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Oily Soil Removal from a Polyester Substrate by Aqueous Nonionic Surfactant Systems

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ABSTRACT

Pure mineral oil soils are removed from polyester substrates by the roll-up mechanism in nonionic surfactant systems, and the process is little affected by hardness ions or builder addition. For a given surfactant system, roll-up and removal efficiency increase with temperature until the cloud point of the nonionic is reached, whereafter a further increase in temperature decreases the rate of roll-up. In general, lower ethoxylated surfactants perform better than higher ethoxylates at low temperature, but the trend is gradually reversed as the temperature is increased. For a given degree of ethoxylation, secondary alcohol ethoxylates are more effective at rolling up mineral oil soils than their primary counterparts. Addition of a small amount of oleic acid to mineral oil soils facilitates the roll-up process (by lowering the oil/water interfacial tension) and minimizes the differences in performance among the various types of unbuilt nonionic surfactants. However, addition of highly alkaline electrolytic builders with these soils promotes oil removal by emulsification, presumably because of charge neutralization and/or transfer of the fatty acid into the aqueous phase. Conditions of high pH and low electrolyte strength inhibit the removal of 5.0% oleic acid in mineral oil soils, as exemplified by studies with added triethanolamine, ammonia, and very diluted NaOH. However, addition of divalent hardness ions to such systems promotes coarse emulsification of the soil, as does addition of relatively high concentrations of monovalent cation salts. A tentative explanation of this phenomenon is proposed. Ionic strength has little effect on the removal of 5.0% oleic acid/mineral oil soils below pH 7, as rapid roll-up is obtained regardless of added electrolytes. Similarly, ionic strength (or pH) has little effect on the removal of mineral oil containing polar, but nonionizing soils such as oleyl alcohol, as rapid roll-up is achieved under a number of conditions.

INTRODUCTION

Detergency mechanisms in anionic surfactant systems have been examined for many years. Of fundamental importance was the early work of Adam (1) who, by using the Young Equation (2), derived expressions relating the contact angles of oily soils to the various surface and interfacial energies in detergent systems. The "rolling-up" process observed by Adam was found to be most applicable to nonpolar soils. Using more complex soil mixtures, Lawrence (3) and others (4-7) discussed the significance of surfactant penetration into the soil, and produced ternary phase diagrams for several surfactant/soil systems. McBain's classical work on solubilization (8) prompted investigations by many other workers (9-15), but most authors have shown that solubilization is of secondary importance in practical systems becuase of the low surfactant to soil ratio.

Emulsification has also received considerable study (16-21), and has been shown to be operative only in systems where a very low oil/water interfacial tension can be obtained. Other ancillary effects, such as osmotic flow (22-23), the role of foam in detergency (24), and molecular complex formation (25) have also been treated.

Studies of nonionic surfactant interactions with oily soil compositions have been more recent. Because of their uncharged character, these surfactants behave somewhat differently from anionic systems. Shinoda (26), for example, has shown that nonionics are much better solubilizing agents for hydrocarbon soils. Scott (5) found that nonionics can achieve maximum detergency at much lower concentrations because of their relatively low critical micelle concentration. Other workers (27-29) have observed considerable variations in soil removal efficiencies between nonionic and anionic systems, showing that nonionics tend to perform best on hydrophobic substrates with nonpolar soils. Although many such practical systems have been characterized, the operative fundamental mechanisms of detergency have received less attention (30). In this paper nonionic surfactant systems will be stressed, and we will investigate the effects of surfactant structure, added builders and temperature on the removal of polar and non-polar soils from a polyester substrate. Interpretations will emphasize the relevant interfacial free energy changes governing soil removal processes.

Several model systems have been devised for studying detergency mechanisms, each with its own particular advantages and limitations. Several workers have related oil removal efficiency to changes in the contact angle of the soil (31-34). These studies have been instrumental in defining the parameters governing the roll-up of oily soils. Radiotagging methods have proven extremely useful in demonstrating the preferential removal of certain polar soils from a complex soil mixture (5,35-38). Still other methods have been used with success (13,39).

In the present studies, the changes in the contact angle and other physical characteristics of oily soil on polyester film submerged in an aqueous detergent solution have been carefully monitored, together with observations of the removal times and mechanisms under accurately controlled conditions. Particulate soil removal processes were not examined.

EXPERIMENTAL

Materials

The Arcoprime 90 white mineral oil was of food grade from Altantic Richfield with a viscosity of 91 S.U.S. at 100 F. Oleic acid and oleyl alcohol were purchased from Fisher Scientific Company and Eastman Kodak, respectively. Triolein was of technical grade from Matheson, Coleman and Bell.

Calsoft L-60 is a linear alkyl benzene sulfonate from

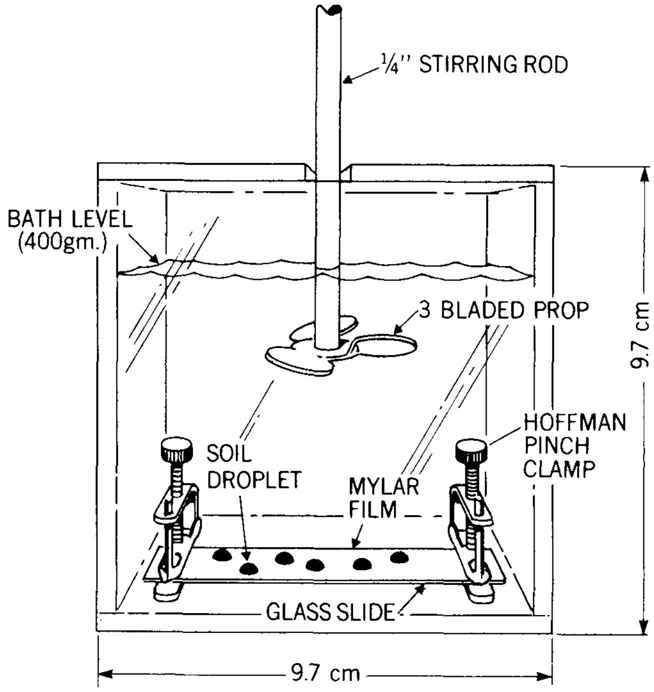


FIG. 1. Pictorial representation of model detergency cell.

Pilot Chemical Company, and the sodium dodecyl sulfate specimen is a high purity product of BDH, Poole, England. The Tide specimen (Procter and Gamble) contained 6.1% phosphorus. The Tergitol surfactants are primary and secondary alcohol ethoxylates from Union Carbide Corporation, and the Neodol surfactants are primary alcohol ethoxylates from Shell Chemical Company. More information on the various surfactants appears in Table I.

Sodium acetate was obtained from Baker, and sodium meta silicate (Uniflow 26) was purchased from Exxon. All other reagents were obtained from Fisher Scientific Company in the highest possible grade.

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

Polyester Mylar film was obtained from Brownell Electric Incorporated in a Type D, 300 gauge. Mylar Type D is a DuPont trade name for polyethylene terephthalate film having a minimum of surface defects.

Procedures

All surface tensions were measured by the Wilhelmy plate method using a platinum plate and a Rosano tensiometer. After equilibrating at 25 ± 0.5 C, the surface was swept with a micro suction-pipette, and the surface tension was measured after 10 minutes of aging. A similar procedure was followed for the interfacial tension studies. Both glass and platinum plates were employed, depending on the wettability characteristics of each in the specific application.

EXPERIMENTAL PROCEDURES – MODEL DETERGENCY STUDIES

Equipment

A model detergency system as shown in Figures 1 and 2 was developed. Figure 1 depicts a specimen transparent plastic cell (9.7 cm^3) which was used to contain 400 grams of the aqueous detergent test solutions. A soiled Mylar film mounted on a conventional glass slide with Hoffman pinch clamps was placed in each cell, which was fitted with a slotted Plexiglas cover to minimize evaporation and heat loss. To increase productivity and allow direct comparisons, a battery of six such cells was used, as pictured in Figure 2. A Phipps and Bird, Inc., 6 Paddle Stirrer, mounted in a Plexiglas constant temperature bath with a slotted double bottom base, was suitably modified so as to provide constant and uniform agitation throughout the cells. The entire apparatus was placed on a Phipps and Bird fluorescent Floc Illuminator to provide adequate lighting in each cell. Constant temperature was mainatinaed with a Haake heater-recirculator to an accuracy of ± 1 at 50 C. A Fisherbrand Dynamix stirrer supplied additional agitation in the bath.

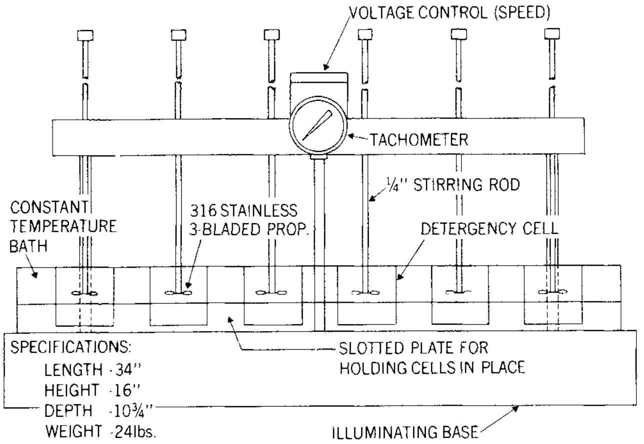


FIG. 2. Pictorial representation of model detergency apparatus.

Cleaning Procedures

Since careful cleaning was found to be essential for obtaining reproducible results, the procedures used are presented in some detail.

All cells and covers were thoroughly cleaned with Tide solution, rinsed exhaustively with tap water and rinsed additionally with doubly distilled water. The cells were covered with fresh filter paper and aluminum foil when not in use. The Hoffman pinch clamps were cleaned with Tide solution, rinsed with tap water and rinsed twice (by soaking) with doubly distilled water. After drying in an oven at 100 C, they were subjected to Soxhlet extraction with absolute ethanol for at least an hour, dried in an oven and stored in a desiccator until use. Care was taken to avoid touching the clean clamps without wearing polyethylene gloves. The microscope slides were cleaned in chromic acid solution, rinsed with tap and doubly distilled water, dried in an oven and stored in a clean, covered crystallization dish until use. All stirrers and shafts were cleaned in chromic acid solution, rinsed completely with tap and doubly distilled water and stored on clean, dry filter paper until use. Cell contamination was periodically monitored by surface tension and conductivity measurements.

Meticulous cleaning of the Mylar was found to be imperative. Initially, films were cleaned according to the methods of Zisman (40) and stored in doubly distilled water until use. However, this procedure produced erratic results, possibly because of varying degrees of surface hydration or contamination from drying in ambient air. Thus, a more rigorous procedure was adopted, wherein the films were soaked (with slight agitation) in a solution of 1.5% sodium dodecylbenzene sulfonate and 1.0% sodium tripolyphosphate at 40-50 C for 30-40 minutes. With Teflon forceps, each film was individually given a 30 second rinse with tap water and again soaked in the cleaning solution. Using the Teflon forceps, each film was then given an exhaustive rinse with tap water and rinsed twice by soaking in doubly distilled water. It was then placed on a clean watchglass and stored in a vacuum desiccator until use. Extreme care was taken to avoid exposure of clean films to ambient air or human touch. Surface purity was monitored by contact angle measurements with a Rame-Hart goniometer.

Test Procedures

The various detergent solutions were prepared and allowed to equilibrate in the constant temperature test bath. Using Teflon forceps and polyethylene gloves rinsed with doubly distilled water, the Mylar films were mounted on the glass slides with pinch clamps. A film was then soiled by placing onto it 2 + 0.005 μl drops of oil from a microsyringe with 6 drops per film. The drops were allowed to spread in air for 30 ± 5 seconds before being submerged in the detergent solution. This was accomplished by holding the top of the clamps and submerging the film quickly through the solution interface, with the film at about a 45° angle to the surface. The films (one per cell) were placed against the back of the cell in every case for best reproducibility. After 15 seconds of submersion without agitation, stirring was commenced at a rate of 60 rpm, which was demonstrated to be uniform throughout the cells by statistically performed tests on soil removal. The above procedure provided satisfactory reproducibility with a minimum of soil drop rupture upon passing through the air/water interface.

Each experiment was performed in duplicate by using two neighboring cells. Thus, the removal times presented in this paper represent the average of 12 drops, that is, two cells with 6 drops per cell. As the bath housed 6 cells, direct comparisons are grouped in sets of 3 in the tables of this paper.

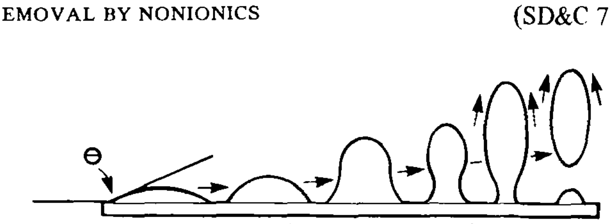
RESULTS AND DISCUSSION

Pure Mineral Oil Soils

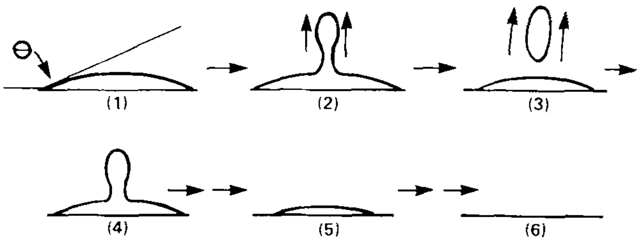
Several workers in the field (5) have shown that nonpolar mineral oil soils are removed primarily by the roll-up process as described by Adam (1) and pictorially presented in Figure 3a (41). The oil droplet, which originally wets the substrate in air, rolls up in the detergent solution and begins to neck and draw, with subsequent removal by hydraulic currents. When the contact angle in the water does not attain a value less than 90°, a small residual drop is observed which undergoes similar removal by a repeat of this process, but requiring much longer times. In general, after submersion the higher the contact angle in the water phase, the larger the residual drop, but when the contact angle in the water is less than 90°, complete detachment may be achieved. Using the Young Equation (2), one can derive an expression relating the extent of roll-up to the pertinent interfacial energies and works of adhesion, as shown in Figure 4 (42). Thus,

$$\cos\theta = \frac{W_{s/w} - \gamma_{w/a} - (W_{s/o} - \gamma_{o/a})}{\gamma_{o/w}} \qquad (4)$$

where $W_{s/w}$ and $W_{s/o}$ are the works of adhesion of the solid to the water and oil, respectively, $\gamma_{w/a}$ and $\gamma_{o/a}$ are the surface tensions of the water and oil, respectively, $\gamma_{o/w}$ is the oil/water interfacial tension, and θ is the contact angle in the aqueous phase. Generally, roll-up, i.e., a high value of cos θ, is favored by a high work of adhesion of the solid to the water, a low aqueous surface tension, a low work of adhesion of the solid to the oil and a low oil/water interfacial free energy.

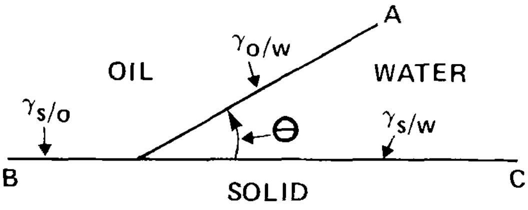


a) Roll-Up and Incomplete Removal of Large Oil Droplet (By Hydraulic Currents) In Detergent Solution when the Contact Angle in the Solution (Θ) Remains 90 < Θ < 180



b) Marginal Roll-Up and Coarse Emulsification Observed with Several Systems. A Rapid Sequence of Droplets is seen to Emerge from the Master Drop (1-5) until the Film becomes Completely Clean (6). The Contact Angle Remains 90 < Θ < 180.

FIG. 3. Oil removal processes observed in various systems.



AT EQUILIBRIUM:

$$\gamma_{s/o} = \gamma_{s/w} + \gamma_{o/w} \cos\Theta_{AC} \qquad (1)$$

SINCE:

$$W_{s/w} = \gamma_{w/a} + \gamma_{s/a} - \gamma_{s/w} \qquad (2)$$

$$W_{s/o} = \gamma_{o/a} + \gamma_{s/a} - \gamma_{s/o} \qquad (3)$$

WE HAVE:

$$\cos\Theta_{AC} = \frac{W_{s/w} - \gamma_{w/a} - (W_{s/o} - \gamma_{o/a})}{\gamma_{o/w}} \qquad (4)$$

FIG. 4. Selected equations governing the roll-up of oily soils.

The effect a surfactant has on the various interfacial energies is dictated by its thermodynamic, as well as surface, activity. Thus, for any given surfactant, we may anticipate an increase in the rate of roll-up and removal with concentration. Figure 5 is a plot of the average removal time (excluding the residual small drop) of mineral oil as a function of concentration at two temperatures for two nonionic surfactants in distilled water. The effects of concentration were most evident at the low end of the concentration scale (< ca. 0.2%). At 25 C, Tergitol 25-L-7, with a cloud point of 50 C (see Table I), was markedly more efficient in oil removal than Tergitol 25-L-9, whose cloud point is 60 C. However, the two surfactants performed almost identically at 40 C, being somewhat more efficient than Tergitol 25-L-7 at 25 C, especially at low concentrations. Since nonionics are known to be most active as they approach their cloud point, these results are in keeping with expectations. The decrease in removal time with concentration reflects increased adsorption at the pertinent interfaces.

Temperature changes are known to affect detergent performance as well as nonionic surfactant activity. Figure 6 shows the variation in roll-up and removal time of mineral oil with temperature for several nonionic surfactants at 0.1% concentration in distilled water. For a given sur-

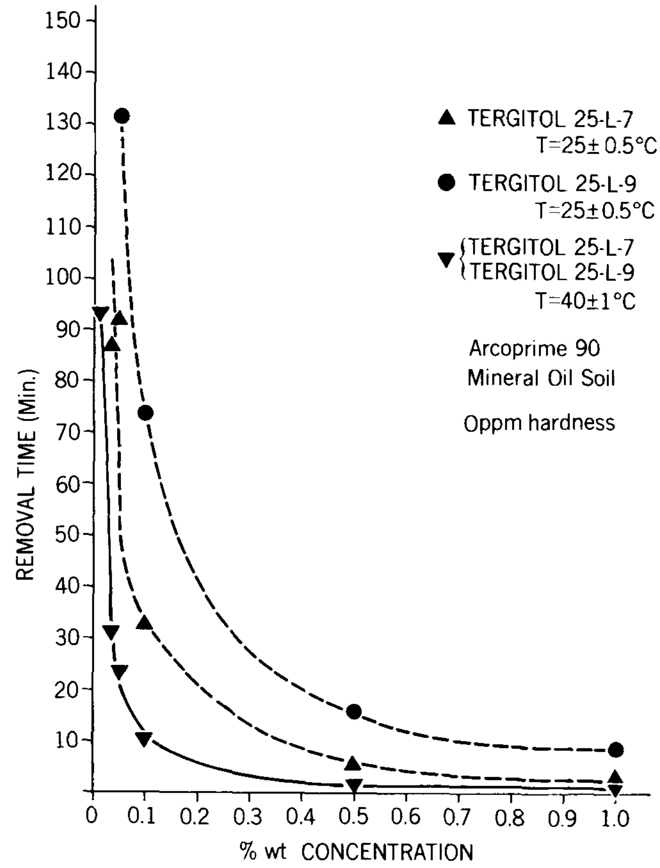


FIG. 5. Removal time vs. concentration for Tergitol 25-L-7 and Tergitol 25-L-9 at 25 and 40 C.

factant, the higher the temperature, the faster the roll-up and removal until the cloud point is reached (see Table I for surfactant descriptions). Above the cloud point, the effective concentration, and thus, the surface and thermodynamic activities of the nonionics are reduced. This behavior was demonstrated by both Terigtol 15-S-7 and Neodol 23-6-5. Even though the soil was obviously more easily removed at higher temperatures (because of reduced viscosity and increased thermal currents) removal times actually increased above the cloud point of these nonionics. Tergitol 25-L-7 and Neodol 25-7 showed improved performance with temperature over the entire range tested, since the temperature did not significantly exceed their respective cloud points. These two surfactants, being very similar in structure, performed equivalently with the variations observed between 30 and 40 C being due, possibly, to differing molecular weight distributions in the hydrophobe or hydrophile. Tergitol 15-S-7 was markedly superior in oil removal to all the other surfactants, especially at low temperatures. Although partly a cloud point effect, other contributing factors will be described later in this paper.

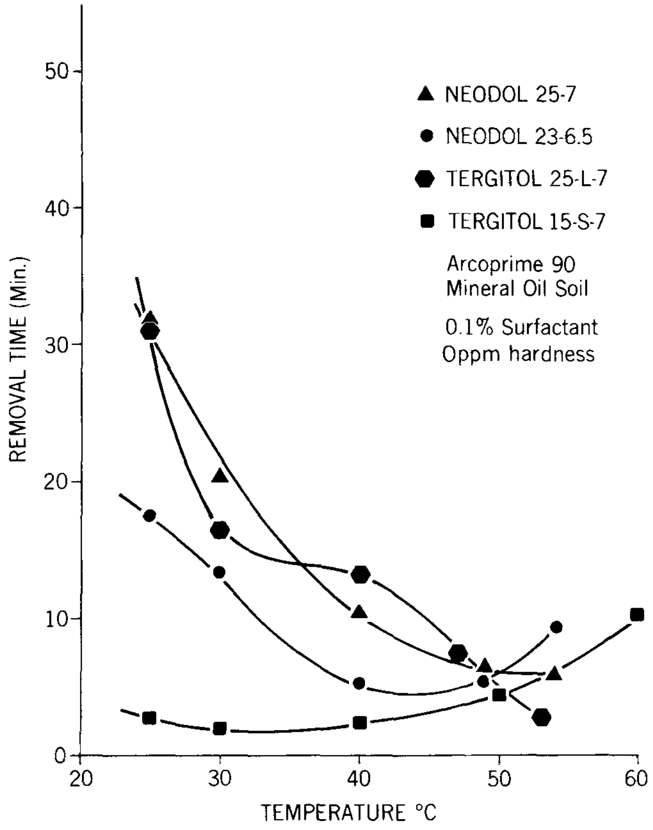


FIG. 6. Removal time vs. temperature for a variety of lower ethoxylated nonionics

Figure 7 gives a temperature profile of oil removal times for three nine mole ethoxylates. In general, the trends were similar to those observed with seven mole ethoxylates, but temperature had more of an effect on surfactant performance. Comparing Figures 6 and 7, we see that the seven mole ethoxylates performed better below 40 C, but the nine mole ethoxylates were superior above this temperature. Tergitol 25-L-9, having the lower cloud point, was noticeably better than Neodol 25-9 at low temperatures,

TABLE I

List of Surfactants

Tradename	and producer	Charge type	Hydrophobe	Average moles ethylene oxide	Cloud point C
Tergitol 25-L-7	Union Carbide Corp.	Nonionic	C_{12}-C_{15} (Primary Alcohol)	7	50
Tergitol 25-L-9		Nonionic	C_{12}-C_{15}	9	60
Tergitol 25-L-12		Nonionic	C_{12}-C_{15}	12	90
Tergitol 15-S-3		Nonionic	C_{11}-C_{15} (Secondary)	3	< 0
Tergitol 15-S-7		Nonionic	C_{11}-C_{15}	7	37
Tergitol 15-S-9		Nonionic	C_{11}-C_{15}	9	60
Tergitol 15-S-12		Nonionic	C_{11}-C_{15}	12	90
Neodol 25-7	Shell Chem. Co.	Nonionic	C_{12}-C_{15} (Primary)	7	52
Neodol 25-9		Nonionic	C_{12}-C_{15}	9	74
Neodol 23-6.5		Nonionic	C_{12}-C_{13}	6.5	45
Calsoft L-60 Alkyl Benzene Sulfonate, Sodium Salt	Pilot Chem. Co.	Anionic	C_{12} alkylbenzene (linear)	—	—
Sodium Dodecyl Sulfate	BDH	Anionic	C_{12} (linear)	—	—

but both surfactants prompted efficient removal above 40 C. Although Tergitol 25-L-9 and Tergitol 15-S-9 have identical cloud points, Tergitol 15-S-9 was far superior in promoting roll-up and removal, especially at low temperatures. Thus, with both the seven and nine mole ethoxylates, the secondary alcohol based surfactants were superior to their primary counterparts.

The superiority of the Tergitol secondary nonionic surfactants may be attributed to at least two factors. The higher critical micelle concentration of the secondaries provides a higher concentration of monomers in solution and, thus, favors an increased rate of adsorption at the various interfaces. Also, the secondary ethoxylates produce a lower oil/water interfacial tension against mineral oil, as seen from Table II. For a given degree of ethoxylation, the surface tensions of the various surfactants are similar, but the interfacial tension against mineral oil is significantly lower for the secondary surfactants. From equation 4 it can be seen that this is likely to result in a lower water/solid contact angle, and thus, more efficient oil displacement by the surfactant solution. It may be noted that in distilled water at 0.1% and 0.5% concentrations respectively, LAS and SDS, two anionic surfactants, exhibited much higher surface tensions and oil/water interfacial tensions than any of the nonionic systems. Equation 4 suggests that this should result in a high contact angle in the water phase and, thus, poor removal. Other workers have, indeed, found that pure mineral oil soils are extremely difficult to roll-up in anionic systems (33).

Mixed Nonionic Surfactants and Pure Mineral Oil Soils

Some authors have shown that a blend of high and low ethoxylated surfactants leads to substantial improvements in detergency (43), presumably by transfer of the lower ethoxylates into the oil phase. Such transfer is theorized as aiding the development of a low oil/water interfacial tension and, thus, promoting emulsification of the soil. As seen in Table III, however, such effects were not observed with blends of Tergitol 15-S-3 and Tergitol 15-S-9 with pure mineral oil soils, even though Tergitol 15-S-3 is readily soluble in the oil. In most cases, addition of Tergitol 15-S-3 resulted in longer removal times with no evidence of emulsification. At 50 C, slower oil removal may have been due to an effective concentration decrease, as addition of a small amount of Tergitol 15-S-3 substantially lowered the cloud point of the Tergitol 15-S-9 solution. At 30 C, although below the cloud point of the solution, the Tergitol 15-S-3 may have been preferentially solubilized in Tergitol 15-S-9 micelles, with little being transferred into the mineral oil. Such being the case, the observed increase in roll-up time with addition of Tergitol 15-S-3 may be expected, since the actual concentration of free Tergitol 15-S-9 would be less in the mixed surfactant systems.

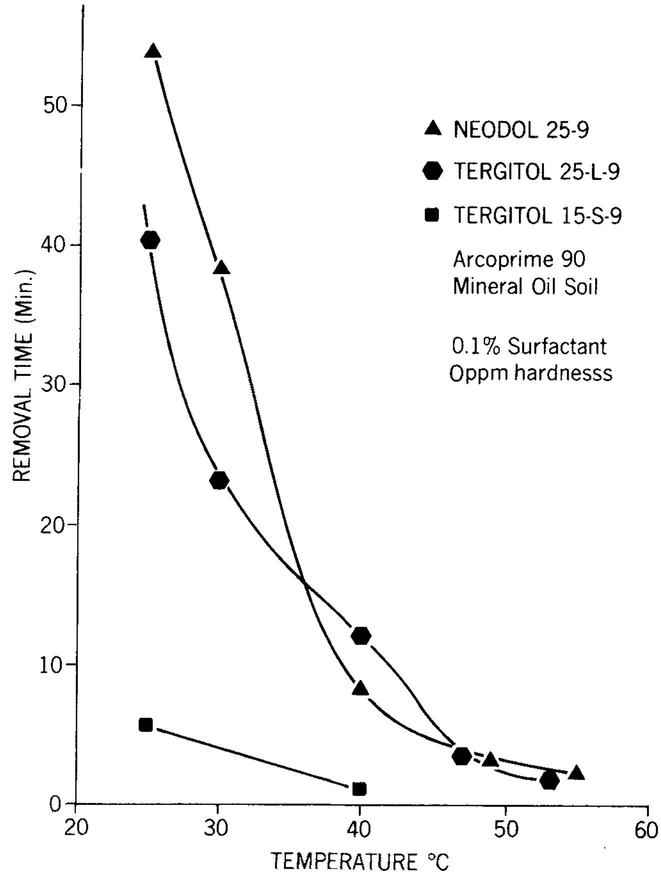


FIG. 7. Removal time vs. temperature for various nine mole ethoxylates.

Hardness and Builder Effects with Pure Mineral Oil Soils

In considering hardness and builder effects with pure mineral oil soils, we may expect relatively small changes in soil removal efficiency compared to that anticipated for more polar soil systems. Indeed, interactions with the nonionic surfactant may be greater than those with the soil. The results of studies with various commercial builders tend to support these assumptions, as shown in Table IV. These tests were performed on a direct comparison basis with

TABLE II

Surface and Interfacial Energies of Various Liquid Solutions at 25 ± 0.5 C[a]

Solution (wt%)	Surface tension (dynes/cm)	Interfacial tension with mineral oil (dynes/cm)
H_2O	72.0	50.2
Arcoprime 90 White Mineral Oil	30.6	---
0.1% LAS (Calsoft L-60)	36.2	7.4
0.5% SDS	38.7	9.6
0.1% Tergitol 15-S-7	29.2	3.1
0.1% Tergitol 15-S-9	30.6	3.6
0.1% Tergitol 15-S-12	31.6	4.7
0.1% Tergitol 25-L-7	28.6	4.6
0.1% Tergitol 25-L-9	29.6	5.0
0.1% Tergitol 25-L-12	32.2	6.0
0.1% Neodol 23-6.5	28.1	4.4
0.1% Neodol 25-7	28.3	4.6
0.1% Neodol 25-9	31.0	5.0

[a]Surfaces aged 10 minutes.

TABLE III

Mixed Nonionic Studies with Pure Mineral Oil Soils[a]

% Tergitol 15-S-9	% Tergitol 15-S-3	T C	Average removal time (sec)
100	0	50	110
98	2	50	210
95	5	50	200
93	7	50	250
92	8	50	680
90	10	50	620
100	0	30	720
98	2	30	1200
95	5	30	650
93	7	30	725
92	8	30	1800
90	10	30	2000

[a] Total surfactant — 0.04 wt%, Hardness — 0 ppm, pH — 6-7.

TABLE IV

Builder and Hardness Effects on Roll-up of Mineral Oil Soils at 50 C with 0.1% Tergitol 25-L-7 Solutions

Builder (wt%)	Hardness (ppm) ($Ca^{2+}/Mg^{2+}=1.5$)	pH[a]	Average removal time (sec)
—	0	(6-7)	150
—	150	(6-7)	115
—	300	(6-7)	190
—	0	(6-7)	200
0.05% TEA	0	9.5	100
0.10% TEA	0	9.6	110
0.05% TEA	0	9.4	120
0.05% TEA	150	9.5	115
0.05% TEA	300	9.5	200
0.05% EDTA (tetra (sodium)	0	10.2	90
0.10% EDTA	0	10.5	110
0.15% EDTA	0	10.6	120
0.05% EDTA	0	10.3	80
0.05% EDTA	150	8.0-7.8*	75
0.05% EDTA	300	8.0-7.7*	170
—	0	(6-7)	95
0.05% $Na_5P_3O_{10}$ (STPP)	0	9.7	70
0.10% $Na_5P_3O_{10}$ (STPP)	0	9.7	80

[a] $pH_{initial}$ = pH final unless noted by *.

0.1% Tergitol 25-L-7 solutions at 50 C. Under all conditions tested, the roll-up mechanism was observed with the formation of a small residual drop as previously discussed. Addition of up to 300 ppm hardness had only marginal effects on removal. The addition of alkaline builders, although known to be capable of salting out nonionic surfactants (44-45), did not have any major effect on the time of removal or its mechanism, with or without hardness ions present.

Binary Soil Systems — Mineral Oil/Oleic Acid

Practical soils contain not only hydrocarbons, but a complex array of various polar constituents, including long chain fatty acids (39). Several authors have shown that the presence of a fatty acid in a nonpolar soil may actually enhance roll-up in anionic systems, even though the pure nonpolar soil shows no roll-up at all (5,34,46). To examine the performance of nonionic surfactants with a more realistic soil, varying amounts of oleic acid were added to mineral oil. Table V presents results of these investigations with 0.05% Tergitol 25-L-7 in distilled water at 50 C. The presence of oleic acid in amounts up to 6.0% led to decreased roll-up times and, although not shown in Table V, minimized the differences between various nonionic surfactants. With 10% oleic acid, however, a combination of roll-up and coarse emulsification occurred, wherein the drops were removed, not as one major droplet, but as a series of small droplets in rapid succession. Pure oleic acid, on the other hand, showed no removal in the time tested, as a high contact angle in the water was maintained. These results are in contrast to what has been observed in studies by other workers (34) with anionic surfactants, wherein oleic acid showed roll-up and removal, but mineral oil did not.

An explanation for the observed behavior with binary soil systems may be found in Table VI which shows that for various nonionic surfactant systems, the oil/water interfacial tension (at 25 C) was markedly lowered with oleic acid in the soil. Equation 4 suggests that this should result in improved roll-up, as, indeed, occurred. Referring once more to Figure 4, addition of oleic acid beyond 6.0% may have increased the work of adhesion of the Mylar to the oil sufficiently to effectively reduce roll-up. However, since the oil/water interfacial tension was still low, coarse emulsification ensued. With pure oleic acid, the roll-up mechanism could not be induced in the nonionic system, perhaps because of a very low solid/oil interfacial tension. Also, since nonionics may be expected to interact much less favorably with a pure polar soil than would anionic surfactant systems, a relatively high oil/water interfacial tension may have been present.

TABLE V

Effects of Oleic Acid Addition on Removal of Mineral Oil Soils[a]

% (wt) Oleic acid in mineral oil	Average removal time (sec)	Mechanism
0	710	Roll-up with small residual drop remaining at long times
0.1 0.5 0.8 1.0 3.0 6.0	345 75 75 60 30 30	Roll-up with small residual drop being removed shortly thereafter. Film appears completely clean at tests' end.
10.0	50	Combination roll-up–emulsification.
100.0	>4500	No removal of the pure oleic acid-drop maintained a low contact angle in the oil.

[a] 0.05% Tergitol 25-L-7. T = 50 C, pH – 6-7, 0 ppm hardness.

TABLE VI

Surface and Interfacial Tensions at 25 ± 0.5 C
(Surface aged 10 minues)

Solution (wt %)	Surface tension (dynes/cm)	Interfacial tension with mineral oil (dynes/cm)	Interfacial tension with 5% oleic acid/mineral oil
Arcoprime 90 mineral oil	30.5	---	---
Arcoprime 90 mineral oil with 5% oleic acid added	30.5	---	---
H_2O	72.0	50.2	18.0
H_2O with 150 ppm Hardness (Ca^{2+}/Mg^{2+} = 1.5)	72.0	50.2	17.0
0.05% TEA	72.0	---	11.5
0.05% TEA + 150 ppm Hardness (Ca^{2+}/Mg^{2+} = 1.5)	72.0	---	6.2
0.1% LAS (Calsoft L-60)	36.2	7.4	2.0
0.1% Calsoft L-60 0.05% TEA	36.2	---	0.9
0.05% Tergitol 25-L-7	28.6	4.8	0.7
0.05% Tergitol 25-L-9	29.6	5.3	0.8
0.05% Tergitol 25-L-12	32.2	6.3	0.9
0.05% Tergitol 25-L-7 0.05% TEA	---	5.1	2.2
0.05% Tergitol 25-L-9 0.05% TEA	---	---	2.5
0.05% Tergitol 25-L-12 0.05% TEA	---	---	2.7
0.05% Tergitol 25-L-7 0.05% TEA, 150 ppm Hardness (Ca^{2+}/Mg^{2+} = 1.5)	---	---	< 0.4
0.05% TErgitol 25-L-7 0.05% EDTA (tetrasodium salt)	---	---	< 0.4

Electrolytic Builder Effects with Binary Soil Systems

Although much evidence can be presented in support of the beneficial role of builders in anionic systems (5,47-49), considerably less exists for nonionic detergents (49). The inherent insensitivity of nonionics to hard water suggests that builders may be of lesser importance, as does the growing acceptability of unbuilt heavy duty liquid detergents based on nonionic surfactants. Indeed, some authors have shown that a considerably greater improvement in detergency is obtained by addition of builders to anionic systems (29), but measurable improvement with nonionics has, in fact, also been shown. Vaughn et al. (50) found that addition of builders to solutions of nonionics in distilled water actually reduces detergency in several cases. Thus, in light of the uncertainty as to the role of builders in nonionic systems, numerous studies were undertaken with 5.0% oleic acid in mineral oil soils, representative results of which are presented in Table VII for alkaline electrolytic builders. In general, the role of the builders was to change the major removal mechanism from roll-up to emulsification. In most cases, small residual soil droplets were observed after the emulsification process, which were subsequently removed by the roll-up mechanism. Detrimental effects of hardness

TABLE VII

Effects of Commercial Electrolytic Builders on the Removal of 5.0% Oleic Acid/Mineral Oil with 0.05% Tergitol 25-L-7 Solutions at 50 C

Builder (wt%)	Hardness (ppm) ($Ca^{2+}/Mg^{2+}=1.5$)	pH[a]	Average removal time (sec) and mechanism
–	0	6-7	20 Roll-up with small residual drop
–	150	6-7	30 Roll-up with small residual drop
0.05% EDTA	0	10.3	100 Rapid emulsification
0.05% EDTA	150	8.0	25 Roll-up with small residual drop
0.1% EDTA	0	10.4	10 Spontaneous emulsification
0.1% EDTA	150	10.4	120 Emulsification
0.05% STPP	0	9.5	200 Roll-up and coarse emulsification
0.1% STPP	0	9.7	100 Emulsification
0.1% STPP	150	9.7	150 Emulsification with significant roll-up
0.05% $Na_2SiO_3 \cdot 5H_2O$	0	10.9	60 Emulsification
0.05% Na_2CO_3	0	10.6	100 Emulsification
0.05% $NaHCO_3$	0	8.4	60 Roll-up with small residual drop
0.5% $NaHCO_3$	0	8.8	200 Coarse emulsification

[a] $pH_{initial} = pH_{final}$.

ions were noted to the extent that the emulsification process was noticeably slowed: with 0.05% sodium-ethylene diamine tetra-acetate (EDTA), addition of 150 ppm hardness lowered the pH of the solution to 8.0, and roll-up was observed; further addition of EDTA to 0.1% raised the pH of the hard water solution and prompted efficient emulsification, but somewhat less so with hardness ions present than absent.

In general, however, little difference in removal time was noted among the unbuilt and built nonionic systems, as removal of the 5.0% oleic acid/mineral oil soil was efficient in all cases. However, as has already been seen with pure oleic acid, other soil systems which are less "optimized" for roll-up may serve to demonstrate the important role of builders, even with nonionic surfactants (these will be referred to in Table X).

Effects of TEA on Polar Soil Removal

One of the most popular sources of alkalinity in the growing heavy duty liquid detergent market is triethanolamine (TEA). This alkanolamine is used widely in its free form, and is also used to neutralize certain anionic surfactant acids, thereby making it a builder worthy of considerable study and discussion. As has already been shown in Table IV, TEA had little effect on the roll-up and removal of pure mineral oil soils in nonionic systems. However, Table VIII reveals that TEA had a remarkable and large *adverse* effect on the removal of the 5.0% oleic acid/mineral oil soils in several surfactant systems in distilled water. In every case, the more TEA present in the absence of added electrolytes, the slower and less complete was the roll-up process, even though the pH of such systems was similar to that of other built systems producing efficient emulsification (see Table VII). Tergitol 25-L-7 solutions containing 0.05% TEA prompted eventual removal, but with large residual drops, and this only after prolonged agitation. The drops slowly rolled up, but maintained a high contact angle in the water. Removal occurred by the continued necking and drawing of the drops caused by buoyancy and agitational forces. Solutions with 0.1% TEA showed only slight roll-up and no removal. Although the removal times for Tergitol 15-S-9 solutions were substantially lower in all cases, the trends were similar, with TEA built systems in the absence of strong electrolytes showing poor roll-up relative to the unbuilt system. TEA had little effect on the removal process in alkyl benzene sulfonate solution, as no removal could be induced in the absence of added electrolyte, with or without TEA.

Surprising results were obtained upon addition of hardness ions at the 150 ppm level to TEA built systems. With a solution of 0.05% Tergitol 25-L-7 and 0.05% TEA, rapid removal by a combination of emulsification and roll-up was observed, which was similar to, but less efficient than that obtained with sodium tripolyphosphate (STPP) of an equal concentration. Figure 3b depicts the removal process, wherein small droplets broke from the master drop in rapid succession until only a small residual drop remained (which was probably oleic acid-impoverished mineral oil). The residual drop was removed at substantially longer times by the roll-up mechanism. The removal times listed in Table VIII represent, as previously, the time required for the bulk of the soil drop to be removed, excluding the residual drop.) With 0.05% Tergitol 25-L-7 solutions in hard water, when the TEA level was increased to 0.1%, more emulsification and even less roll-up character was observed. Similar results were observed for Tergitol 15-S-9.

Turning now to LAS systems, we see (Table VIII) that TEA had little effect on the inefficient removal of the 5.0% oleic acid/mineral oil soil in distilled water systems – substantial oil residues remained even after very long times. With 0.1% LAS in hard water in the absence of TEA, instantaneous removal by a coarse emulsification process was observed, with the film becoming completely clean. This process was impeded somewhat by the presence of TEA, to the extent that small residual drops now remained.

To further examine the unusual effects observed with TEA, studies were made in nonionic systems under varying conditions of pH and electrolyte strength, as listed in Table IX for 0.05% Tergitol 25-L-7 solutions in distilled water at 50 C. With a constant TEA concentration of 0.05%, addition of as little as 0.005% of an electrolytic "cobuilder" was found to have a definite effect in decreasing the removal time without significantly affecting pH. However, under these conditions a rather inefficient roll-up process was observed, leaving a large residual drop. Cobuilder effectiveness was found to increase with concentration and seems to be proportional to sodium content, since NaCl was the best performer tested. At the 0.05% level, NaCl led to a coarse emulsification of the soil by a process that was similar to (but less efficient than) that observed upon addition of 150 ppm divalent hardness ions. Increasing the concentration of TEA to 0.5% in the absence of a cobuilder or added electrolyte served to raise the pH to well above that which achieved emulsification with electrolytic builders, but only a slow, inefficient roll-up with a large residual drop was observed.

In an effort to determine the generality of the "TEA

TABLE VIII

Effects of Tea on Oil Removal with 5.0%
Oleic Acid/Mineral Oil Soils at 50 C

Detergent (wt)	Hardness (ppm) ($Ca^{2+}/Mg^{2+}=1.5$)	pH[a]	Removal time (sec) and mechanism
0.05% Tergitol 25-L-7	0	6-7	20 Roll-up with small residual drop
0.05% Tergitol 25-L-7 0.05% TEA	0	9.4	2230 Inefficient roll-up with large residual drop
0.05% Tergitol 25-L-7 0.1% TEA	0	9.6	>4000 No removal – high contact angle in the water maintained
0.05% Tergitol 25-L-7 0.05% TEA	150	9.4	60 Slight roll-up and coarse emulsification
0.05% Tergitol 25-L-7 0.1% TEA	150	9.7	60 Coarse Emulsification
0.05% Tergitol 15-S-9	0	4.7	25 Roll-up with small residual drop
0.05% Tergitol 15-S-9 0.05% TEA	0	9.4	700 Inefficient roll-up with large residual drop
0.05% Tergitol 15-S-9 0.05% TEA	150	9.3	60 Slight roll-up and coarse emulsification
0.1% LAS (Calsoft L-60	0	7.0	>2400 No removal observed; contact angle in the water remained high
0.1% LAS 0.05% TEA	0	9.4	>2400 No removal observed; contact angle in the water remained high
0.1% LAS 0.1% TEA	0	9.6	>2400 No removal observed, contact angle in the water remained high
0.1% LAS	150	8.0	Coarse emulsification – instaneous; film completely clean in a few seconds
0.1% LAS 0.05% TEA	150	9.4	Some coarse emulsification upon submersion; substantial residual soil maintained
0.1% LAS 0.1% TEA	150	9.6	Some coarse emulsification–inconsistent integrity in residual drops

[a] $pH_{initial} = pH_{final}$.

effect," tests were performed with other builders with which a combination of high pH and low electrolyte concentration could be achieved. Ammonia, which can be considered the "parent" amine of TEA, provided results similar to those observed with TEA in 0.05% Tergitol 25-L-7 solutions, as shown in Table IX. Added alone to a nonionic surfactant solution, ammonia provides a high pH and low electrolyte concentration, and poor soil removal by an inefficient roll-up process was observed. Addition of 0.05% NaCl to such systems led to rapid removal by the coarse emulsification process shown in Figure 3b, as was seen with TEA.

NaOH was also used to provide a high pH and relatively low electrolyte concentration, and the results were similar to those observed with TEA and NH_3, although less pronounced. NaOH systems at 1×10^{-4}M, having a pH similar to that of 0.05% TEA, showed some modest improvement in removal times over TEA systems. However, further addition of sodium ions (0.05% NaCl) prompted a marked improvement in soil removal by the coarse emulsification process previously discussed. Increasing the concentration of NaOH in the presence of NaCl provided conditions for rapid emulsification of the soil. In summary, in all nonionic systems tested, conditions of high pH and low electrolyte concentration resulted in poor roll-up and no emulsification, but addition of strong electrolytes to such systems prompted rapid removal by a coarse emulsification process.

Nonionic systems of pH less than 7 were also tested to determine electrolyte effects, and the results of these studies are also listed in Table IX. Ionic strength appeared to have no observable effect on oil removal below pH 7, as rapid, efficient roll-up and coarse emulsification mechanisms were both found to be operative under these conditions. Small droplets began to break off from the master drop soon after submersion, but the master drop also underwent efficient roll-up, so that the original 2 μl drops were seen to be totally removed as three subdroplets in rapid succession. This action may be expected in instances where a low oil/water interfacial tension is combined with a relatively high work of adhesion of the water to the solid.

Many of the effects of high pH and low electrolytic strength may be rationalized on the basis of data in Table VI, which lists surface and interfacial tensions for selected, relevant systems. Addition of 0.05% TEA to distilled water solutions of 0.05% Tergitol 25-L-7 (or Tergitol 25-7-9, or, 25-L-12) was found to increase the oil/water interfacial tension. As previously seen in equation (4), a rise in the oil/water interfacial tension may be expected to reduce roll-up, and certainly inhibit emulsification. Thermodynamically, a rise in the oil/water interfacial tension detracts from removal by any process, since the free energy change accompanying soil removal is given by

$$\Delta G = \gamma_{w/o} + \gamma_{s/w} - \gamma_{s/o} \ (51) \qquad (5)$$

However, the increased oil/water interfacial tension cannot be the sole factor preventing oil removal in TEA built Tergitol 25-L-7 systems with no added electrolyte. The oil/water interfacial tension of 2.2 dynes/cm for such systems, with 5.0% oleic acid in mineral oil soils, is below that for pure mineral oil (5.1 dynes/cm) under similar conditions, but mineral oil was found to roll-up quite effectively. For reasons not readily apparent, conditions of high pH and low electrolyte concentration appear to augment the effective adhesion of the mineral oil/oleic acid soil to the Mylar surface in nonionic aqueous systems.

Addition of 150 ppm hardness or other electrolytes to TEA built nonionic systems resulted in an extremely low

TABLE IX

Studies of the Effects of pH and Electrolyte Concentration on Removal of 5.0% Oleic Acid/Mineral Oil Soils with 0.05% Tergitol 25-L-7 Solutions at 50 C[a]

Builder	$pH_{initial}$	pH_{final}	Removal time (sec) and mechanism
---	6-7	6-7	20 Roll-up with small residual drop
0.05% TEA 0.005% EDTA	9.8	9.5	1500 Inefficient roll-up with large residual drop
0.05% TEA 0.005% STPP	9.7	9.5	675 Inefficient roll-up with large residual drop
0.05% TEA 0.005% NaCl	9.5	9.3	600 Roll-up with large residual drop
0.05% TEA 0.05% NaCl	9.5	9.5	300 Coarse emulsification
0.5% TEA	10.1	10.2	2100 Inefficient roll-up with large residual drop
0.0005% NH_3	9.4	8.9	1500 Inefficient roll-up with large residual drop
0.005% NH_3	9.9	9.9	>2500 High contact angle in the water maintained
0.0005% NH_3 0.05% $NaCl^3$	9.2	8.9	60 Roll-up and coarse emulsification
1 x 10^{-4}M NaOH	9.6	9.3	1425 Inefficient roll-up with large residual drop
1 x 10^{-4}M NaOH 0.005% NaCl	9.5	9.2	280 Inefficient roll-up with large residual drop
1 x 10^{-4}M NaOH 0.05% NaCl	9.4	9.1	30 Coarse emulsification
1 x 10^{-3}M NaOH 0.05% NaCl	10.6	10.6	100 Rapid emulsification
1 x 10^{-1}M CH_3COOH 1 x 10^{-1}M $CH_3COO\text{-}Na^+$	4.7	4.7	20 Rapid roll-up and coarse emulsification film became clean by 40
1 x 10^{-3}M HCl	2.9	2.9	25 Rapid roll-up and coarse emulsification; film became clean by 40
1 x 10^{-3}M HCl 0.05% NaCl	2.9	2.9	25 Rapid roll-up and coarse emulsification; film became clean by 40

[a] 0 ppm Hardness.

TABLE X

Removal Studies with Other Soil and Detergent Systems at 50 C

Detergent (wt%)	Hardness (ppm)[a]	pH[b]	Soil	Average removal time (sec) and mechanisms	
---	0	7.0	0.2% oleic acid/ mineral oil	>4200	High contact angle in the water maintained
---	0	7.0	0.5% oleic acid/ mineral oil	>4200	
---	0	7.0	3.0% oleic acid/ mineral oil	>4200	
---	150	7.0	0.2% oleic acid/ mineral oil	>4200	High contact angle in the water maintained
---	150	7.0	0.5 oleic acid/ mineral oil	>4200	
---	150	7.0	3.0% oleic acid/ mineral oil	>4200	
0.05% Tergitol 25-L-7	0	6-7	5.0% oleyl alcohol/ mineral oil	120	Rapid roll-up with small residual drop
0.05% Tergitol 25-L-7 0.05% TEA	0	9.4	5.0% oleyl alcohol/ mineral oil	90	
0.05% Tergitol 25-L-7 0.05% EDTA	0	10.4	5.0% oleyl alcohol/ mineral	100	
0.05% Tergitol 25-L-7	0	6-7	Triolein	>5000	Marginal roll-up
0.05% Tergitol 15-L-7 0.05% TEA	0	9.6	Triolein	>5000	
0.05% TErgitol 25-L-7 0.05% EDTA	0	10.5	Triolein	575	Complex formation

[a] 3:2 Ratio of Ca^{2+}/Mg^{2+}.

[b] $pH_{initial} = pH_{final}$.

oil/water interfacial tension, which as is expected, prompted removal by necking, drawing and coarse emulsification of the soil. The low oil/water interfacial tension in such systems is apparently connected with charge neutralization of the ionized fatty acid (by added electrolyte) at the interface, allowing the formation of a more coherent mixed film with the nonionic surfactant and/or facilitating transfer of the ionized fatty acid across the aqueous interface. Thus, the need for an appropriate counterion for the fatty acid in alkaline solutions is demonstrated.

The poor removal of 5.0% oleic acid/mineral oil soils with LAS systems alone, or containing TEA and no electrolyte, may also be related to the relevant interfacial tensions. Although Table VI shows that the oil/water interfacial energy was significantly lowered by addition of TEA to an LAS solution, no removal or improvement in roll-up was noted. The poor roll-up qualities of such systems are evidently determined by several interfacial contributions, and may involve a relatively low work of adhesion of their solutions to the Mylar and their relatively high surface tension. However, the low oil/water interfacial tension might be expected to promote emulsification of the soil, which was not observed in the absence of added electrolytes. In this case, we suspect inadequate transfer of surfactant across the interface, which is felt to be a prerequisite for effective soil removal, or, as before, an insufficiently coherent interfacial film is present. In the presence of hardness ions, these conditions change, and LAS systems with no builder showed complete and rapid removal by a coarse emulsification of the soil, With TEA added to such systems, emulsification still occurred but substantial residual drops were observed. Apparently, a preferential removal of the fatty acid (and some mineral oil) occurred, leaving the residual soil droplets composed of fatty acid depleted mineral oil. Such effects have been reported by other workers using similar systems (5,52).

OTHER STUDIES

Several other tests were performed in an effort to substantiate some of the previously developed arguments. Table X shows that with no surfactant present in the aqueous phase, increasing amounts of oleic acid in mineral oil soils had adverse effects on roll-up. From Table VI we see that such addition of oleic acid to mineral oil significantly lowered the oil/water interfacial tension, which in most cases has been associated with improved roll-up. However, the conditions are somewhat different in non-detergent systems, since the work of adhesion of water to hydrophobic Mylar film is very low, making the numerator in equation (4) more negative. If it were to become negative, roll-up would be favored by a high oil/water interfacial tension. Indeed, pure mineral oil was found to roll-up much more than mineral oil with added polar constituents in non-detergent systems. However, pure mineral is extremely difficult to remove under such conditions, because the work of adhesion of the Mylar to the oil is much greater that its adhesion to water.

In support of the studies made with nonionic surfactant solutions of low electrolyte concentration, a limited number of tests were carried out with a polar, but non-ionizing constituent in the oil. Considering previously discussed results, 5.0% oleyl alcohol in mineral oil soils should be expected to undergo rapid roll-up regardless of pH or electrolyte strength. As seen in Table X, this was observed. Such rapid roll-up may be attributed to the low oil/water interfacial tension in such systems, which was found to be 1.6 dynes/cm at 25 C for a solution of 0.05% Tergitol 25-L-7 and 0.05% TEA. (Note that although this value is lower than that of pure mineral oil soils, it is not much different from that observed with 5.0% oleic acid in mineral oil under the same conditions.)

Triolein, which is known to be a difficult soil to remove from hydrophobic substrates (5,43), was also used as a model soil. As expected, 0.05% Tergitol 25-L-7 alone could elicit no removal, and only marginal roll-up. With TEA present, the drops became viscous after several minutes, taking on a semi-solid appearance, but no removal was observed. However, in EDTA-built systems the viscous nature of the drops was assumed much faster, with subsequent removal via necking and drawing. A large residual drop remained which was removed by a series of such processes until the film became completely clean (2000 seconds). Apparently, the high pH provided by EDTA aided the penetration of the surfactant into the soil, which undoubtedly contained a small amount of hydrolyzed acid, and this resulted in eventual soil removal. TEA also produced enhanced penetration, but to a more limited extent.

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