1,3-dioxacyclanes in organic solvents (18). Among the dialkyl substituted derivatives of 1,3-dioxolane, (VIa) and (VIb), the *cis*-isomer is oxidized at a higher rate than the *trans*-isomer. This result is consistent with the higher susceptibility of *cis*-isomers to hydrolysis (19). Among the four isomeric glycerol derivatives (VIIa–VIId), the *cis*-dioxolane is oxidized at the highest rate and the *trans*-dioxane at the lowest. We did not find any results on the ozonation reaction of glycerol acetals in the literature. It seems specific and worth noticing, however, that the rates of acidic hydrolysis of isomeric acetals (VIIa–VIId) decrease in the order: *cis*-dioxolane > *trans*-dioxolane > *trans*-dioxane > *cis*-dioxane with the relative rate constants 9.8:5.6:1.4:1 (20).

The investigations shed some light on the oxidative degradation of cyclic acetal-type surfactants in an aqueous environment. The results can provide an additional choice criterion of appropriate derivatives of 1,3-dioxacyclanes as hydrophobic intermediates for surfactant manufacturing.

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Surfactants for Hard-Surface Cleaning: Mechanisms of Solid Soil Removal[1]

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Soil-submersion tests were performed with several solid, organic soils to examine the effects of surfactant structure on soil removal. Results show that hydrophobe size and Hydrophile-Lipophile Balance (HLB) affect soil removal processes. Data also indicate that soil removal first requires penetration of the surfactant (and associated water molecules) into the soil. After this liquefaction process begins, other processes (e.g., emulsification, mechanical action, reduction in soil adhesion) can commence which actually remove soil.

There are three principal mechanisms for removing soil from hard surfaces (Fig. 1). Detergency, or surface-chemical processes, employ surfactants to achieve soil removal. In contrast, mechanical processes use some sort of physical means (abrasion, etc.), and chemical processes involve the use of solvents. In most applications, soil removal is achieved through detergency because it offers a more cost-effective and versatile approach. Most detergency processes, however, rely on some degree of mechanical action to achieve soil removal. Some also rely on chemical solvation of the soil to aid in soil removal (e.g., addition of caustic to saponify and solubilize natural oils and fats).

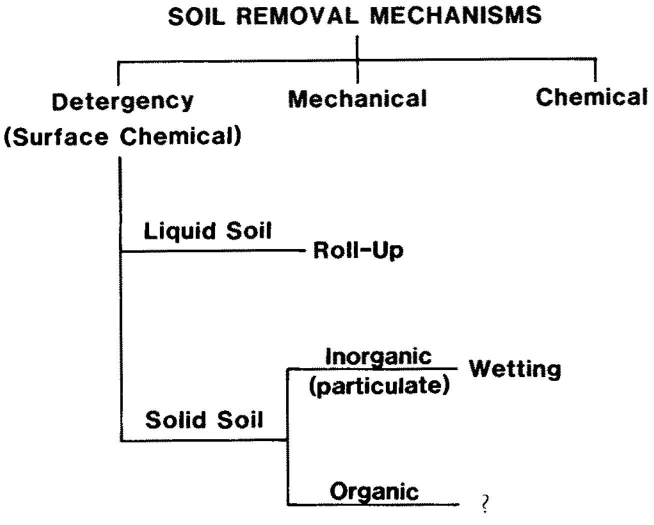

FIG. 1. Major mechanisms involved in the removal of soils from hard surfaces.

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[1] Presented at the 76th Annual AOCS meeting in May 1985 in Philadelphia, PA.

Different surface-chemical mechanisms can be classified according to the type of soil removed. Liquid (oily) soils generally are removed through a "roll-up" mechanism (1). Solid, inorganic (particulate) soils are removed via a wetting mechanism which lowers adhesion between the soil and substrate surface (2). However, the mechanisms involved in removal of solid, organic soils such as greases, waxes and fats, are not well understood.

Diffusion of surfactant into soil has been suggested as a possible mechanism by which surfactants remove solid, organic soils (3). Penetration of surfactant (and associated water molecules) into soil causes it to swell and soften (liquefy). Liquefaction allows soil to be removed more easily through some mechanical process, and permits soil removal via emulsification. This study examines the effect of surfactant structure (molecular weight, carbon chain length, ethylene oxide content) and surfactant type (nonionic vs. anionic) on its ability to penetrate and remove solid, organic soils. The relationship between soil removal and surfactant-soil HLB (Hydrophile-Lipophile Balance) also is discussed, and a model characterizing the soil removal process is presented.

EXPERIMENTAL

Soil submersion tests were performed to measure the relative ability of surfactants to penetrate and/or remove various organic soils. Each test consisted of suspending preweighed soiled-substrate coupons in a series of identical 200-ml solutions of 1.00% (wt/wt) surfactant. Each coupon was submersed at a specific time relative to the length of time desired for submersion. All coupons were removed from their solutions simultaneously, allowed to air-dry for two hr and then reweighed to determine the change in soil-substrate weight. Data were plotted as a function of time submersed in surfactant.

Thin aluminum coupons (3.8 cm in diameter, ∼275 mg in weight) were used as the soil substrate. A 1″ loop of 36 gauge Chromel wire (∼8 mg) was attached to the edge of each coupon for suspending it in solution.

Tests were performed on the three soils listed in Table 1. (Paraffin wax also was examined, but only small, non-reproducible changes in soil weight were observed.)

TABLE 1

Soils Used in Submersion Tests

Soil	Source	Soiling temp. (°F)	Typical soil wt (mg)
Anhydrous lanolin[a]	Mallinckrodt, St. Louis, MO	170	350 +/− 50
Cetyl (hexadecyl) alcohol	Alfol 16 alcohol, Vista Chemical Co., Houston, TX	140	200 +/− 25
Stearin grease (refined lard)	PFAU refined white grease stearin, Geo. Pfau & Sons Co., Jefferson, IN	130	350 +/− 50

[a] Sebaceous excretion of sheep (wool fat).

Soiled coupons were prepared by dipping them in melted soil. Only those soiled coupons falling within a specific weight range and having a visibly uniform layer of soil were used.

The surfactants used in the soil submersion tests are listed in Table 2. All were of commercial quality.

For reference, soil removal was also examined in deionized water. (No significant changes in soil weights were observed.)

Soil-substrate weights were obtained using a 0.1-mg top-loading balance (Sartorius, Model 1602 MP). A tared wire cradle was used to suspend and weigh the coupons on the balance pan.

RESULTS AND DISCUSSION

Development of the test outlined in the previous section was a major step in the study. Submersion times of up to 24 hr were necessary to observe significant differences in the penetration and soil removal properties of various surfactants. Under typical use conditions, however, other factors, such as agitation, abrasion, higher surfactant concentrations, etc., would accelerate the rates observed under static conditions.

All soil-substrate weight data are normalized with respect to surface area (constant 22.7 cm^2) and not soil weight. Because of the methodology employed in soiling the substrate coupons, differences in initial soil weight often exceed the changes observed in weight after submersion in surfactant. However, as shown in Table 3, changes in soil weight occurring during submersion are primarily a function of surface area, and not soil weight.

Test reproducibility varied somewhat depending on the soil and surfactant employed. Although it was not routinely measured, results with replicate solutions (Table 3) showed less than a 10% variation. In addition,

TABLE 2

Surfactants Used in Submersion Tests

Nonionic surfactants

Surfactant	Alcohol base	% EO	Moles EO
8-60	C_8, linear, primary	60	4.5
12-55[a]	C_{12}, linear, primary	55	4.7
12-60	C_{12}, linear, primary	60	6.3
12-70	C_{12}, linear, primary	70	9.8
12-80	C_{12}, linear, primary	80	17
NPE-60	Nonylphenol	60	7.5
NPE-65	Nonylphenol	65	9.0
NPE-75	Nonylphenol	75	15

Anionic surfactants

Surfactant	Avg. carbon chain length	Avg. mol. wt.	Typical % 2-phenyl isomer content
C_{11} LAS	11.4	339	28.6
C_{12} LAS	12	343	14.5
C_{13} LAS	13	363	11.5

[a] 1:1 Blend of C_{12}-50% EO/C_{12}-60% EO surfactants.

each series of tests described below was performed in such a way as to maximize reproducibility (all submersion tests were performed simultaneously using the same batch of soiled coupons).

SOIL REMOVAL VS. SURFACTANT STRUCTURE

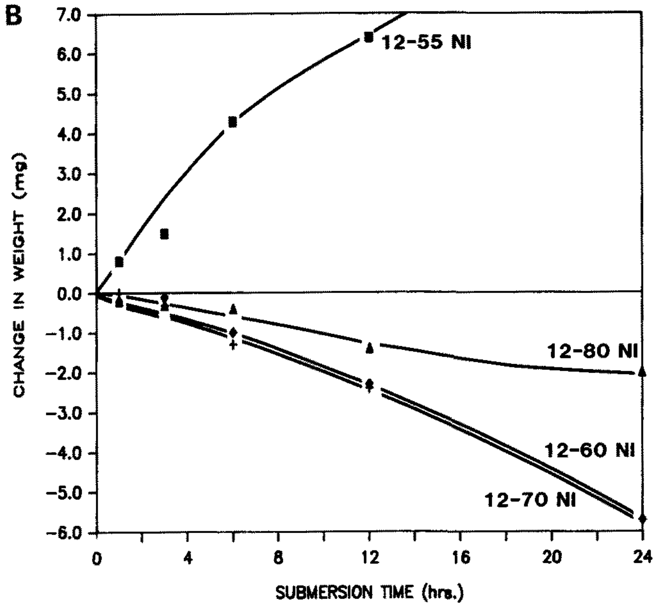
Effect of nonionic EO content (HLB). The effects of ethylene oxide (EO) content on lanolin, cetyl alcohol and stearin grease soils are shown in Figure 2. With anhydrous lanolin (Fig. 2A), all surfactants produce an initial increase in soil weight, indicating surfactant penetration into the soil has occurred. As expected, the initial rate of penetration is a function of surfactant solubility. As EO content (water solubility) is reduced, penetration increases because surfactant is more strongly adsorbed at the soil-water interface. After 24 hr of submersion, however, the 70% and 80% EO surfactants show a net increase in soil weight, and the 55% and 60% materials show a net decrease in soil weight. Because the 55% EO (HLB = 11) and the 60% EO (HLB = 12) surfactants are best suited to emulsify lanolin [optimum HLB = 12 (4)], soil removal appears to involve an emulsification-type mechanism. A pre-emulsification process

TABLE 3

Effect of Soil Weight on Submersion Tests

With 1 hr submersion				
Wt (g) coupon	Wt (g) soil	Wt (g) soil + coupon	Wt (g) after 1 hr submersion	Change in soil wt (mg)
0.2851	0.3187	0.6038	0.6072	3.4
0.2813	0.2969	0.5782	0.5814	3.2
0.2834	0.2489	0.5323	0.5355	3.2
0.2826	0.2875	0.5729	0.5761	3.2

With 6 hr submersion				
Wt (g) coupon	Wt (g) soil	Wt (g) soil + coupon	Wt (g) after 6 hr submersion	Change in soil wt (mg)
0.2822	0.2640	0.5462	0.5508	4.6
0.2849	0.2336	0.5185	0.5232	4.7
0.2837	0.3015	0.5852	0.5902	5.0
0.2832	0.2534	0.5366	0.5411	4.5



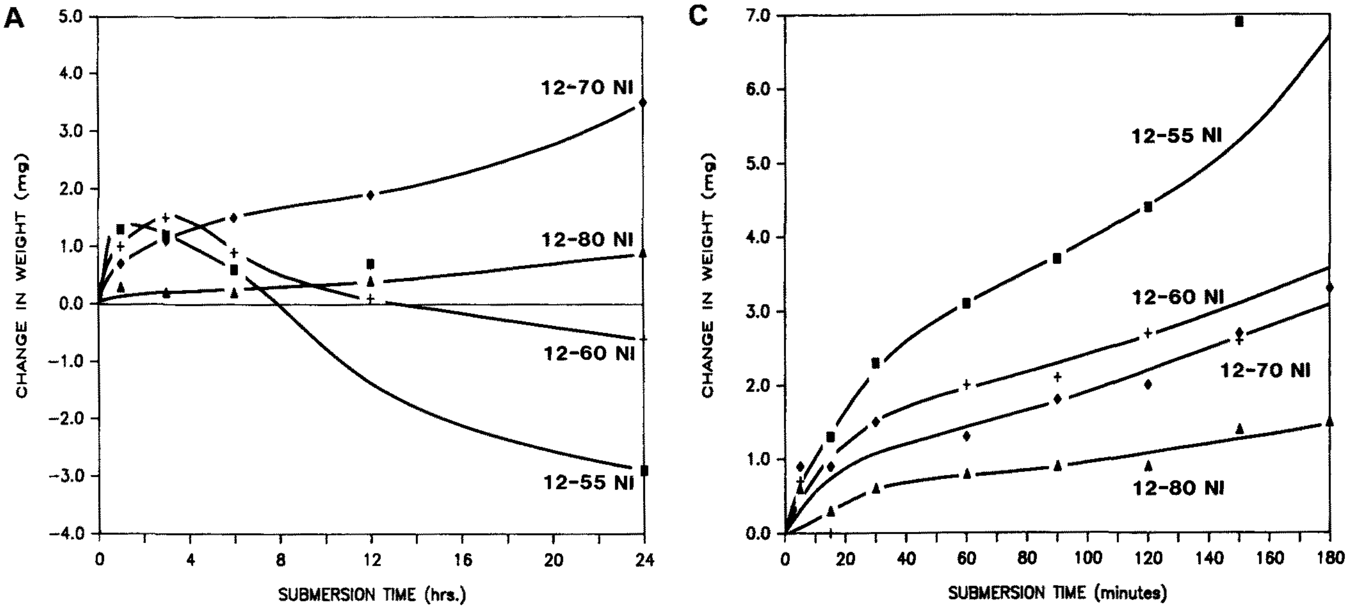


FIG. 2. Effect of ethylene oxide content (of C_{12} alcohol nonionic) on soil-substrate weight with (A) lanolin, (B) cetyl alcohol, and (C) stearin grease soils.

must also be involved because solid material cannot, by definition, be emulsified. This pre-emulsification step apparently involves surfactant penetration because effective soil removal does not begin until after a certain degree of penetration has occurred. In addition, the fact that the curves obtained with the 55% and 60% EO surfactants show a peak or maximum in soil weight suggests that at least two different processes (one which increases soil weight and one which decreases soil weight) are taking place simultaneously.

With cetyl alcohol (Fig. 2B), different trends are observed. While 60%, 70% and 80% EO surfactants reduce soil weight, the 55% EO surfactant significantly increases soil weight (18.6 mg after 24 hr submersion, which corresponds to an increase of approximately 9.5%). These results are also a function of the ability of surfactants to penetrate and emulsify the soil. The 55% EO surfactant is the least water-soluble (most oil-soluble) surfactant. It shows the greatest increase in soil weight because it is best able to penetrate the soil but least effective in emulsifying it (optimum HLB for cetyl alcohol = 14–15). In contrast, the 70% EO surfactant does not penetrate well, but it is the most effective in emulsifying the soil, so it shows the greatest decrease in soil weight.

In comparison to lanolin, initial penetration of the soil does not appear to be required before effective soil removal takes place. However, it is likely that some degree of penetration does occur in conjunction with the soil removal process, but that its effect on soil weight is masked by that of the soil removal process itself. As long as the rate of soil removal exceeds the rate of penetration (weight gain), a net loss in soil weight will be observed.

Results with stearin grease are less conclusive because of the rapidity by which surfactants penetrate the soil. Submersion times greater than 180 min could not be used reliably, because the soil would often swell and soften to the point where it would break up during removal from solution. As shown in Figure 2C, a lower EO content yields a higher rate of penetration.

Similar trends are observed with nonylphenol ethoxylates (Fig. 3).

Effect of nonionic hydrophobe size. The effect of nonionic carbon chain length (C_8 vs C_{12}) is shown in Figure 4. A shorter chain length produces a significant increase (at least initially) in the rate of surfactant penetration with all three soils. A shorter chain hydrophobe apparently increases the ability of the surfactant to diffuse through solid, organic soils.

The results obtained with cetyl alcohol (Fig. 4B) also illustrate the relationship between soil removal and surfactant penetration. Although the 12-60 NI is better suited to emulsify soil (because of its longer chain length), the 8-60 NI is observed to be better at removing cetyl alcohol. This is evidently a result of its significantly higher rate of penetration. After some degree of penetration has occurred, the soil removal process is accelerated due to the change in the emulsification behavior of the soil.

Effect of Butyl Cellosolve. Butyl Cellosolve (ethylene glycol monobutyl ether) is often used in conjunction with nonionic surfactants, especially nonylphenol ethoxylates, to improve the solvency characteristics of the hard-surface cleaner. The effect of Butyl Cellosolve (BC) was

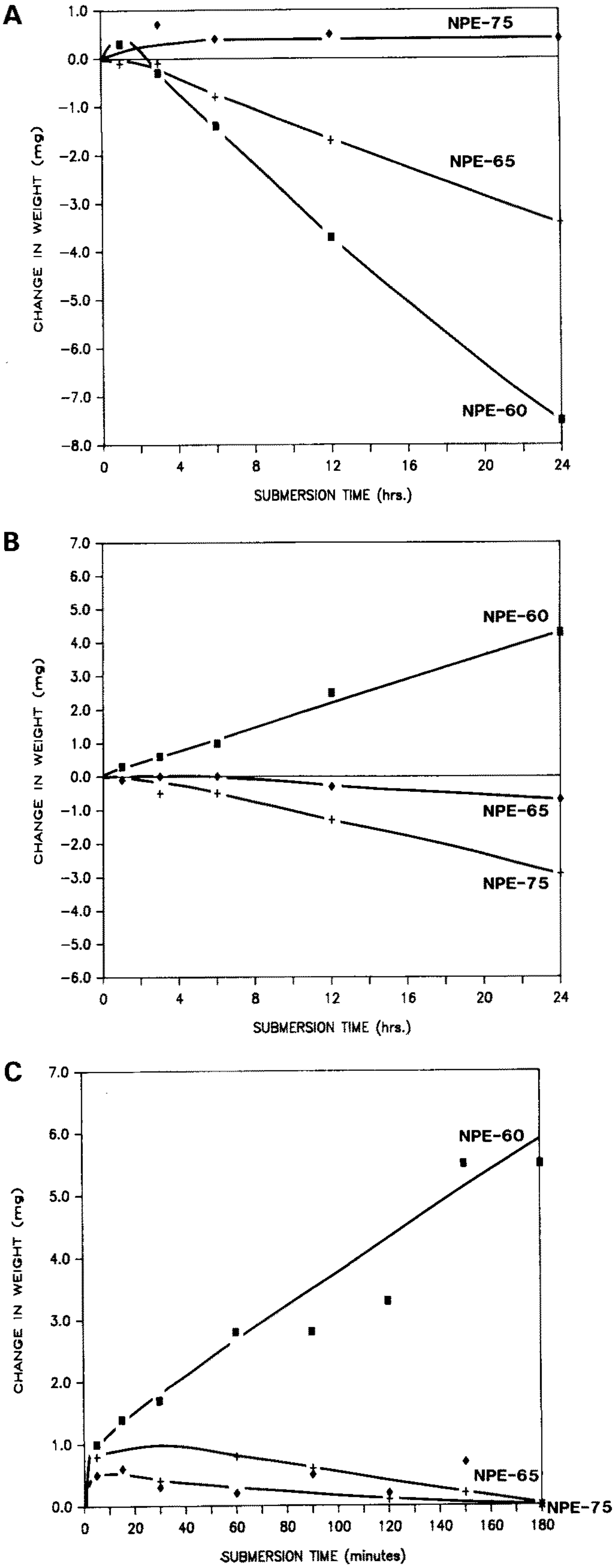


FIG. 3. Effect of ethylene oxide content (of nonylphenol ethoxylate) on soil-substrate weight with (A) lanolin, (B) cetyl alcohol, and (C) stearin grease soils.

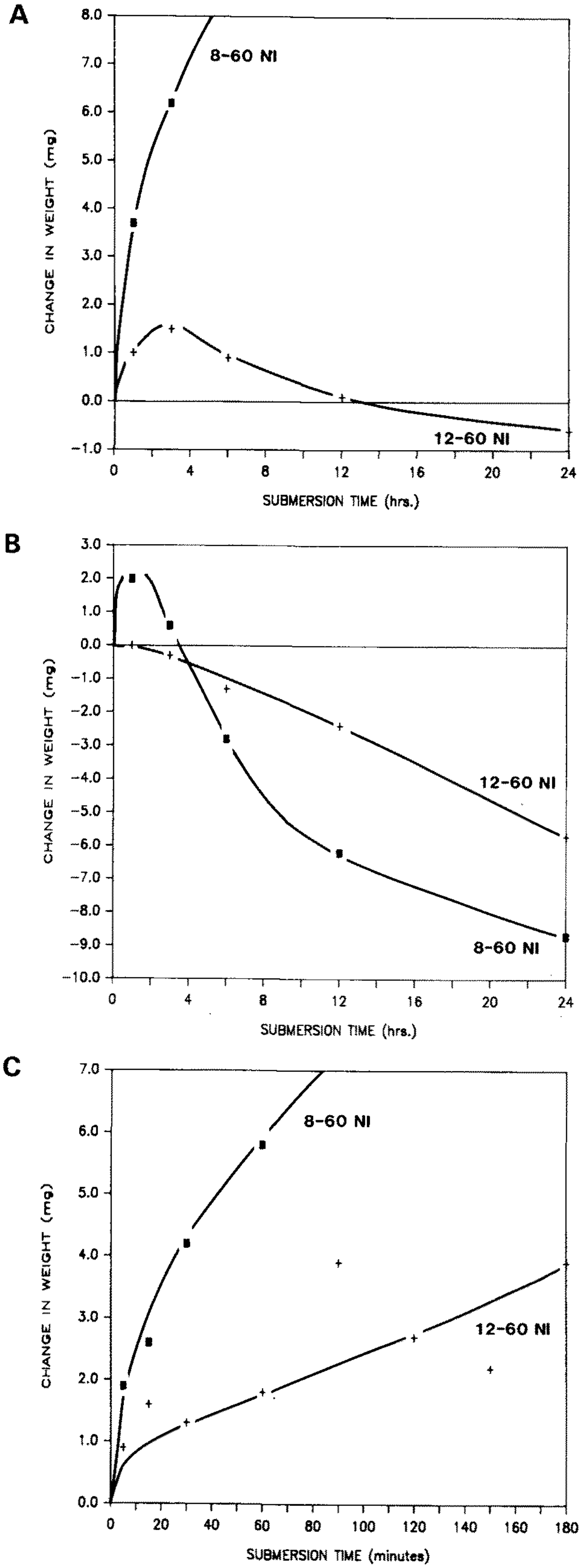


FIG. 4. Effect of carbon chain length (of C_{12} alcohol nonionic) on soil-substrate weight with (A) lanolin, (B) cetyl alcohol, and (C) stearin grease soils.

examined by comparing the penetration/soil removal performance of NPE and several NPE/BC blends. In summary, results showed that partial substitution of surfactant by BC produces only a slight increase in the initial rate of penetration and a slight decrease in the rate of soil removal.

Effect of LAS molecular weight. The performances of three different molecular weight linear alkylbenzene sulfonates (LAS) are shown in Figure 5. On lanolin soil (Fig. 5A), all LAS materials show a capacity to remove soil, especially C_{13}-LAS. As observed with nonionic surfactants, the rate of soil removal is related to the ability of the surfactant to emulsify the soil. C_{13}-LAS, because of its longer chain length, is the better emulsifier and consequently is best in promoting soil removal.

The unexpected increase in weight occurring with C_{13}-LAS between 12 and 24 hr submersion is of particular interest because it illustrates a different aspect of the relationship between surfactant penetration and soil removal. Although the 24-hr data point was suspect initially, other data (Fig. 6A, etc.) suggest that an increase in the rate of penetration does occur after a certain degree of soil removal has taken place. This appears to be the result of preferential extraction of specific soil species by the surfactant. Because lanolin is a complex mixture of esters and polyesters (of high molecular weight alcohols and fatty acids), it is reasonable to assume that certain soil components are more easily emulsified. The rapid removal of these components would logically cause an initial surge in the rate of soil removal.

The effect of LAS molecular weight observed with cetyl alcohol (Fig. 5B) differs from that observed with lanolin. Although C_{13}-LAS remains best at soil removal, significant differences in performance are observed between C_{12}- and C_{11}-LAS. Apparently the greater rate of initial penetration observed with C_{11}-LAS is responsible for its ability to remove soil at a faster rate than C_{12}-LAS. The reason for this faster penetration rate, however, is not understood.

Results with stearin grease (Fig. 5C) show that surfactant penetration is a function of surfactant solubility. Increasing LAS molecular weight decreases water-solubility (increases oil-solubility), which results in a corresponding increase in the ability of the surfactant to penetrate the soil. Consequently, C_{13}-LAS shows the most rapid increase in soil weight, followed by C_{12}-LAS, and finally C_{11}-LAS.

Effect of LAS solubility (addition of Mg^{+2}). In addition to increasing hydrophobe carbon chain length, LAS solubility can be reduced through the addition of divalent cations such as Mg^{+2} and Ca^{+2}. The effect of Mg^{+2} was examined by comparing the penetration and soil removal properties of C_{12}-LAS vs C_{12}-LAS + 0.006 M Mg^{+2}. This concentration of magnesium (with 1% LAS) gives a LAS:Mg^{+2} molar ratio of 2:1.

With lanolin (Fig. 6A), the addition of Mg^{+2} increases the rate of initial soil removal and the overall rate of surfactant penetration. As previously discussed, the unusual curve obtained with the LAS/Mg^{+2} blend results from the rapid removal of specific soil components during the early stages of submersion. Cetyl alcohol and stearin grease soils both show that the addition of Mg^{+2} dramatically increases the rate of soil penetration. With cetyl alcohol (Fig. 6B), soil weight increases by more than 29% after

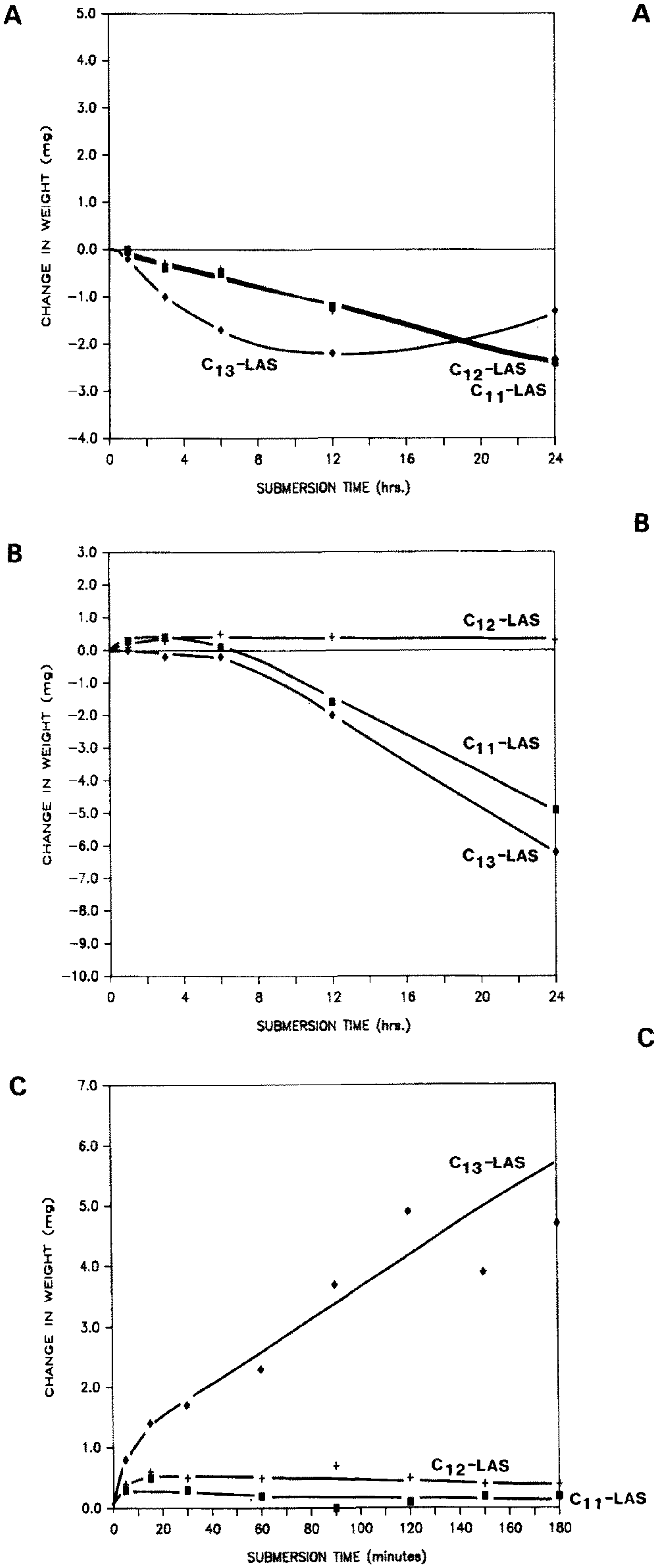
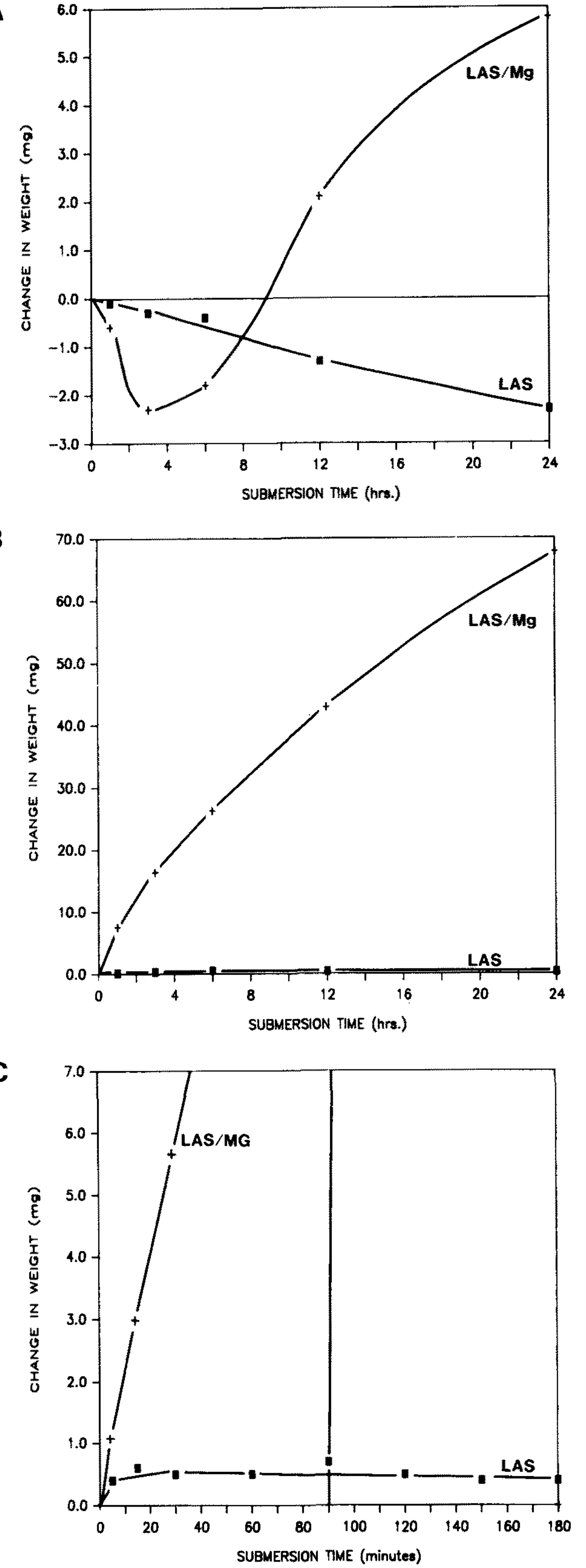


FIG. 5. Effect of LAS carbon chain length on soil-substrate weight with (A) lanolin, (B) cetyl alcohol, and (C) stearin grease soils.



A

B

C

FIG. 6. Comparison between C_{12}-LAS and a 2:1 (molar) blend of C_{12}-LAS and Mg^{+2} with (A) lanolin, (B) cetyl alcohol, and (C) stearin grease soils.

24 hr submersion. With stearin grease (Fig. 6C), penetration proceeds rapidly until the soil, as a whole, breaks away from the substrate coupon. (Apparently, sufficient surfactant and water diffuse through the soil to reduce soil-substrate adhesion). These results suggest that combinations of LAS and Mg^{+2} would be very effective in applications where soil-softening is important.

The fact that Mg^{+2} can complex with alcohol soil components via Lewis acid-base interactions may play a role in the results discussed above.

CORRELATION OF DATA WITH MECHANICAL ABRASION TESTING

Other studies using traditional performance tests show that changes in surfactant molecular structure which increase penetration rate also lead to improved hard-surface cleaning (3,5). Surfactant penetration apparently prepares (softens) the soil for mechanical removal, as discussed below.

MECHANISMS OF SOIL REMOVAL

The results discussed above suggest soil removal is a two-step process (Figs. 7 and 8). Liquefaction, the key step in the mechanism, involves penetration of surfactant (and associated water molecules) into the soil. This soil-softening process prepares the soil for other processes which actually remove soil from the substrate. These secondary processes include emulsification, the reduction of soil-substrate adhesion by wetting the substrate surface, and simple agitation or mechanical abrasion.

The mechanism described above also suggests several ground rules for developing hard-surface cleaners to remove solid, organic soils.

(i) Products used in applications involving some degree of mechanical action should use a surfactant which maximizes penetration (soil-softening). This can be accomplished by minimizing both surfactant hydrophobe size and water-solubility. Both nonionic (e.g., 8-60 NI) and anionic (e.g., $Mg[LAS]_2$) surfactants are effective, although their relative performance appears to depend upon soil composition.

(ii) In applications involving static soil removal, the ability of the surfactant to emulsify the soil should be maximized. This is best accomplished by matching the HLB of the surfactant to that of the soil.

(iii) In some applications, it may be beneficial to use a blend of surfactants which maximize penetration and emulsification.

The soils used in the experiments discussed above all contain polar components. The fact that paraffin wax (nonpolar) was found to be insensitive to submersion suggests that soil removal may involve polar attraction of the surfactant to the soil surface.

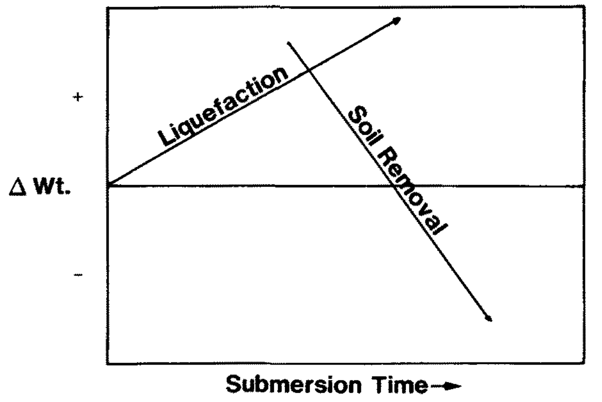


FIG. 7. Plot correlating soil weight with soil removal processes.

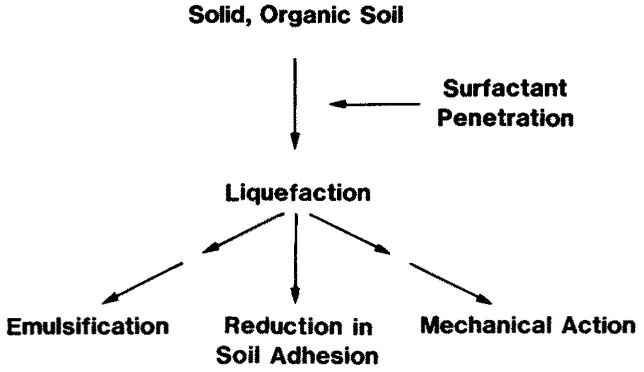


FIG. 8. Proposed model correlating surfactant penetration (liquefaction) with soil removal processes.

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