♣Optimization of Nonionic Surfactants for Hard-Surface Cleaning

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ABSTRACT

The hard-surface cleaning performance of various nonionic homologs was evaluated as a function of carbon chain length, ethylene oxide (EO) content, blending and concentration. Results show carbon chain length to be very important to hard-surface cleaning. Performance significantly increases as carbon-chain length decreases, probably as a result of an increase in solvency properties as carbon chain length is decreased. EO content is also important, particularly if nonionics with longer carbon chain lengths are used. Surfactant concentration (dilution) has little effect on the optimum ethylene oxide content but significantly affects the optimum carbon chain length of the hydrophobe. With 5% homolog solutions, the optimally performing nonionic contains a C6 hydrophobe, but with 0.2% solutions, the optimal carbon chain length is shifted to the C8-C10 range. This is thought to result from a trade-off between the surfactant and solvent properties of the nonionic. Overall results show the optimal nonionic for hard-surface cleaning to consist of a blend of C6, C8 and C10 alcohols ethoxylated to a 50% EO level. Commonly used surfactant systems, e.g., alkylphenol ethoxylates and alkylphenol ethoxylate (APE)-butyl cellosolve (BC) blends, were also examined. Results show that alkylphenol ethoxylates give relatively poor performance compared with lower molecular weight linear nonionics because of the large size of their hydrophobe. Under concentrated use, a synergism does exist between APE and BC, but under dilute conditions, the addition of BC is ineffective. BC does not help the performance of low molecular weight nonionics. Surfactant-soil diffusion studies indicate that surfactant penetration of the soil may be the primary mechanism involved in the hard-surface cleaning of solid soils.

INTRODUCTION

Many surfactants are used in hard-surface cleaners. One popular surfactant system consists of a mixture of alkylphenol ethoxylate (APE) and butyl cellosolve (BC). Although the question of biodegradability has prevented the widespread use of APE in laundry products, their availability and relatively low cost have made them attractive to manufacturers of hard-surface cleaners. BC is often added to APE-based cleaners to enhance their grease-cutting properties. The nature of this enhancement has been assumed to be the result of the solvency properties of butyl cellosolve.

Another popular surfactant system for hard-surface cleaners is a mixture of nonionics that vary in ethylene oxide (EO) content. Usually an oil-soluble ethoxylate is added to improve performance on oily soils and a water-soluble nonionic is present for cleaning particulate soil and to solubilize the nonwater-soluble ethoxylate. This approach assumes that the optimum nonionics for cleaning oily soils and particulate soils are different.

Little evidence is available to justify either surfactant system. Consequently, this study was designed to determine the effect of surfactant composition on performance in order to determine the optimum nonionic for hard-surface cleaning.

The approach used was to first develop a reproducible and representative test for measuring the hard-surface cleaning performance of various materials using soils and substrates commonly encountered by the consumer. The performances of several series of nonionic homologs varying

in ethylene oxide content were then tested to determine the effect of nonionic composition on hard-surface cleaning. The effects of other variables, e.g., surfactant concentration and blending, were also examined. Commercially available surfactants were then evaluated to determine which nonionic system is best for hard-surface cleaning applications.

EXPERIMENTAL

Performance Testing

Hard-surface cleaning performance was tested using a Gardner Straight Line Washability and Abrasion Machine that was modified to improve reproducibility and permit the simultaneous testing of 3 different cleaning solutions. Figures 1 and 2 illustrate the experimental setup.

Mohair strips (1½" × 8") were attached to Lucite® blocks giving a 1½" × 3½" cleaning surface. Each block was fitted into a weighted holder. All 3 weighted mohair cloth assemblies weighed 575 ± 10 g.

Mohair cloth (National Novelty Brush Company, Lancaster, PA) was used instead of brushes or sponges because it is inexpensive, can be discarded after use, gives more reproducible results and represents a compromise between the 2 conventional materials.
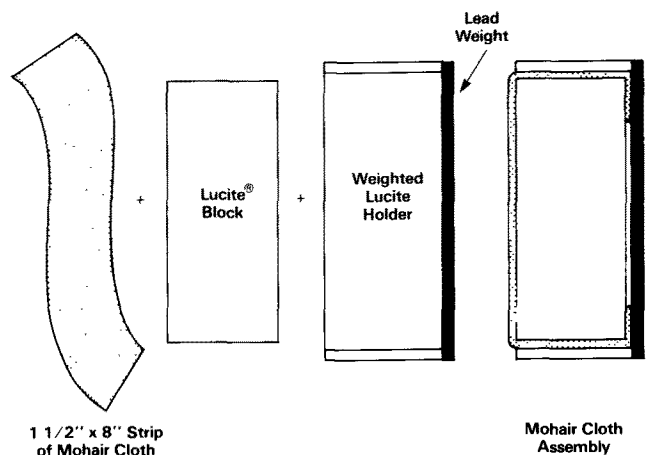

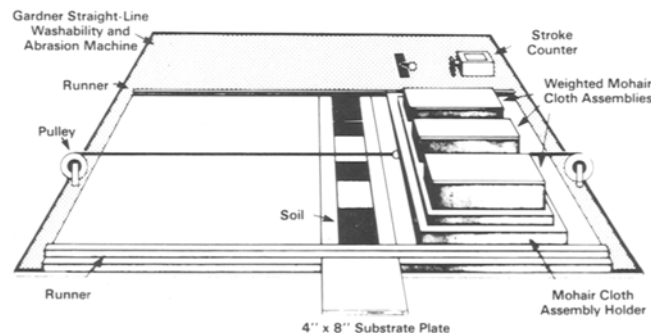FIG. 1. Schematic showing construction of mohair cloth assembly.

FIG. 2. Schematic of hard-surface cleaning test apparatus.

Each mohair assembly was placed in ca. 50 mL of pre-mixed solution for ca. 15 sec. The assemblies were then transferred to the sample assembly holder and the test apparatus started. Cleaning resulted from the solution-wetted mohair strips passing over the soil-substrate plate. Cleaning continued until one test area subjectively approached the reflectance of the unsoiled substrate.

The cleaning index (relative cleaning performance) was determined by dividing the difference between the reflectance (Rd) of the soiled substrate and the clean substrate by the number of test strokes:

$$\text{Cleaning Index (CI)} = \frac{(\text{Rd clean}) - (\text{Rd soiled})}{\text{Number Test Strokes}}.$$

A sample calculation of CI is shown in Table I. A higher CI indicates better cleaning performance.

CI values are relative and reflect the performance of the test solutions under a given set of conditions. Results within a single test varied by less than ca. 10%. To correlate results among different tests, one of the formulations of a given series was employed in each run as a reference. Also, because the number of test strokes vs CI is nonlinear, the number of test strokes for each soil was kept constant when testing a series of similar surfactant solutions. For example, when grease soil was employed, 10 test strokes were used when testing 5% surfactant solutions, whereas 20 test strokes were used when testing their dilutions (1:30). Using a specific number of test strokes for all tests was impossible because different solutions and soils required different degrees of mechanical abrasion. The soils used to test cleaning performance are listed in Table II.

Each soil was applied to a 2 in. wide center strip of the substrate. The substrate consisted of a 4″ × 8″ sheet of 1/8 in. masonite covered with 2 coats of a white latex semigloss paint. The grease-carbon soil was applied to the substrate using a brush and was smoothed to a uniform film using a strip of mohair cloth stretched over the edge of a thin plate. The black wax soil was applied by making multiple passes over the soil area using a straight edge. The soil was then melted using a heat gun and the soil spread evenly over the surface with a piece of cloth. Particulate soiled substrate was made by simply rubbing an excess of graphite powder over the surface area.

TABLE I

Example of Cleaning Index Calculation for Evaluation of Hard-Surface Cleaning Performance

Sample	Soiled Rd	Cleaned Rd	Number of test strokes	CI
A	4.1	37.6	10	3.4
B	5.2	67.2	10	6.2 (Best)
C	4.7	49.3	10	4.5

For solution A, $\text{CI} = \dfrac{\text{Cleaned Rd} - \text{Soiled Rd}}{\text{Number Test Strokes}} = \dfrac{37.6 - 4.1}{10} = 3.4.$

TABLE II

Soils Used in Testing Hard-Surface Cleaning Performance

Soil type	Brand
Grease	Conoco "Super-Sta" Grease With 1% Carbon Black
Wax	Blaisdell 373-T Black Wax Marker
Particulate	Fisher Grade No. 38 Graphite Powder

Before use, the reflectance of each soiled plate was measured using a Gardner (Model XL20) colorimeter. The reflectance of each region to be cleaned was measured to determine soil uniformity.

Soil/Surfactant Interaction Study

The effect of submersing a solid soil in a surfactant solution on soil weight was examined. Thin aluminum plates (4 cm in diameter) were dipped in melted lard (Pfau "Peacock" Refined White Grease Stearine). Ca. 200 mg of lard covered each plate in a thin uniform film. The aluminum-lard plates were suspended in various 5% surfactant solutions. Periodically, each plate was withdrawn from solution, allowed to drain and its weight recorded using a Cahn (Model 2000) microbalance. Change in weight vs time was recorded.

Lard soil was employed because it is solid at room temperature and can be melted to provide a simple means of applying an even, thin film of soil. Grease and wax soils used in performance testing were unacceptable.

RESULTS AND DISCUSSION

The effect of nonionic composition on hard-surface cleaning was tested using several series of C6, C8, C10, C12 and C14 nonionic homologs that varied in EO content. The nonionic homologs were derived from ALFOL® alcohols and were ethoxylated in our laboratory.

Effect of Carbon-Chain Length

The effect of alcohol carbon-chain length on the hard-surface cleaning of grease, wax and particulate soils is shown in Figures 3A, B, and C. Two series of 5% nonionic homologs were tested: one with 40% EO, the other with 60% EO. Although both series are plotted together, each was tested independently. Comparisons should not be made between the 2 series. The CI range given for each soil represents the difference between well-cleaned substrate and soiled (untested) substrate.

As shown, cleaning performance decreases dramatically on all soils as carbon chain length is increased. This is probably caused by an increase in the solvent character of the nonionic surfactant as size of the hydrophobe decreases. Ethoxylates made from C2 and C4 alcohols are known to be relatively good solvents. However, surface activity decreases as size of the hydroprobe decreases. A C4 ethoxylate with 40% EO shows very poor performance because it is a poor surfactant. The C6 homolog apparently gives optimal performance because it has the best combination of surface activity and solvency.

Effect of EO Content

The effect of EO content on cleaning performance is shown in Figures 4A, B and C. Because lower molecular weight is important to cleaning performance, only C6, C8 and C10 homolog groups were tested. Each group contained 4 nonionics made from the same molecular weight alcohol that were ethoxylated to 30%, 40%, 50% and 60% EO levels. Each group was tested separately using 5% surfactant solutions.

The optimum EO content for cleaning the grease soil (Fig. 4A) is shown to be ca. 50% adduct. The C10 series is most affected by change in EO. The better performing C6 series of nonionics show a much smaller effect indicating carbon chain length is more important to cleaning performance than EO.

A different trend is observed with the wax soil (Fig. 4B). The C10 series of nonionics is not affected by EO content and the C8 series shows only a slight decrease in performance as EO increases. The most significant change in clean-
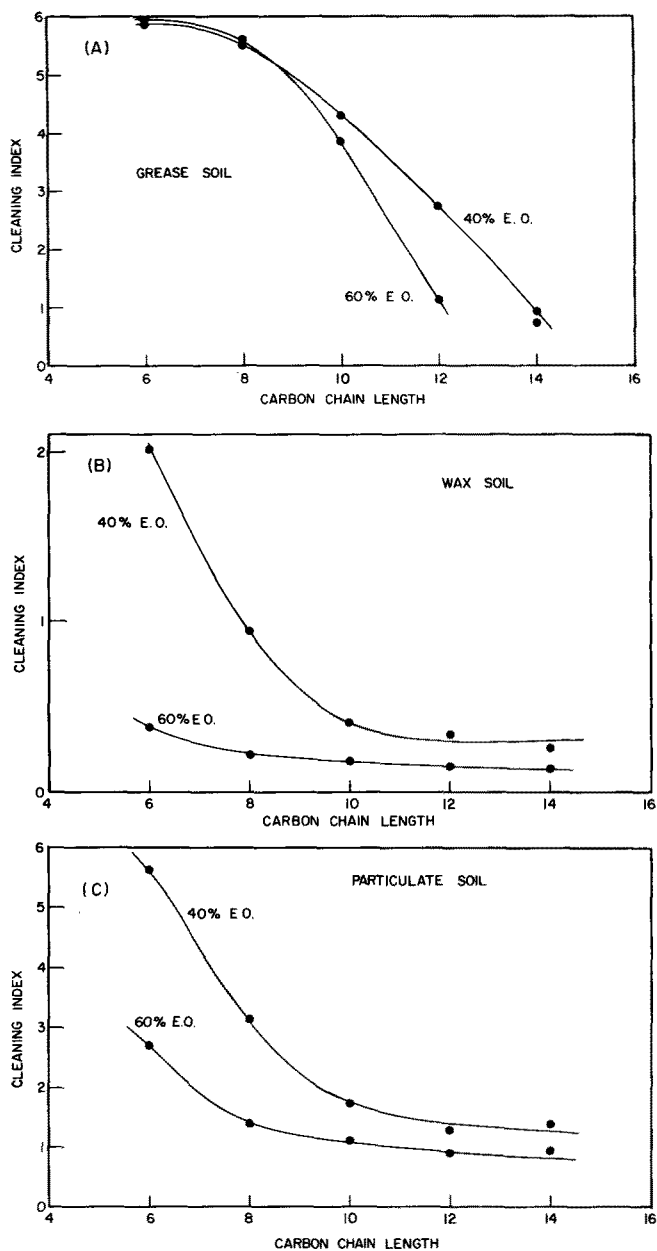
FIG. 3. Hard-surface cleaning performance of nonionic homologs (5% solutions) as a function of carbon chain length on: (a) grease soil; (b) wax soil; (c) particulate soil.
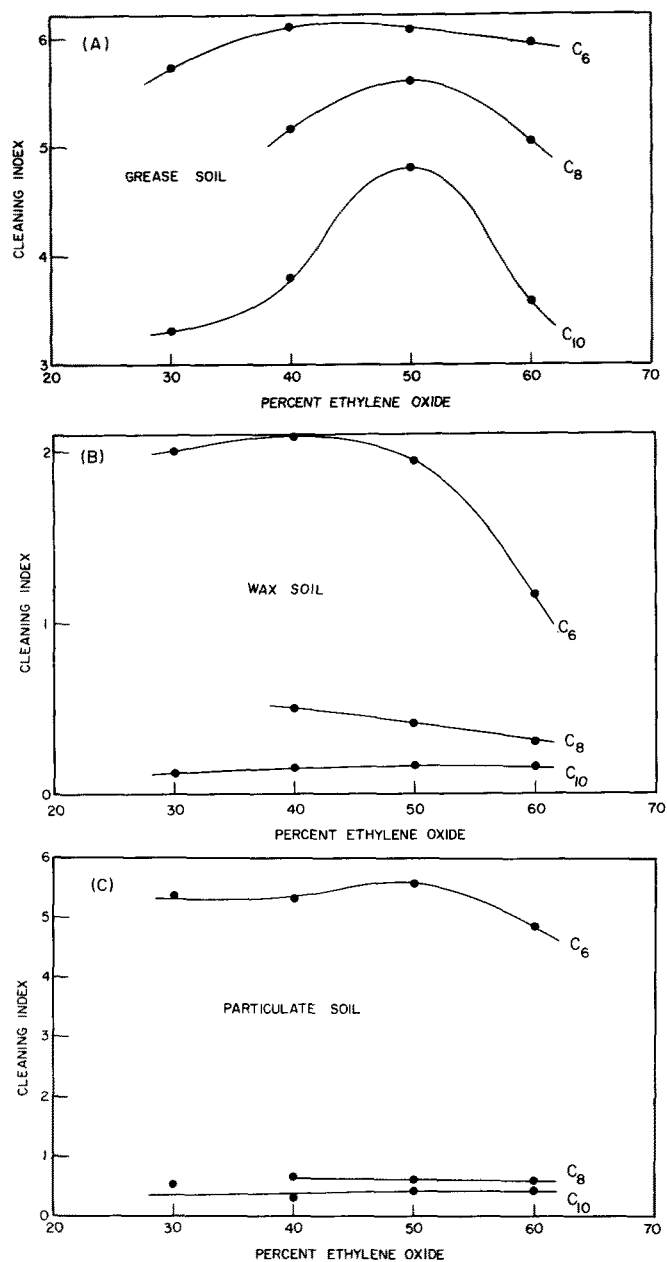

FIG. 4. Hard surface cleaning performance of nonionic homologs (5% solutions) as a function of ethylene oxide content on: (a) grease soil; (b) wax soil; (c) particulate soil.

ing performance occurs with the C6-60% EO nonionic, which shows poorer performance than its lower EO counterparts. The other C6 materials show good cleaning performance, indicating that oil-soluble nonionics are best for cleaning waxy soils.

Results on particulate soil (Fig. 4C) show trends similar to those observed with the wax soil. EO content does not greatly affect the performance of the C8 and C10 series of nonionics and only slightly affects the performance of the C6 materials. The optimum C6 nonionic contains a 50% EO adduct.

Effect of Dilution

Because many hard-surface cleaners are used in diluted form, the effects of carbon chain length and EO content were examined using 1:30 (0.17%) dilutions of the previously described 5% nonionic homolog solutions.

Figures 5A and B show the effect of dilution on the

relationship between cleaning performance and carbon chain length. Again, comparisons should not be made between the 2 curves shown in each figure because they were obtained using different numbers of test strokes.

As shown, under dilute concentration the optimum carbon chain length is shifted from a C6 nonionic to a C8-10 material. This is probably the result of the C8 and C10 homologs being better surfactants than the C6 nonionic. The C6 material is best at high concentrations where plenty of surfactant is available for lowering interfacial tension, but under dilute conditions, the advantage it has in having a shorter chain length is insufficient to make up for its relatively poorer surface activity. This suggests a trade-off between the solvency properties of a nonionic surfactant and its surface activity. Reducing carbon chain length appears to increase the solvent properties of a nonionic, which are important to cleaning performance. However, under dilute concentrations, better surfactant proper-
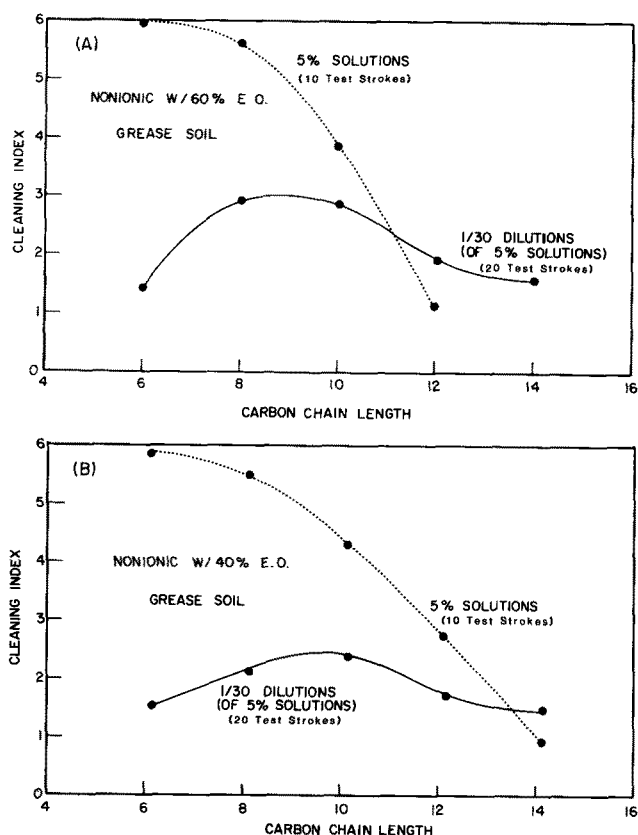
FIG. 5. Effect of dilution on the hard-surface cleaning performance of nonionic homologs containing: (a) 60% ethylene oxide; (b) 40% ethylene oxide (using grease soil).
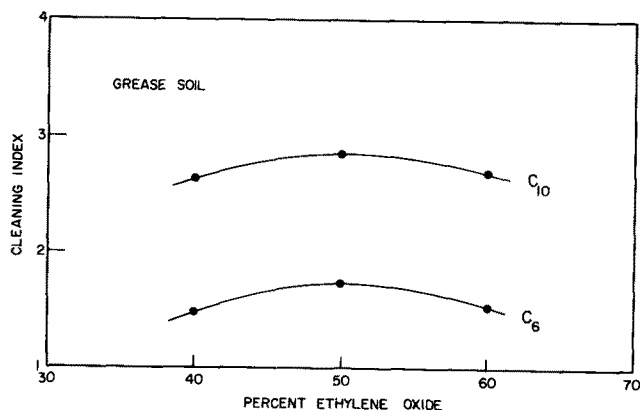

FIG. 6. Hard surface cleaning performance of diluted nonionic homologs (0.17% solutions) as a function of ethylene oxide content.

ties are required to concentrate the nonionic at the soil-water interface where it is needed. This requires a slightly larger hydrophobe.

The effect of EO content on cleaning performance using diluted homologs is shown in Figure 6. The optimal EO content is a 50% EO adduct. Because the 50% nonionics are sparingly water soluble, they will more readily reside at the soil-water interface. This concentration of the surfactant at the interface would logically improve performance.

Trends similar to those shown in Figures 5 and 6 (with grease soil) were observed with the wax and particulate soils.

Effect of Blending

The effect of blending was tested by comparing the cleaning performance of a C8-50 (% EO) nonionic to a 1:1 blend

TABLE III

Effect of Blending on Hard-Surface Cleaning Performance

	Percentage increase in cleaning index (relative to C8-50 nonionic)		
Blend	Grease oil (%)	Wax oil (%)	Particulate soil (%)
1:1 C6-50/C10-50	12	21	28
1:1 C8-40/C8-60	5	17	48

of C6-50 and C10-50 homologs and to a 1:1 blend of C8-40 and C8-60 homologs. The relative performance of each blend in comparison to the C8-50 homolog is given in Table III.

As shown, blending aids performance, especially on the wax and particulate soils. This is presumably because the soils themselves are heterogeneous in nature. Logically, heterogeneous surfactants would provide better cleaning.

Nonionic Optimization

Based on the results of the homolog studies, the optimum nonionic under fairly concentrated conditions would consist of a C6 alcohol with ca. 50% EO. The best nonionic for performance under dilute conditions would be derived from a C8-10 alcohol, also with 50% EO. For hard-surface cleaning, overall, a nonionic consisting of a C6, C8 and C10 alcohol blend with 50% EO would give optimal performance at a variety of use concentrations.

Evaluation of Commercial Nonionics

A series of commercial (ALFONIC®) nonionics were tested on each soil to determine if the trends observed with the nonionic homologs are observed with commercially available surfactants. Table IV lists the compositions of the nonionics tested.

Because the CI range depends on soil type, results are given as they relate to the performance of the best performing nonionic. This allows a single scale to be used for evaluating performance on all soils.

Test results are shown in Figure 7. As expected, the C6-10-50% EO nonionic (610-50) performs best on all 3 soils because of its lower carbon chain length. In general, cleaning performance follows the same trend of decreasing performance with increasing hydrophobe size. EO content also affects performance, especially on particulate soil. The performances of the C12-14 surfactants (1412-40, 1412-60 and 1214-70 nonionics) on particulate soil show that cleaning improves as EO content is increased. This is contrary to the trend observed with nonionic homologs. Apparently, with particulate-type soils, EO content becomes more important when using surfactants having greater carbon chain lengths. The opposite trend is seen on wax soil. The 1216-22 nonionic performs well on wax soil, confirming previous results showing oil-soluble nonionic surfactants to clean best. Although the effect of EO content is important, optimal performance is primarily a function of carbon chain length.

The performance of the 610-50 nonionic was compared with that of the popular nonylphenol ethoxylate-BC blend using the following built formulation: 5 to 15% Surfactant; 10% SXS (As is); 5% TKPP; 2% Metasilicate (As is); q.s. Water.

Formulations containing 5%, 10% and 15% 610-50 nonionic were tested vs a formulation containing 10% nonylphenol ethoxylate (NPE) and 5% BC. For reference, a formulation containing 15% NPE was included. The NPE used contained 9½ mol EO.

TABLE IV

Nonionics Used in Performance Testing

Nonionic	Alcohol blend*	Average carbon chain length	Percentage of EO	Moles EO
610-50	C6, C8 and C10	C8.6	50	3.1
1012-60	C10 and C12	C10.5	60	5.6
1214-70	C12 and C14	C12.7	70	10.3
1216-22	C12, C14 and C16	C12.9	22	1.3
1412-40	C12 and C14	C13.4	40	3.1
1412-60	C12 and C14	C13.6	60	6.9

*Linear, primary alcohols.

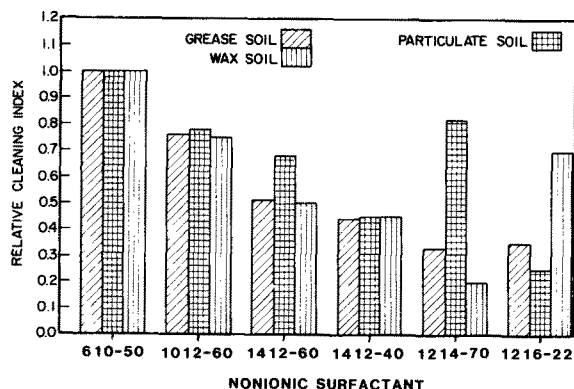

FIG. 7. Relative hard-surface cleaning performance of commercial nonionics on grease, wax and particulate soils (5% solutions).

FIG. 8. Comparison of the hard-surface cleaning performance of ALFONIC® 610-50 nonionic, nonylphenol ethoxylate (9½ mole) and a nonylphenol ethoxylate/butyl cellosolve mixture (using 1/3 dilutions of built formulations on grease soil)

FIG. 9. Comparison of the hard-surface cleaning performance of ALFONIC® 610-50 nonionic, nonylphenol ethoxylate (9½ mole) and a nonylphenol ethoxylate/butyl cellosolve mixture (using 1/30 dilutions of built formulations on grease soil).

Test results are shown in Figures 8 and 9. At 1/3 dilution, the performance of the NPE formulation is significantly poorer than that of all the other materials. This is probably the result of the relatively large size of its hydrophobe. The 10% NPE-5% BC formulation performs much better, indicating that a synergism exists between them. Because BC is itself a poor surfactant, the increase in performance of the NPE-BC mixture is probably caused by the solvency properties imparted by the BC. Even with this synergism, the performance of the NPE-BC formulation is significantly poorer than the 15% 610-50 nonionic formulation.

With 1:30 dilutions, a synergism between NPE and BC is not evident. Under dilute conditions, little of the BC probably resides at the soil-water interface. Consequently, performance decreases so that the 15% NPE formulation out-performs the NPE-BC mixture. However, the 15% 610-50 nonionic formulation still gives significantly better performance than the NPE formulation.

The results of these tests indicate that a mixture of NPE and BC is not the best surfactant system available for hard-surface cleaning. The advantages for using a lower molecular weight surfactant are obvious. Either performance can be improved or equal performance can be achieved with significantly less active ingredients.

A variety of other commercially available surfactants were tested, including many octylphenol and NPE. The trend observed relating carbon chain length to performance was evident throughout the study. In summary, the 610-50 nonionic was found to perform better than all the other surfactants tested.

Tests were also performed to determine the effect of blending the 610-50 nonionic with BC. Performance was observed to decrease (dilution effect) as nonionic was partially replaced with butyl cellosolve. Apparently, lower molecular weight nonionics have sufficient soil solvency properties and do not need BC to aid performance.
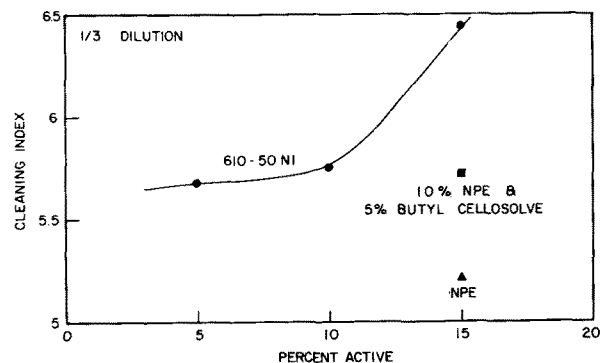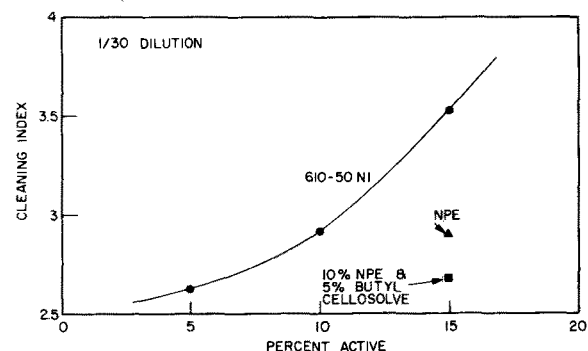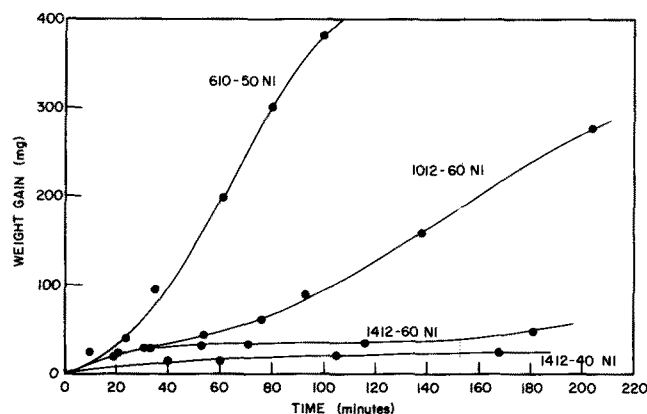

FIG. 10. Change in soil weight vs time for lard soil submersed in 5% solutions of several commercial nonionics.

Soil-Surfactant Interaction Study

The physical interaction between a nonionic surfactant and a solid soil was examined by measuring the change in weight of lard soil vs time submersed in various nonionic solutions. Test procedures are explained in the experimental section of this report.

As shown in Figure 10, lard soil increases in weight when submersed in nonionic surfactant solutions. The rate of soil weight gain is greatest for 610-50 nonionic surfactants. As surfactant carbon chain length is increased, the rate of soil weight gain decreases.

The fact that soil weight does not decrease indicates that soil solubilization is not the primary process for removing the soil. Because soil weight increases, the key soil removal process may involve penetration or dissolution of the surfactant into the soil. Soil penetration would explain why hard-surface cleaning performance is strongly related to carbon chain length. Surfactant penetration would cause soil to swell and soften, allowing it to be more easily removed. Surfactants with smaller hydrophobes would logically penetrate or dissolve into soil at a faster rate, resulting in an improvement in cleaning performance.

♣ Factors Affecting Oil/Water Interfacial Tension in Detergent Systems: Nonionic Surfactants and Nonpolar Oils

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ABSTRACT

Because earlier model detergency studies have shown that oil/water interfacial tension is critically important in oil removal processes, factors affecting the interfacial tension between detergent-range nonionic surfactant solutions and paraffin oil have been examined. For a given hydrophobe, equilibrium interfacial tension values increase with the length of the ethylene oxide chain in the hydrophile, because of the attendant decrease in overall surface activity. For a given degree of ethoxylation, commercial nonylphenol ethoxylates reduce interfacial tension more effectively than their secondary alcohol-based counterparts, and these in turn are more effective than commercial primary alcohol ethoxylates. Furthermore, monodisperse primary alcohol ethoxylates reduce interfacial tension more effectively than broad-range ethoxylates with similar cloud points. This observed order of effectiveness is attributed in part to variations in the extent of fractionation that occur as nonionic surfactants divide between the oil and water phases. Equilibrium interfacial tension values produced by commercial nonionic surfactants are significantly more dependent on concentration and temperature than those obtained with monodisperse ethoxylates. However, the time-course for lowering interfacial tension exhibited by monodisperse ethoxylates varies with concentration and temperature to a greater extent than that displayed by commercial products. These findings are accounted for by the combined effects of the changes in relative surface activity and partitioning that occur as the concentration and temperature are varied. An imidazoline-based quaternary fabric softener markedly increases the interfacial tension immediately following phase contact, whereas equilibrium values are only slightly higher in the presence of the softener. Apparently, preferential adsorption of the softener occurs at the interface, followed by adsorption of the nonionic surfactant at the new softener/water interface. Builders and electrolytes have no significant effect on the interfacial tension between aqueous nonionic surfactant solutions and paraffin oil. Terg-O-Tometer results demonstrate the correlation between oil/water interfacial tension and detergency.

INTRODUCTION

Previous investigations (1,2) have shown that nonpolar oils are removed from polyester substrates submerged in nonionic surfactant solutions by the roll-up process originally described by Adam (3). Using the Young equation (4), an expression relating the extent of roll-up, i.e., the equilibrium contact angle in the aqueous phase ($\theta_{w/s}$), to the solid/water ($\gamma_{s/w}$), solid/oil ($\gamma_{s/o}$), and oil/water ($\gamma_{o/w}$) equilibrium interfacial tensions may be cast in the form:

$$\cos\theta_{w/s} = \frac{\gamma_{s/o} - \gamma_{s/w}}{\gamma_{o/w}}. \qquad [1]$$

Model studies have demonstrated the utility of this relationship in explaining relative performance differences among nonionic surfactants (1,5). These investigations also revealed that although the resultant force acting at the 3 phase point of contact ultimately determines the value of $\theta_{w/s}$ for a given substrate and oil, variations in $\theta_{w/s}$ are usually caused by changes in $\gamma_{o/w}$. Consequently, an examination of factors affecting $\gamma_{o/w}$ is instrumental in developing an understanding of the performance properties of nonionic surfactants.

In this report, factors affecting interfacial tension in systems of interest to the detergent industry are examined. The effects of surfactant concentration and structure on the time-course of interfacial tension lowering are delineated. Because warm- and cool-water launderings are becoming more prevalent, temperature effects are also considered. Also, in view of the growing market for detergents with built-in fabric-softening capabilities, the effects of softeners on interfacial tension are cursorily treated. Finally, a brief discussion of the effects of builders and electrolytes on interfacial tension provides a basis for future research. In selected instances, the practical implications of the data and the correlation with laboratory detergency evaluations are addressed.

EXPERIMENTAL

Interfacial tensions were measured using the spinning drop technique (6) under conditions where the infinite length assumption was valid. In the time-course of interfacial tension lowering studies, time zero corresponds to the time spinning of the drop begins; generally, a 6-8 μL drop of oil