly exhibit a high contact angle (in water) on both Teflon FEP and Mylar substrates in unbuilt surfactant systems. Builder addition lowers the oil/water interfacial tension and thereby prompts necking and drawing action.

## INTRODUCTION

In our previous work (1) we described a model detergency system wherein the changes in the contact angle and other physical characteristics of oily soil on polyester film, submerged in an aqueous detergent solution, could be observed. The effects of temperature, water hardness, surfactant and builders were examined for pure mineral oil and selected binary soils. Removal times and mechanisms were recorded under carefully controlled conditions and the results were rationalized on the basis of interfacial tension considerations. As was the case in these early studies, this work emphasizes pure mineral oils. Extensive studies of the effect of surfactant concentration on removal time have been carried out. Furthermore, since practical soils contain several polar constituents (2), oleyl alcohol and triolein have now been examined.

In an effort to define the role of the substrate in the detergency process, selected model studies with a hydrophobic fluorocarbon film have been performed. Interfacial tension and contact angle measurements have again proven useful in aiding interpretation of the results.

## EXPERIMENTAL

### Materials

Arcoprime 70 and Arcoprime 90 are food grade white

mineral oils from Atlantic Richfield having viscosities at 38 C of 70 and 85 SUS, respectively. Reagent grade oleyl alcohol was obtained from Eastman Kodak and technical grade triolein was supplied by Matheson, Coleman and Bell. All other reagents were purchased from Fisher Scientific Company in the highest available grade.

Calsoft L-60 is a linear dodecyl benzene sulfonate (Na<sup>+</sup> salt) of Pilot Chemical Company. Polytergent SL-62 is an alcohol alkoxyate product from Olin Chemical and Triton X-100 is an octylphenol ethoxyate produced by Rohm and Haas. The Tergitol surfactants are primary alcohol, secondary alcohol and nonyl phenol ethoxylates marked by Union Carbide Corporation. The Tide detergent from Procter and Gamble contained 6.1% phosphorus whereas the Wisk formulation of Lever Brothers was phosphate-free. More information on the surfactants employed appears in Table I.

Polyester Mylar (300 gauge, Type D) is a DuPont trade-name for polyethylene terephthalate film having a minimum of surface defects; this film was purchased through Brownell Electric Incorporated. The tetrafluoroethylene-hexafluoropropylene copolymer, Teflon FEP, was purchased from DuPont as smooth, clear, 500 gauge, amorphous film.

Water was preboiled under basic conditions and twice distilled from basic potassium permanganate.

### Procedures—Surface and Interfacial Tensions

All surface tensions were measured by the platinum Wilhelmy plate method with an electrobalance-recorder apparatus. Unless otherwise stated, all reported surface tensions represent equilibrium values. Mylar plates used in the contact angle studies were cleaned by the Soxhlet extraction procedure subsequently described under Model Detergency Studies.

Most equilibrium oil/water interfacial tensions were measured by the Wilhelmy plate technique. Because serious experimental difficulties were encountered with platinum, viz., dewetting, glass plates were used. After the oil and water phases were equilibrated, the interface was swept with a microsuction pipette. The plate was then wetted with the aqueous phase and lowered through the oil into the interface. The oil/water interfacial tension was recorded at first contact with the interface, since selected studies revealed that no appreciable time effects could be observed in the surfactant concentration range of interest. In cases where current results differ slightly from previously reported values obtained with a less sensitive procedure (1), the recent findings are considered the most reliable.

A few oil/water interfacial tensions were measured using the spinning drop apparatus (3). Agreement between the methods is fairly good (1); the spinning results are considered the more reliable in the low interfacial tension range of interest. Because of experimental difficulties with the Wilhelmy plate method and because of the time-consuming nature of the spinning drop technique, only a few oleyl alcohol and triolein systems were examined.

TABLE I  
List of Surfactants

Trade name	Producer	Structural type	Cloud point C (1.0% solution)
Tergitol 25-L-7	Union Carbide	C <sub>12</sub> -C <sub>15</sub> primary alcohol ethoxylate	50
Tergitol 25-L-9			60
Tergitol 25-L-12			90
Tergitol 15-S-7	Union Carbide	C <sub>11</sub> -C <sub>15</sub> secondary alcohol ethoxylate	37
Tergitol 15-S-9			60
Tergitol 15-S-12			90
Tergitol NP-9	Union Carbide	Nonyl phenol ethoxylate	54
Tergitol NP-10			63
Nonionic X	Union Carbide (experimental)	C <sub>12</sub> -C <sub>15</sub> primary alcohol alkoxyate	60
Triton X-100	Rohm and Haas	Octyl phenol ethoxylate	65
Polytergent SL-62	Olin Chemical	Primary alcohol alkoxyate	62
Calsoft L-60 (LAS)	Pilot Chemical	Sodium dodecyl benzene sulfonate (linear)	—

### Procedures—Model Detergency Studies

The model detergency system and its use have been previously detailed (1). Briefly, the apparatus consisted of a battery of 6 transparent detergency cells, each with 400 g of surfactant solution in a constant temperature bath. A soiled film mounted on a glass slide was placed in each of the cells and the detergency action noted through visual observations. A constant and uniform agitation rate of 60 rpm was provided in each cell. Six 2- $\mu$ l soil drops were used per film and each experiment was performed in duplicate, so that a total of 12 data points was obtained for each test condition.

The meticulous cleaning procedure for Mylar films has been described previously (1). The procedure involved soaking the films in 1.0% sodium tripolyphosphate and 1.5% sodium dodecyl benzene sulfonate at 40-50 C with subsequent thorough water rinsing, followed by storage in a vacuum desiccator. Because of their porosity and extreme hydrophobicity, the Teflon FEP films were cleaned via Soxhlet extraction with hexane/ethanol (50:50, v/v). After 4-5 hr of extraction at ca. 60 C, the films were carefully removed and stored in a vacuum desiccator until used. As with Mylar, surface cleanliness was monitored by contact angle measurements.

The remaining model detergency equipment (cells, stirrers, clamps, slides) was cleaned as in our previous studies (1).

## RESULTS AND DISCUSSION

### Pure Mineral Oil Soils on Mylar

Several workers (1,4) have shown that nonpolar mineral oil soils are removed from synthetic substrates primarily by the roll-up mechanism described by Adam (5). Based on the Young equation (6), an expression relating the extent of roll-up to the pertinent interfacial tensions is easily derived (1), so that under equilibrium conditions:

$$\cos \theta_{W/S} = \frac{\gamma_{S/O} - \gamma_{S/W}}{\gamma_{O/W}} \quad (1)$$

where  $\gamma_{S/O}$ ,  $\gamma_{S/W}$  and  $\gamma_{O/W}$  represent the solid/oil, solid/water and oil/water interfacial tensions, respectively, and  $\theta_{W/S}$  is the contact angle in the aqueous phase. Upon submersion in the aqueous phase, the oil droplet, which originally wets the substrate in air, rolls up to an extent governed by the component forces of this equation. Subse-

quent removal occurs via necking and drawing caused by hydraulic currents and buoyancy. When the contact angle in the water does not attain a value significantly less than 90°, only partial removal is observed in agitated systems and the small residual drop undergoes removal by a repetitive process requiring much longer times. The reported removal times pertain to the first removal process unless otherwise noted.

The various interfacial tensions governing the roll-up process are dependent on several parameters (1), such as substrate and/or oil polarity, temperature, surfactant structure and concentration. We have recently sought to characterize the dependence of roll-up and removal on surfactant concentration above the critical micelle concentration (cmc). Implicit in our studies is the assumption that the greater the extent of roll-up, i.e., the lower the contact angle in the water phase, the more easily, and therefore the more quickly the oil droplets will be removed. Figure 1 shows the results of these studies for 5 nonionic surfactants

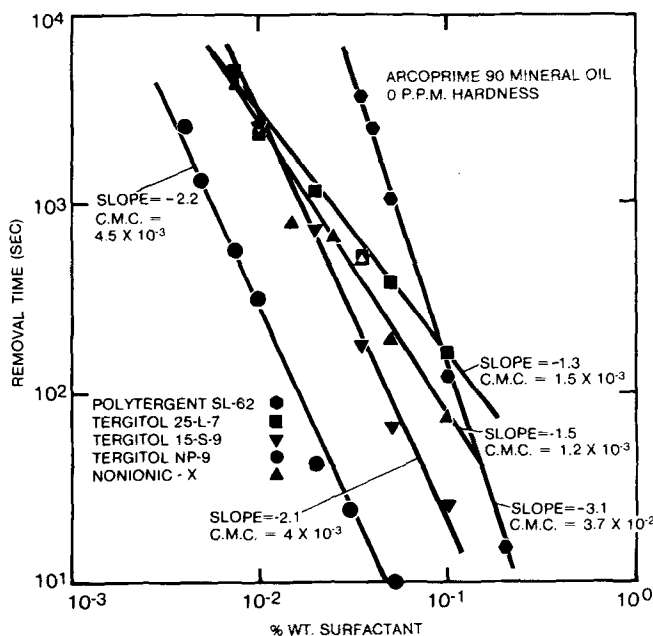


FIG. 1. Removal time vs concentration for selected nonionic surfactants at 50 C using mineral oil soils on Mylar.

at 50 C, using Arcoprime 90 mineral oil soil on Mylar. Although relative surfactant efficiencies vary greatly with concentration, a linear relationship between log removal time and log concentration is observed in each case. Tergitol NP-9 is the most effective surfactant over the entire range, but its performance falls off rapidly near the cmc; indeed, no removal was observed in any system below the cmc.

In an effort to explain the observed effect of concentration on removal time, the dependence of the pertinent interfacial tensions on concentration was investigated. Figure 2 presents the relationship between surface tension and concentration for 2 representative surfactants at 25 C. The surface tension is relatively constant over the concentration range of interest (i.e., above the cmc), and thus cannot readily account for our findings. Similar results were observed at 60 C. However, since the rate of surface tension lowering is expected to vary with concentration, time effects were investigated at 25 and 60 C over a range of concentrations. Figure 3 depicts typical behavior, wherein, for Tergitol 15-S-9 at 25 C, marked time effects are observed only well below the cmc ( $4 \times 10^{-3}\%$ ). Above the cmc, time effects are nearly immeasurable and therefore do not explain the dependence of removal time on concentration.

It is desirable to obtain an estimate of the dependence on surfactant concentration of  $\gamma_{S/W}$ , the solid/water interfacial tension, which appears in the numerator of equation (I). Although not directly measurable, certain deductions concerning  $\gamma_{S/W}$  can be made by determining the adhesion tension for the surfactant solution on the Mylar surface. For a drop of aqueous solution on Mylar, the Young equation (6) can be cast in the form:

$$\gamma_{W/A} \cos \theta_{W/A} = (\gamma_{S/A} - \gamma_{S/W}) \quad \text{[II]}$$

where  $\gamma_{S/A}$ ,  $\gamma_{S/W}$  and  $\gamma_{W/A}$  are the solid/air, solid/water and water/air interfacial tensions, respectively, and  $\theta_{W/A}$  is the contact angle in the aqueous phase. Using Mylar Wilhelmy plates the adhesion tension,  $\gamma_{W/A} \cos \theta_{W/A}$  can be directly measured. Since  $\gamma_{W/A}$  is known from similar measurements with platinum plates where  $\cos \theta_{W/A} = 1$ ,  $\cos \theta_{W/A}$  for Mylar can be obtained. On the assumption that  $\gamma_{S/A}$  is a constant (7), i.e., no (change in) "spreading pressure" is registered at the solid/air interface, any change in  $(\gamma_{S/A} - \gamma_{S/W})$  actually reflects a change in  $\gamma_{S/W}$ . Table II lists the results of measurements to pursue this approach with pertinent nonionic surfactants. For each surfactant,  $\gamma_{W/A} \cos \theta_{W/A}$  does not vary significantly with concentration above the cmc and it can be concluded that  $\gamma_{S/W}$  is effectively constant. In other words, this parameter does not provide an explanation of the variation in soil removal with concentration shown in Figure 1, nor does the time variation of the wetting of Mylar by the surfactant solutions: Figure 4 shows that rather low equilibrium contact angles ( $\theta_{W/A}$ ) on Mylar are rapidly attained with 0.1% surfactant solutions at 25 C. Similar behavior is observed at other concentrations above the cmc.

Since the dependence of removal time on concentration cannot be explained by considering aqueous surface tension or solid/water interfacial tension changes, we now turn to the oil/water interfacial tension,  $\gamma_{O/W}$  (8). Figure 5 reveals a definite dependence of  $\gamma_{O/W}$  on surfactant concentration above the cmc for each of the nonionic surfactants examined in Figure 1. Although the slopes of the lines in Figure 5 are not as variable as those in Figure 1, surfactants which show the most pronounced dependence of  $\gamma_{O/W}$  on concentration also tend to exhibit the most marked dependence of removal time on concentration.

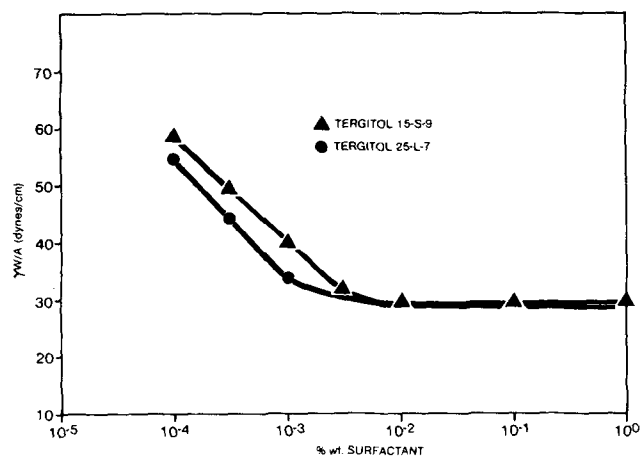


FIG. 2. Surface tension vs concentration for typical nonionic surfactants at 25 C.

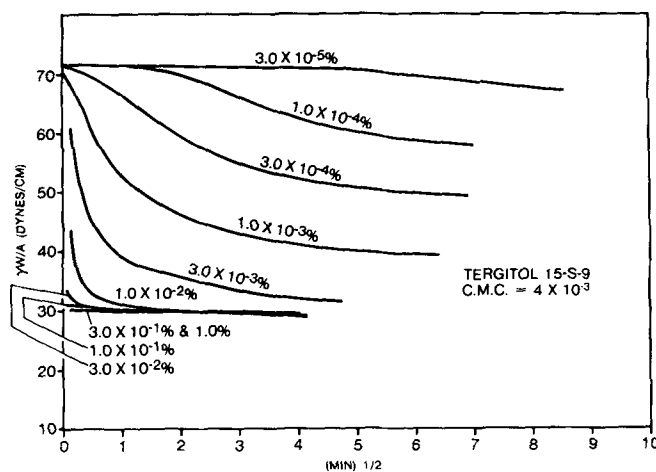


FIG. 3. Rate of surface tension lowering as a function of surfactant concentration at 25 C for Tergitol 15-S-9.

Furthermore, a relationship between cmc and slope seems apparent, especially in Figure 1, wherein surfactants having the highest cmc tend to display the largest slopes. It is also of interest that the relative surfactant efficiencies in Figure 1 show a direct dependence on the relative  $\gamma_{O/W}$  values in Figure 5; the surfactant producing the lowest  $\gamma_{O/W}$  at a given concentration, viz., Tergitol NP-9, is most efficient in the removal studies whereas the surfactant providing the highest  $\gamma_{O/W}$ , viz., Polytergent SL-62, is least efficient. However, it can also be seen from Figures 1 and 5 that 2 surfactants compared at concentrations yielding the same interfacial tensions do not necessarily yield the same removal times, implying that  $\gamma_{S/W}$  also plays a significant role in dictating roll-up efficiency. Although the removal times in Figure 1 are for 50 C and the  $\gamma_{O/W}$  values in Figure 5 correspond to 25 C, selected  $\gamma_{O/W}$  measurements at 50 C indicate that the dependence of  $\gamma_{O/W}$  on concentration remains agreeable with the deductions just given.

In most cases, it may be assumed that  $\gamma_{S/O}$ , the solid/oil interfacial tension, is relatively constant for a given soil and substrate in surfactant systems exhibiting relatively low oil solubility. Referring to Equation I, if  $\gamma_{S/O} - \gamma_{S/W}$  is sensibly unaltered with concentration, a decrease in  $\gamma_{O/W}$  is expected to result in an increased  $\cos \theta_{W/S}$  and thus promote more efficient roll-up. Since the absolute values

TABLE II

Contact Angle Studies with Mylar Wilhelmy Plates<sup>a</sup>

Surfactant	Wt%	$\gamma_{W/A}$ (dynes/cm)	$\gamma_{W/A} \cos \theta_{W/A}$ (dynes/cm) = ( $\gamma_{S/A} - \gamma_{S/W}$ )	$\cos \theta_{W/A}$
Tergitol 15-S-9	1.0	29.5	28.5	0.966
"	0.1	29.2	28.5	0.976
"	0.01	29.2	28.3	0.969
Tergitol NP-9	1.0	31.6	30.6	0.968
"	0.1	31.3	30.6	0.978
"	0.01	30.7	29.9	0.974
Tergitol 25-L-7	1.0	28.1	27.7	0.986
"	0.1	28.1	27.8	0.989
"	0.01	28.6	28.1	0.983
Tergitol 25-L-9	1.0	28.7	28.3	0.986
"	0.1	28.7	28.3	0.986
"	0.01	29.0	28.3	0.976
Nonionic X	1.0	30.9	30.2	0.977
"	0.1	31.0	30.2	0.974
"	0.01	31.5	30.0	0.952
Polytergent SL-62	1.0	30.3	29.5	0.974
"	0.1	29.6	28.9	0.976
"	0.01	37.2	30.2	0.812
Calsoft L-60 (LAS)	0.1	35.4	33.5	0.946
—	—	71.9	22.2	0.309

<sup>a</sup>Temp = 25 C. $\theta_{W/A}$  = Contact angle in the surfactant solution on Mylar in air. $\gamma_{W/A}$  = Surface tension of surfactant solution. $\gamma_{S/A}$  = Solid/air interfacial tension. $\gamma_{S/W}$  = Solid/water interfacial tension.

of  $\gamma_{O/W}$  are in all cases rather low, a seemingly small change of 1-2 dynes/cm can result in a significant variation in  $\cos \theta_{W/S}$ . The experimental results thus strongly suggest a relationship between the time of removal of the oil drops and the magnitude of the oil/water interfacial tension, both of which decrease with increasing surfactant concentration above the cmc. While the mechanism linking these parameters is not established, it can be said that the rate effects observed do not appear to involve changes in transport rates of surfactant in the aqueous phase as the concentration increases above the cmc since: (a) our surface tension measurements show that once the cmc is attained adsorption at the liquid/air interface is extremely rapid; likewise, contact angle studies reveal that adsorption at the solid/water interface occurs very quickly. Although the time course of interfacial tension was not formally determined, it was obvious experimentally that the adsorption at the oil/water interface is also rapid above the cmc. Furthermore, agitation of the aqueous solution would serve to further enhance the rate of adsorption at the relevant interfaces; and (b) in those systems where diffusion at and

above the cmc is expected to be most rapid, i.e., for members with the highest cmc, the effects of concentration on removal time above the cmc are most pronounced. The opposite would have been expected if diffusion to the interface was the rate-determining factor.

These results suggest that, in our agitated system with a simple geometry wherein a small oil drop is exposed to an overwhelming volume of aqueous solution, the rate of adsorption per se is not limiting. This situation could, of course, be different under real laundering conditions because the complexity of the fabric/soil geometry could slow the diffusion process markedly.

As further evidence of the importance of  $\gamma_{O/W}$  in determining the relative roll-up efficiencies of various surfactants, we compare removal times and oil/water interfacial tensions for a number of systems. Table III lists oil/water interfacial tensions for selected surfactants and Arcoprime 70 mineral oil. For aqueous solutions of a series of surfactants possessing a common hydrophobe at a temperature below the cloud point, increasing the ethoxylation produces an increase in  $\gamma_{O/W}$ . Similarly, removal

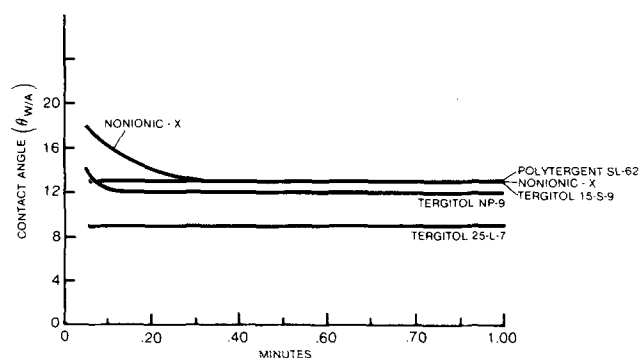


FIG. 4. Contact angle as a function of time for 0.1% nonionic surfactant solutions at 25 C on Mylar.

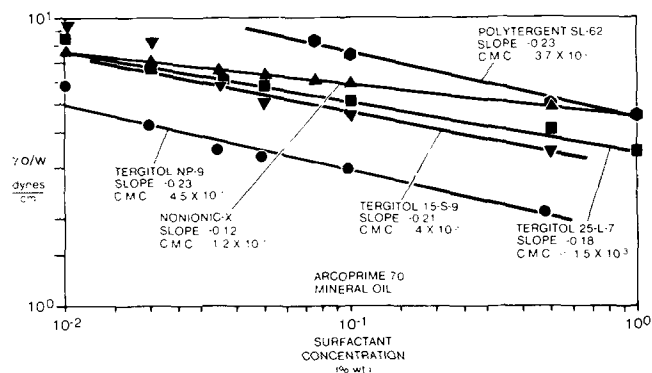


FIG. 5. Oil/water interfacial tension as a function of surfactant concentration at 25 C for selected nonionic surfactants.

TABLE III

Oil/Water Interfacial Tensions for Arcoprime 70 Mineral Oil

Surfactant	Wt%	Temp (C)	$\gamma_{O/W}$ (dynes/cm)
Tergitol 25-L-7	0.05	25	5.7
Tergitol 25-L-9	0.05	25	5.9
Tergitol 25-L-12	0.05	25	6.6
Tergitol 25-L-7	0.05	50	5.2
Tergitol 25-L-9	0.05	50	5.1
Tergitol 25-L-12	0.05	50	5.4
Tergitol 15-S-9	0.05	25	5.0
Tergitol 15-S-12	0.05	25	6.0
Tergitol 15-S-9	0.05	50	4.9
Tergitol 15-S-12	0.05	50	5.2
Tergitol NP-9	0.05	25	3.8
Tergitol NP-10	0.05	25	4.1
Triton X-100	0.05	25	4.6
Tergitol NP-9	0.05	50	4.4
Tergitol NP-10	0.05	50	4.1
LAS	0.1	25	8.1
LAS	0.1	50	9.1
Nonionic-X	0.05	25	6.3
Polytergent SL-62	0.1	25	7.4

studies have shown that increasing the ethoxylation results in increased removal time in many cases (1). Furthermore, secondary alcohol ethoxylates with a given degree of ethoxylation produce lower  $\gamma_{O/W}$  values than their primary counterparts and have also been shown to be much more effective in rolling-up mineral oil soils. Since Table II shows that the adhesion tensions for Tergitol 15-S-9 and Tergitol 25-L-9 are very similar, it follows from Equation I that  $\gamma_{O/W}$  is the dominant factor. We have already shown that nonyl phenol ethoxylates with a given degree of ethoxylation produce the lowest  $\gamma_{O/W}$  values observed and are also the most efficient in prompting roll-up. (Fig. 1) In addition, nonyl phenol ethoxylates also produce a high adhesion tension, as shown in Table II. No other surfactant tested seems capable of simultaneously providing a low  $\gamma_{S/W}$  and a low  $\gamma_{O/W}$ . Table III shows that, for a given nonionic surfactant,  $\gamma_{O/W}$  generally decreases with increasing temperature. Removal times in previous model studies displayed a similar temperature dependence (1). As stated previously (1), no removal is observed in model studies using linear alkyl benzene sulfonate (LAS) at normal use concentrations. Table II reveals that this is in spite of the high adhesion tension, i.e., low  $\gamma_{S/W}$ , with Mylar substrates. Table III,

however, shows that  $\gamma_{O/W}$  is relatively high in such systems, thus accounting for the observed effects.

#### Pure Mineral Oil Soils—Teflon FEP Substrates

Teflon FEP Type A 500 gauge film provides a model surface for fabrics treated with soil and/or water-repellent fluorinated finishes (9). Since such fabrics present an unusually difficult laundering problem (10-13), Teflon FEP is useful in demonstrating the relevance of solid surface free energy in detergency.

Table IV lists studies with pure mineral oil on Teflon FEP at 50 C. Without exception, the oil spreads from an initial contact angle of  $62 \pm 2^\circ$  to near 0 (or  $180^\circ$  as measured in the water) upon submersion in the aqueous phase. However, in nonionic systems, necking and drawing lead to an apparent contact angle less than  $180^\circ$  and incomplete removal by agitation. In light of Equation I,  $\gamma_{S/O} - \gamma_{S/W}$  is undoubtedly negative in all of these systems, allowing  $\cos \theta$  to approach -1. With nonionic surfactants, sufficient lowering of  $\gamma_{O/W}$  eventually prompts partial removal via necking and drawing and the observed order of removal times is consistent with  $\gamma_{O/W}$  values listed in Table III.

Anionic surfactants produce much higher interfacial tensions and no removal via necking and drawing is observed.

#### Oleyl Alcohol Soils

Since fatty alcohols are present in natural soils (14), oleyl alcohol has been examined with both Mylar and Teflon FEP substrates. Results are shown in Tables V and VI, respectively. With Mylar substrates, none of the surfactant systems provides effective oil removal. In several instances the drops slide or "creep" on the film surface, and subsequent coalescence is sometimes observed. In LAS systems, partial removal via necking and drawing sometimes follows coalescence, but a high contact angle in the water is maintained in all cases. Although conditions of high pH cause the drops to assume a milky appearance, little improvement in oil removal is noted. With Teflon FEP substrates, Table VI shows that nonionics again fail to elicit oil removal whereas LAS-based systems provide reasonable removal, especially at high pH. With nonionic systems, the drops actually spread upon submersion from an initial contact angle of  $60 \pm 2^\circ$  in air to near 0 (or  $180^\circ$  as measured in the water). The drops do not spread as much in the anionic systems and partial removal occurs via necking and drawing.

The results of these studies with both nonionic and anionic systems may be rationalized on the basis of Equa-

TABLE IV

Removal Studies on Teflon FEP with Arcoprime 90 Mineral Oil Soils

Detergent (wt%)	pH	Removal time and mechanism
0.05% Tergitol 25-L-7	6.3	No removal is observed within 4200 sec. Drops spread upon submersion so that a high contact angle in the water is reached and maintained. Marginal necking and drawing are observed.
0.1% LAS (Calsoft L-60)	6.0	
0.15% Tide	9.9	No removal within 5100 sec. is observed. Drops spread upon submersion so that a high contact angle in the water is reached and maintained. No appreciable necking or drawing occur.
0.05% Tergitol 15-S-9	5.9	
0.05% Tergitol NP-9	6.1	~2875 seconds { Partial removal occurs via necking and drawing, resulting in a large residual drop. A high contact angle in the water is reached and maintained.
		~2520 seconds {

Temp =  $50 \pm 1$  C, at 0 ppm hardness.

## OILY SOIL REMOVAL

TABLE V

Model Studies with Oleyl Alcohol Soils on Mylar at 50 C

Detergent (wt%)	pH	Removal time and mechanism
0.05% Tergitol 25-L-7	6.8	No removal is observed within 3200 sec. A high contact angle in the water is maintained. Drop "creep" on the film surface is observed in some systems.
0.05% Tergitol NP-9	6.2	
0.05% Tergitol 25-L-7 0.05% STPP	9.8	
0.05% Tergitol 25-L-7 0.05% STPP 150 ppm Hardness	8.4	
0.05% Tergitol 25-L-7 0.05% TEA	9.5	
0.1% Wisk	9.2	
0.1% LAS	8.0	Partial removal is observed within 4000 sec, after the drops "creep" and coalesce (but only via an inefficient necking and drawing process). A high contact angle in the water is maintained.
0.1% LAS 0.05% TEA	9.5	
0.1% LAS 0.05% STPP	9.7	
0.15% Tide	9.8	Partial removal is observed with 1100 sec. via a necking and drawing process. However, a high contact angle in the water is maintained.

TABLE VI

Model Studies with Oleyl Alcohol Soils on Teflon FEP at 50 C

Detergent (wt%)	pH	Removal time and mechanism
0.05% Tergitol 25-L-7	5.9	No removal is observed within 4200 sec. A high contact angle in the water (near 180°) is reached quickly and maintained. No necking or drawing is observed.
0.05% Tergitol 15-S-9	5.8	No removal is observed within 4200 sec. A high contact angle in the water (near 180°) is reached and maintained. Substantial necking and drawing occur.
0.05% Tergitol NP-9	6.1	
0.1% LAS	6.1	650 sec 100 sec 190 sec Upon submersion a relatively low contact angle in the water is maintained; removal occurs via necking and drawing. The residual drops are subsequently removed by a repeat process.
0.15% Tide	9.7	
0.1% LAS 0.05% Na <sub>2</sub> CO <sub>3</sub>	10.5	
0.1% Wisk	9.1	No removal occurs within 5000 sec. A high contact in the water is reached and maintained; only marginal necking and drawing action are noted.
0.05% Tergitol 25-L-7 0.05% Na <sub>2</sub> CO <sub>3</sub>	10.3	No removal is observed within 5000 sec. A high contact angle in the water (near 180°) is quickly reached and maintained. No necking or drawing is observed. A whitish texture is developed soon after submersion.
0.05% Tergitol 25-L-7 0.05% STPP	9.5	

tion I. For 0.05% Tergitol 25-L-7 at 25 C, Table VII shows that an oil/water interfacial tension of 5.1 dynes/cm was obtained by the spinning drop technique. (The plate method could not be used in nonionic/oleyl alcohol systems because of dewetting problems.) With Mylar substrates, while pure mineral oil soils possessing similar  $\gamma_{O/W}$  values are easily removed by the roll-up process, oleyl alcohol maintains a high contact angle in the water, i.e.,  $\cos \theta_{W/S}$  approaches -1. This implies that the numerator in Equation I ( $\gamma_{S/O} - \gamma_{S/W}$ ) is negative and suggests that  $\gamma_{S/O}$  for oleyl alcohol on Mylar is relatively low. Thus, even though  $\gamma_{O/W}$  is also relatively low, no roll-up is observed, and the marginal necking and drawing actions observed in some systems are inadequate for removal.

With Teflon substrates, although the absolute values of the various interfacial tensions are different, the same relative conditions exist; because the numerator in Equation I is negative, no roll-up is observed and the marginal necking and drawing actions are again unable to elicit removal. Systems containing LAS produce somewhat different results in that, although a high contact angle in the water is maintained with both Mylar and Teflon substrates, partial removal via necking and drawing does occur in many cases. Table VII suggests that this phenomenon is related to an unusually low  $\gamma_{O/W}$  upon first contact of the 2 phases. A violent swirling motion in the oil phase near the interface (which is not observed in similarly built nonionic systems) is observed for the first few min of contact of

TABLE VII

Oil/Water Interfacial Tensions at 25 C

Detergent (wt%)	Oil	$\gamma_{O/W}$ (dynes/cm)
0.05% Tergitol 25-L-7 <sup>a</sup>	Oleyl alcohol	5.1
0.1% LAS	Oleyl alcohol	6.4 (5-min aging) 7.0 (60-min aging)
0.1% LAS 0.05% STPP	Oleyl alcohol	3.9 (5-min aging) 6.0 (60-min aging) 6.4 (20-hr aging)
0.1% LAS 0.05% TEA	Oleyl alcohol	5.0 (10-min aging) 5.8 (2-hr aging)
0.1% LAS 0.05% Na <sub>2</sub> CO <sub>3</sub>	Oleyl alcohol	2.8 (5-min aging) 4.6 (60-min aging)
0.15% Tide	Oleyl alcohol	4.4 (5-min aging) 5.4 (20-hr aging)
0.05% Tergitol 25-L-7	Triolein	4.7
0.05% Tergitol 25-L-7 0.05% STPP	Triolein	< 1
0.1% LAS	Triolein	3.2
0.1% LAS 0.05% TEA	Triolein	< 1

<sup>a</sup>Spinning drop method.

the 2 phases. Given sufficient time, Table VII shows that the very low  $\gamma_{O/W}$  initially measured subsequently rises with time. This initial, low  $\gamma_{O/W}$  and the swirling motion apparently produce conditions favorable for necking and drawing within the first few min of submersion, especially with Teflon FEP substrates. The likely presence of oxidation products in the oil is expected to help produce a further lowering of  $\gamma_{O/W}$  in high pH systems and thus the observed builder effects seem quite rational.

The oleyl alcohol drops that are not readily removed in these systems develop a white, gelatinous appearance after several min (sometimes hr) of submersion. The drops are subsequently removed through slow "complex" formation

at the solution/oil droplet interface. Once formed the complex slowly disperses as a white, fluffy, cloud-like phase, thus providing the opportunity for further growth at the new interface. This process continues until the film is clean, requiring anywhere from a few hr to a few days. Other workers have reported liquid crystals in similar systems (15, 16). However, because of time and viscosity limitations, such liquid crystal formation is not expected to be an important operative mechanism in detergency.

### Triolein Soils

Since triglycerides comprise a significant fraction of natural oily soils (14), several workers have examined their detergency mechanisms with various substrates (15,17-19). Most of these authors have shown that triglycerides are difficult to remove from synthetic fabrics and that they thereby represent a practical choice for a model oily soil. Consequently, extensive studies have been made with both Mylar and Teflon FEP substrates, selected results of which appear in Tables VIII and IX, respectively. With Mylar at 50 C unbuilt surfactant systems show no removal and a high contact angle (in water) is maintained. Upon alkaline builder addition, extensive necking and drawing are observed in most systems. Teflon FEP substrates provide somewhat similar net results. Initially, the oil contact angle is  $68 \pm 2^\circ$ , but upon submersion in an unbuilt surfactant system, a  $0^\circ$  contact angle (or  $180^\circ$  as measured in the water) is quickly reached and maintained. In built surfactant systems of sufficiently high alkalinity, partial removal occurs quickly before the drops can spread, but after spreading occurs, residual drops are very persistent. Although builder variability determines the removal efficiency of a given surfactant system, nonionics are more effective than anionics in most cases.

The results of these tests with both Teflon FEP and Mylar substrates may be explained following arguments similar to those previously applied to oleyl alcohol soils. Table VII shows that even though the  $\gamma_{O/W}$  values for triolein with unbuilt surfactant systems are low compared to similar systems with mineral oil, a high contact angle

TABLE VIII

Model Studies with Triolein on Mylar at 50 C

Detergent (wt%)	pH	Removal time and mechanism
0.05% Tergitol 15-S-9	5.6	No removal is observed within 4600 sec. A high contact angle in the water is maintained.
0.05% Tergitol 25-L-7	6.0	
0.1% LAS	6.1	
0.05% Tergitol NP-9	6.0	1360 sec — Removal occurs via roll-up, necking and drawing, with a substantial residual drop. A repeat process is noted for the residual drop at long times.
0.05% Tergitol NP-9 0.05% Na <sub>2</sub> CO <sub>3</sub>	10.5	240 sec. Upon submersion the drops adopt an intense white color; subsequent removal occurs by a necking and drawing process. A substantial residual drop is observed.
0.05% Tergitol 25-L-7 0.05% Na <sub>2</sub> CO <sub>3</sub>	10.5	
0.1% LAS 0.05% Na <sub>2</sub> CO <sub>3</sub>	10.3	
0.05% Tergitol NP-9 0.05% Na <sub>2</sub> CO <sub>3</sub>	10.4	
150 ppm Hardness		
0.05% Tergitol 25-L-7 0.05% TEA	9.6	No removal occurs within 4000 sec. A high contact angle in the water is maintained. A white gelatinous appearance is noted, especially with hardness ions present.
0.05% Tergitol 25-L-7 0.05% TEA	9.3	
150 ppm Hardness		

TABLE IX

Model Studies with Triolein Soils on Teflon FEP at 50 C

Detergent (wt%)	pH	Removal time and mechanism
0.05% Tergitol 25-L-7	6.0	No removal is observed within 6000 sec. A high contact angle in the water is reached quickly and maintained.
0.05% Tergitol NP-9	6.2	
0.1% Wisk	9.1	
0.1% LAS	6.0	No removal occurs within 5100 sec. A contact angle which is somewhat lower (in water) than with nonionics is observed.
0.1% LAS	10.5	
0.05% Na <sub>2</sub> CO <sub>3</sub>	9.7	Immediate partial removal occurs upon submersion by a rapid sequential break-off from the master drop. The residual drops develop a white color and are subsequently removed by necking and drawing.
0.15% Tide	10.6	
0.05% Tergitol 25-L-7		
0.05% Na <sub>2</sub> CO <sub>3</sub>		

in the water persists in the unbuil surfactant systems. From Equation 1 we see that  $\cos \theta_{W/S}$  must therefore approach -1, and it can be further deduced that  $\gamma_{S/O}$  is relatively low. Table VII also shows that the necking and drawing action observed in most built systems is attributable to a substantial lowering of  $\gamma_{O/W}$  upon builder addition. This effect presumably is at least partially caused by the presence of hydrolysis and oxidation products in the triolein.

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