Alcohol Ethoxycarboxylates—Mild, High-Foaming Surfactants for Personal-Care Products[1]

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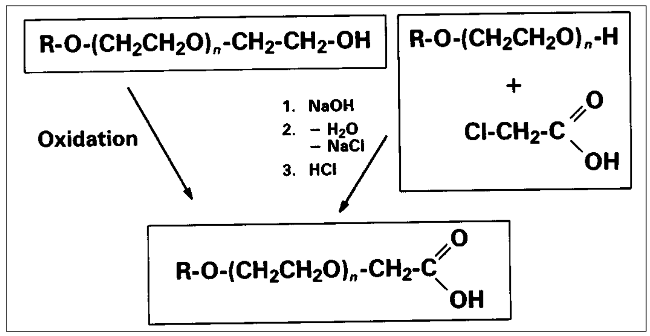
ABSTRACT: Alcohol ethoxycarboxylates (AEC) may be derived from alcohol ethoxylates (AEO) either by reaction of the nonionic surfactant with monochloroacetic acid (MCAA) or by oxidation. If MCAA is used, a $–CH_2COOH$ unit is added to the AEO. When an AEO is oxidized, the terminal $–CH_2OH$ group is selectively converted to –COOH. By use of proprietary carefully controlled oxidation technology, a variety of AEC surfactants have been synthesized. These surfactants exhibit good foaming and excellent lime soap dispersion, and they allow formulation of high-quality personal-care products. Starter formulations have been investigated with AEC, both in shampoos and liquid hand cleaners. These formulations had the viscosity and foaming found in a survey of commercially available products. A shampoo and a liquid soap formulation with AEC were subjected to *in-vitro* assays to assess the potential for irritation to the skin or eyes. The assay results predict these formulations to cause minimal irritation, similar to commercial products.
JAOCS 74, 25–31 (1997).

KEY WORDS: Alcohol ethoxycarboxylates, foaming, hand cleaner, *in-vitro* assay, personal-care products, shampoo, surfactants, viscosity.

An alcohol ethoxycarboxylate (AEC) can readily be made on a commercial basis from the salt of monochloroacetic acid (MCAA) (1), but the process for making these surfactants has been greatly simplified by proprietary oxidation technology (2). AEC has been reported to be especially useful in shampoo and other personal-care products because the surfactant produces a pleasing creamy lather, and the formulations exhibit mildness to the skin and low eye irritation potential (3). Because of the ability to make high-quality AEC, the use of these surfactants in both shampoos and liquid hand cleaners has been investigated. The data reported here include foaming, viscosity, and expected mildness of these two types of AEC-containing formulations.

As displayed in Scheme 1, the oxidation route is a much more efficient synthesis of these surfactants. The AEC (acid form) was obtained directly from the reactor as a nonviscous, easily pumped material. In contrast, the procedure based on MCAA required more processing steps to isolate a comparable product, and in general, the final AEC was not as pure.



SCHEME 1

Research was undertaken to establish how well AEC could partially replace alcohol ethoxysulfate (AEOS) in prototype shampoos and hand cleaners. Information collected included: foaming and viscosity results for simplified formulations with AEOS and mixtures of AEOS with AEC; foaming and viscosity results for hand cleaners that include soap and AEC; and *in vitro* assay data on pure surfactants and formulations to evaluate the potential for skin and eye irritation.

EXPERIMENTAL PROCEDURES

The comparison surfactants were obtained from a variety of sources and each is identified by both chemical description and trade name in Table 1. Laboratory chemicals were obtained from standard commercial sources and used as received. All solution concentrations are percentage by weight of the solute in deionized water.

AEC composition and purity were established with standard methods, including ^{13}C nuclear magnetic resonance (NMR). 1,4-Dioxane content was measured with a headspace capillary gas chromatography technique.

The SEN foaming device (SEN, Incorporated, Portage, MI), Figure 1, was a useful way of measuring "flash foam." A surfactant solution (0.1 wt%) was agitated by pumping, and air was admitted to the recycle line to assist in generating foam. The time required to generate 20 cm of foam was

[1]Presented at the AOCS 86th Annual Meeting & Expo, May 7–11, 1995, San Antonio, Texas.

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TABLE 1
Identification of Chemicals

Chemical description[a]	Trade name	Acronym
$C_{12,13,14,15}$ alcohol-3 EO sulfate, sodium salt	NEODOL® 25-3S[b]	AEOS
$C_{12,13}$ alcohol 4 EO carboxylate	NEODOX™ 23-4[b]	AEC 23-4
$C_{12,13,14,15}$ alcohol 6 EO carboxylate	NEODOX™ 25-6[b]	AEC 25-6
$C_{12,13}$ alcohol 6 EO carboxylate	NEODOX™ 23-6[b]	AEC 23-6
$C_{12,13,14,15}$ alcohol sulfate, sodium salt	NEODOL® 25S[b]	AS
Fatty acid alkanol amide	Ninol® 49CE[c]	Amide
C_{12} linear alkyl-benzene sulfonate	Witconate® 1260[d]	C_{12}-LAS
Sodium cocoyl isethionate	IGEPON® AC-78[e]	Na Coco Isethionate (SCI)
Cocoamidopropyl betaine	Monateric® CAB[f]	Betaine
Ethylenediaminetetraacetic acid, sodium salt	EDTA[g]	EDTA
Fatty acids	C-110 Coconut fatty acid[h]	Soap

[a]EO, ethylene oxide; AEC, alcohol ethoxycarboxylates; AEOS, alcohol ethoxysulfate. [b]Shell Chemical Co. (Houston, TX). [c]Stepan Inc. (Northfield, IL). [d]Witco Co. (New York, NY). [e]Rhône-Poulenc (Cranberry, NJ). [f]Mona Industries (Patterson, NJ). [g]Mallinckrodt (St. Louis, MO). [h]Procter & Gamble (Cincinnati, OH).

recorded. Thus, in the context of shampoos and hand soaps, faster times are preferred.

Lime soap dispersion was measured by the literature procedure (4,5). Surfactant and formulation viscosities were measured with a Brookfield Model DV-II+ viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA).

Dynamic spray foaming was measured in the Shell-designed device depicted in Figure 2. A surfactant solution was pumped through a spray nozzle at controlled pressure. General comments on the use and results from this type of foam test have been published (6,7).

Hardness tolerance was determined by titrating calcium ions into aqueous solutions of the surfactants. The solution turbidity was monitored with a PC800 (Brinkmann Instruments Ltd., Toronto, Canada) dipping probe colorimeter (8–10).

A variety of commercial brands of handcleaners and shampoos was purchased and tested to establish an expected range for SEN foaming rate and viscosity. The foaming rates were: handcleaners, 52–274 s/20 cm; and shampoos, 81–271 s/20 cm. The viscosity ranges were: hand cleaners, 3,900–85,000 cP; and shampoos, 1,000–8,700 cP. These results were the basis for the "commercial range" shown in selected graphs.

RESULTS AND DISCUSSION

Surfactant properties of AEC. Table 2 shows selected properties of a typical AEC (acid) compared to the sodium salt of an AEOS. It was necessary to compare AEC (acid) to AEOS (sodium salt) because the alcohol ethoxy-sulfuric acids were not stable unless stored in the cold. Even if kept cold, AEOS (acid) was a thick paste and decomposed slowly. As displayed in the table, the AEC acid was a nonviscous liquid at approximately 90% active matter. As depicted in Figure 3, typical aqueous dilutions of AEC in the acid form have substantial gel regions. This gel from AEC is likely an advantage, as it is commonly perceived that thick, viscous formulations of shampoos and handcleaners are more effective.

Foaming was another attribute of AEC that was dramati-

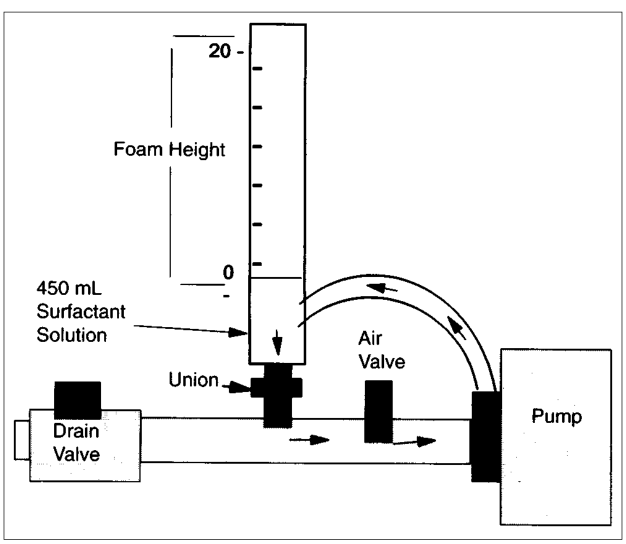

FIG. 1. SEN (SEN, Incorporated, Portage, MI) foam tester.

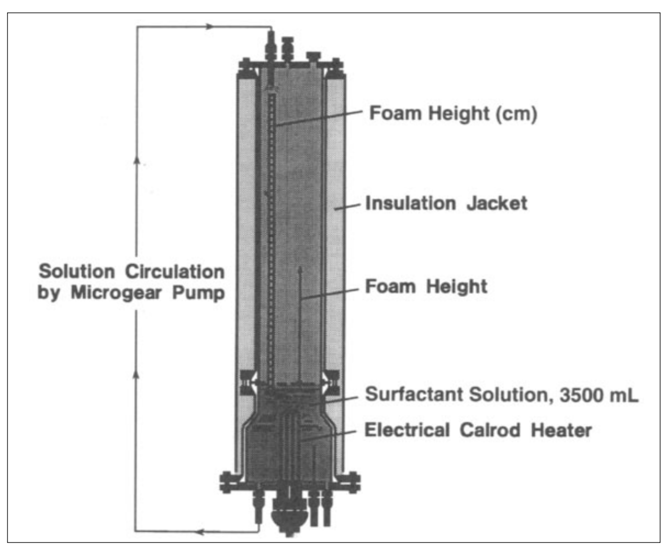

FIG. 2. Shell spray foam apparatus.

TABLE 2
Surfactant and Physical Properties of AEOS (sodium salt) and AEC (acid)[a]

	Surfactants[a]			
Property	AEOS	AEC 23-4	AEC 23-6	AEC 25-6
Pour point (°C)	5	2	0	9
pH (5% AM)[a]	8.5–10	3–4	3–4	3–4
1,4-Dioxane (ppm on AM)	<75	<1	<1	<1
% wt solution without gel	28	>90	>90	>90
Viscosity in cP	6500	280	355	445
at 25°C (AM)	(70)	(92)	(95)	(95)

[a]AM, active matter. See Table 1 for other abbreviations.

cally affected by pH. Figure 4 shows a comparison of the spray foam generated from AEC 23-4 in the acid form and after neutralization to pH >8 with NaOH. The level of foam displayed for the AEC (sodium salt) was the same as observed in the same test device with AEOS.

An important property for surfactants in selected personal-care applications is lime soap dispersion. Results for representative AEC are displayed in Figure 5. The lime soap dispersing power was the same for AEC (acid) and the AEC carboxylate anion (sodium salt). For personal-care products, the carboxylate form was required to enhance foaming. However, lime soap dispersion at a pH = 6.5 ± 0.2 would be an important attribute for products buffered to enhance skin compatibility.

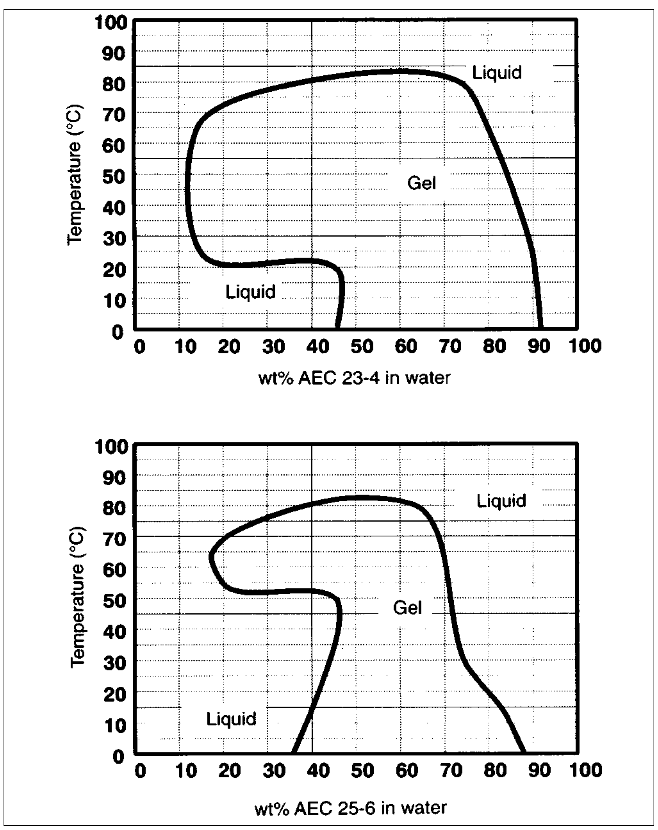

FIG. 3. Gel curves for AEC 23-4 and AEC 25-6.

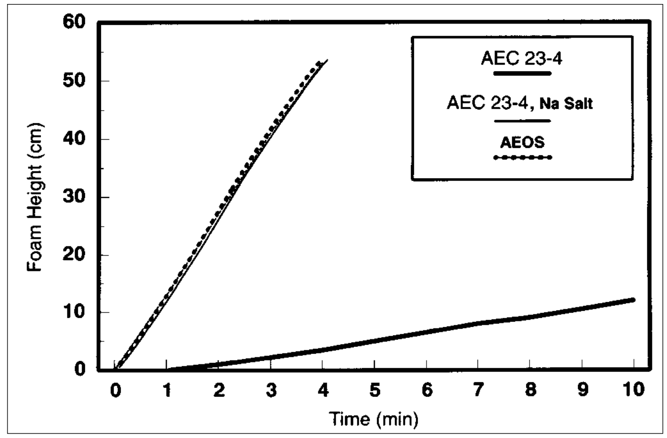

FIG. 4. Dynamic spray foam height for AEC 23-4 (0.1% wt in distilled water).

Lack of sensitivity to water hardness or other electrolytes is a widely reported advantage of AEC (11,12). Figure 6 is a depiction of the water hardness tolerance of typical AEC. As noted in the Experimental Procedures section, this evaluation employed a dipping probe colorimeter to monitor solution turbidity. Thus, as insoluble calcium salts form with a surfactant such as LAS, the presence of the dispersed solid was detected by the colorimeter. For both AEC and AEOS, the solution remained clear.

Handcleaners ("liquid soaps"). Three different handcleaner formulations were made and evaluated. As displayed in Table 3, in a paired evaluation, AEC was substituted for alcohol sulfate. In a different type of cleaner, AEC was used in combination with AEOS and coconut soap (Table 4). These formulations were selected to use AEC in combination with AEOS. This strategy was selected to maximize the opportunity to observe synergy between these two components. Further, with AEOS present, the possibility exists to use salt thickening, should a given formulation exhibit inadequate viscosity.

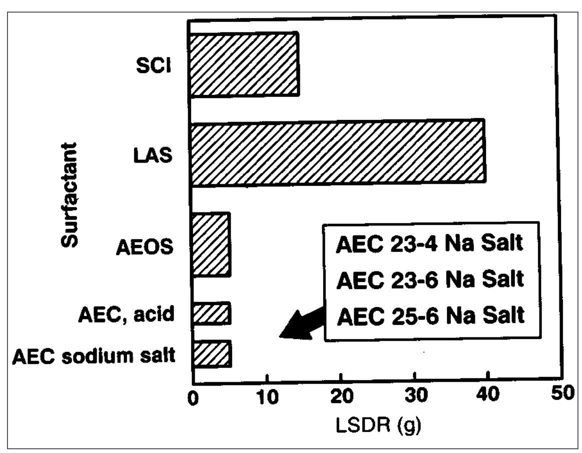

FIG. 5. Lime soap dispersion. LSDR is the number of grams of surfactant required to disperse the lime soap formed from 100 g of sodium oleate in water with a hardness equivalent of 333 ppm as $CaCO_3$.

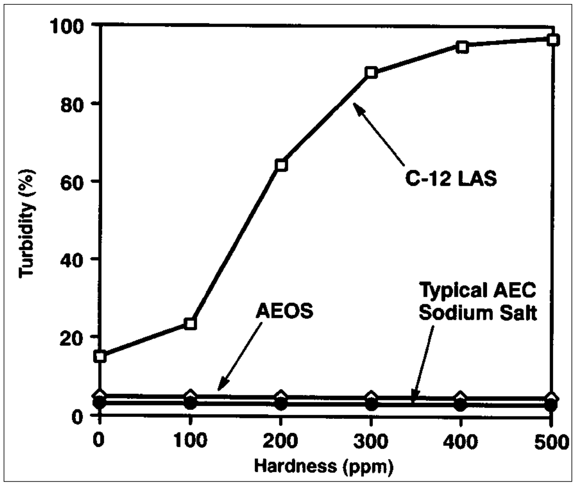

FIG. 6. Hardness tolerance as measured by solution turbidity.

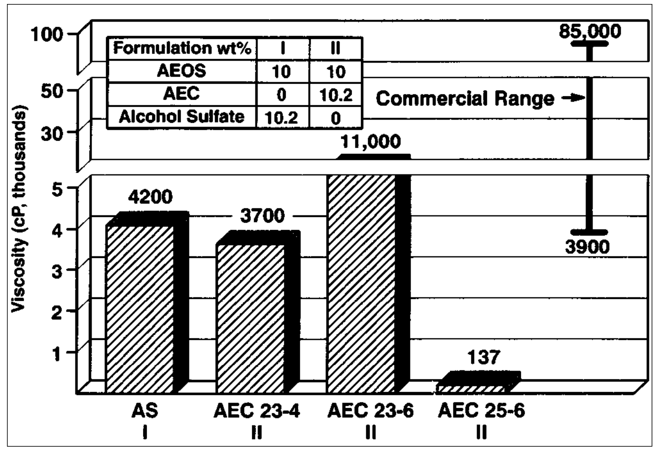

FIG. 7. Viscosity of prototype liquid soaps.

The viscosity results with Formulations I and II are shown in Figure 7. Not surprisingly, Formulation I was within the range for the surveyed commercial products. Only one example of Formulation II, made with AEC 25-6, had inadequate viscosity. The product with AEC 25-6 could likely be made more viscous by the addition of a small amount of NaCl.

The SEN foaming results with these formulations are in Figure 8. All AEOS- and AEC-containing formulations foamed well, with all products foaming at a speed comparable to the best commercial product evaluated. This exceptional foaming performance should allow an individual formulator to easily add aloe or other skin conditioning agents. It was notable that the foams generated from commercial products and the prototype formulations were very stable. The SEN device is stopped after 20 cm of foam has been made. This foam was composed of small cells, and the foam height did not diminish measurably after 5 min.

Figure 9 shows the viscosity data from the use of AEC in Formulation III. All AEC formulations exhibited viscosities within the range observed for the commercial samples. AEC 25-6 gave excellent viscosity in this formulation, whereas the viscosity was low in Formulation II (Fig. 7). This phenomenon was deduced to be a peculiar function of the specific ingredients because the foaming of AEC 25-6 was excellent in all formulations.

Figure 10 compares the SEN foaming data for the liquid soaps. The AEC performed well, not as fast as the fastest commercial product but substantially faster than the slowest.

TABLE 3
Formulations of Test Liquid Handcleaners

	wt%
Formulation I	
AEOS	10
Alcohol sulfate	10.2
Fatty acid Alkanolamide	5.0
Cocamidopropyl betaine	1.5
EDTA	0.2
Glycerin	1.0
Water	to 100
Formulation II	
AEOS	10
AEC	10.2
Fatty acid alkanolamide	5.0
Cocamidopropyl betaine	1.5
EDTA	0.2
Glycerin	1.0
Water	to 100

TABLE 4
Liquid Handcleaner Formulation with AEOS, AEOS, AEC, and Soap

Formulation III	wt%
AEC	10
AEOS	5.0
Coconut soap	5.0
Fatty acid alkanolamide	5.0
Cocamidopropyl betaine	1.5
EDTA	0.2
Glycerin	1.0
Water	to 100

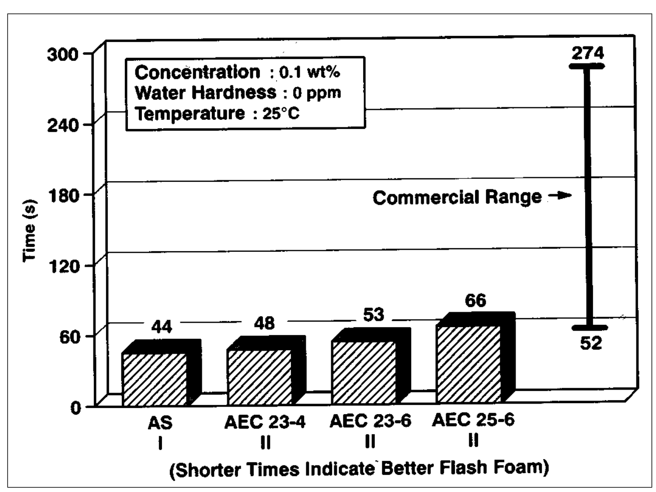

FIG. 8. SEN foam rate of liquid soaps. See Figure 1 for company source.

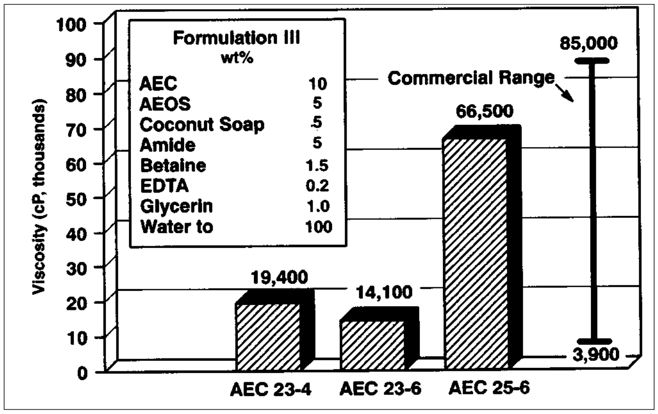

FIG. 9. Viscosity of liquid soaps.

TABLE 5
Formulations of Test Shampoos[a]

	wt%
Formulation IV	
AEOS	15
Fatty acid alkanolamide	2.1
Cocamidopropyl betaine	7.5
Ethanol	1.0
Water	to 100
Formulation V	
AEOS	7.5
AEC	7.5
Fatty acid alkanolamide	2.1
Cocamidopropyl betaine	7.5
Water	to 100

[a]See Table 1 for abbreviations.

Prototype shampoo formulations. Table 5 shows the shampoo products evaluated in this work, Formulations IV and V. The strategy was to replace half of the AEOS with AEC and document the effect of this change on foaming and viscosity. Collected in Figure 11 are the viscosity data for the prototype shampoos. Formulation IV was very thick, while the formulation made with AEC 25-6 might not have sufficient viscosity. As with the liquid soap formulations, the presence of AEOS should allow this AEC 25-6-containing shampoo to be thickened by the addition of salt.

Figure 12 shows that the prototype shampoo formulations developed for this work gave excellent foaming results. All prototype products foamed substantially faster than the commercial range. As with the prototype handcleaners, these foaming levels are expected to allow introduction of conditioners and other ingredients.

In vitro *assay data for skin and eye irritation.* As reported by Van Paasen (13), the mildness of AEC is especially suited for cosmetic use. Further, AEC has been advocated for use in contact lens cleaning solution because of exceptionally low eye irritation potential (14). AEC 23-4 has been evaluated in two different *in vitro* assays, and the results are discussed in conjunction with data from the same assays on certain prototype formulations.

To understand the utility of AEC in personal-care products, it was decided to select a few formulations and conduct *in vitro* irritation assays. The assays chosen were: Bovine Corneal Opacity and Permeability (BCOP) and EpiDerm™ (both available from Microbiological Associates, Inc., Rockville, MD). Published results with both assays indicate that these laboratory tests predict the relative eye and skin irritation, respectively, that might occur in actual use of personal-care products (15–17). In brief, the BCOP method uses an opacitometer and spectrophotometer to measure induction of opacity and fluorescein permeability (epithelial cell damage) in corneas harvested from slaughterhouse animals. The EpiDerm™ method measures the time required to reach 50% cytotoxicity from the test substance exposure to a stratified and cornified human keratinocyte culture, a human epidermal construct. For the EpiDerm™ method, longer times equate to milder test substances.

In Table 6, the EpiDerm™ scores have been reported for the pure surfactants used in this research. Additionally listed are data from the prototype handcleaners (evaluated at 10% concentration). Two control surfactants were studied at 1% concentration. These controls are a nonylphenolethoxylate 9EO (NPEO-9) and sodium lauryl sulfate (SLS). In this assay,

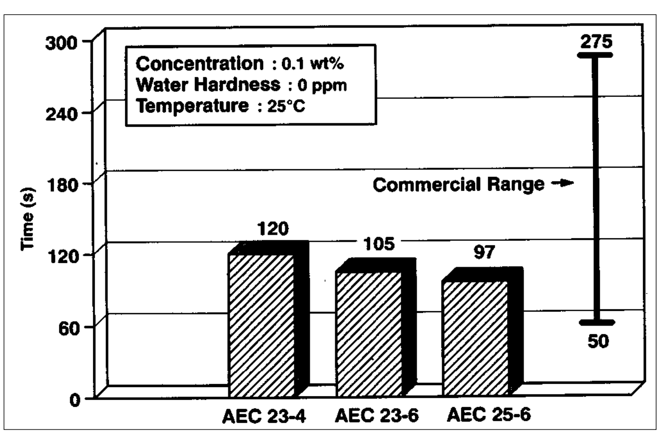

FIG. 10. SEN foam rate of liquid soaps. See Figure 1 for company source.

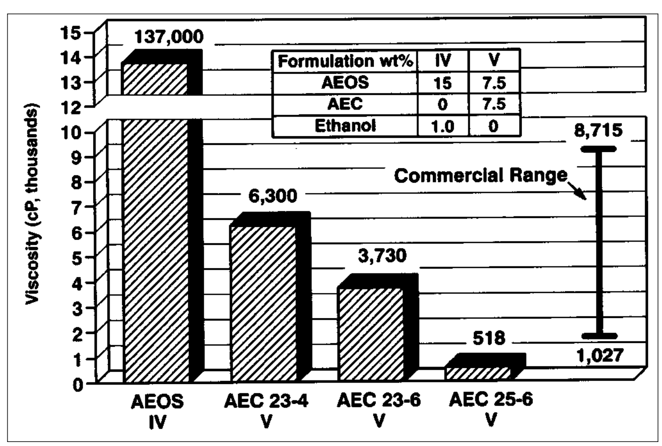

FIG. 11. Viscosity of prototype shampoos.

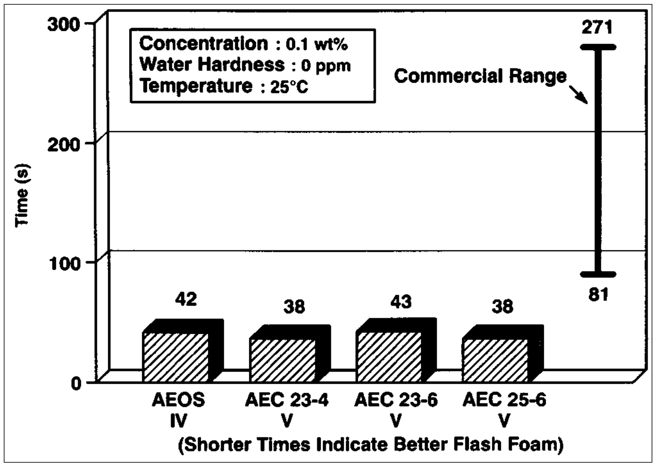

FIG. 12. SEN foam of prototype shampoos. See Figure 1 for company source.

the larger the time to reach half viability, the less irritant is the material. The AEOS handcleaner ("liquid soap") gave an EpiDerm™ value of about four, while the formulation based on AEC 23-4 gave a score of slightly less than seven. Both formulations would be considered mild skin irritants under these conditions.

Collected in Table 7 are the EpiDerm™ data acquired during this research for prototype shampoos. As noted above, higher scores are characteristic of "milder" products. The AEC and AEOS shampoos both gave scores of about ten, suggesting that the formulations are similar in irritation potential. These EpiDerm™ results suggest that either surfactant could be used to make a shampoo product that would be expected to have minimal skin irritation.

Displayed in Table 8 are the prototype shampoo formulations evaluated at 10% concentration in the BCOP assays. In this assay, increasing *in vitro* scores are indicative of increasing eye irritation potential. In analyzing the data in Table 8, BCOP scores less than 25 are classified as "mild irritant" (18), and these scores are close to zero or nonirritant. Based on this scale, all surfactants and formulations are classified into this category. Because these surfactants do not cause significant changes in opacity, an alternate evaluation may be made based on the mean permeability scores alone (15). In other studies, permeability scores alone on several shampoos correlated well with rabbit maximum average Draize scores (15). These mean permeability scores are not significantly different, supporting the conclusion that AEC can be readily substituted for AEOS in shampoo formulations without changing the eye irritation potential.

The formulations made and assayed in this research are predicted to have a similar degree of mildness to products made only with AEOS. Based on the literature that suggests mildness for AEC, an optimized formulation could be less irritating (13,14,19). In any case, the BCOP assay allows the laboratory chemist to rapidly evaluate test formulations. BCOP assays in concert with EpiDerm™ scores would be expected to aid the formulator in evaluating products for expected skin and eye interactions.

Implications for future of formulations. AEC surfactants have been evaluated for use in cleaning products in contact with the skin (or possibly the eye). AEC were found to have many useful attributes: (i) low viscosity at room temperature, for ease of handling; (ii) high foaming, as the sodium salt; (iii) good lime soap dispersion, in either the protonated or carboxylate anion form; and, (iv) low potential for eye and skin irritation.

TABLE 6
***In Vitro* Skin Irritation Evaluation of Surfactants and Handcleaner Formulations[a]**

Test material	EpiDerm™ [MTT_{50} h]	pH
10% AEOS	5.56	7.0
10% AEC 23-4	4.19	6.5
AEOS handcleaner, Formulation I	4.16	n.d.
AEC handcleaner, Formulation II	6.60	n.d.
1% NPEO-9	5.67	n.d.
1% Sodium lauryl sulfate	<2	n.d.

[a]Handcleaner formulations were tested at 10% aqueous concentration of the formulation where EpiDerm™ scoring scale is <1, severe; 1–3.9, moderate; 4–11.9, moderate to mild; 12–24, very mild; >24, generally not irritating, ET_{50} (h) and expected *in vitro* irritation, respectively. n.d. = Not determined.

TABLE 7
***In Vitro* Skin Irritation Evaluation of Surfactants and Shampoo Formulations[a]**

Test material	EpiDerm™ [MTT_{50} h]	pH
10% AEOS	5.56	7.0
10% AEC 23-4	4.19	6.5
AEOS handclearner, Formulation 1	10.0	6.1
AEC handcleaner, Formulation II	10.7	6.5
1% NPEO-9	5.67	n.d.
1% Sodium lauryl sulfate	<2	n.d.

[a]Shampoo formulations were tested at 10% aqueous concentration of the formulation where EpiDerm™ scoring scale is <1, severe; 1–3.9, moderate; 4–11.9, moderate to mild; 12–24, very mild; >24, generally not irritating, ET_{50} (h) and expected *in vitro* irritation, respectively.

TABLE 8
***In Vitro* Eye Irritation Evaluation of Surfactants and Shampoo Formulations[a]**

Test material	Opacity value	Permeability: Change in O.D.	Permeability: 15 × Change in O.D.	BCOP *in vitro* score
10% AEOS	1.8	0.281	4.2	6.0
10% AEC	0.8	0.343	5.1	5.9
AEOS shampoo	−1.6	0.177	2.7	1.1
AEC shampoo	−1.0	0.269	4.0	3.0
100% Ethanol	39.5	0.961	14.4	53.9

[a]*In vitro* bovine corneal opacity and permeability assay. O.D. = optical density. Shampoo formulations were tested at 10% aqueous concentration of the formulation. *In vitro* score = mean opacity value + 15 × mean permeability value. *In vitro* score: from 0 to 25, mild irritant; from 25.1 to 55, moderate irritant; from 55.1 and above, severe irritant.

Formulations with AEC were high-foaming and had viscosity values within the range typically expected of such products. *In vitro* assays of formulations indicated that AEC-containing products will be mild with respect to potential skin and eye irritation. Future use of AEC will allow optimization of products for foaming, easy dispensing, and mildness.

ACKNOWLEDGMENT

We thank Ann C. Williams for assisting in preparing this manuscript for publication.

REFERENCES

1. Cripe, T.A., U.S. Patent 5,233,087, Aug. 3, 1993, assigned to the Procter & Gamble Co.
2. Fried, H.E., U.S. Patent 5,162,579, Nov. 10, 1992, assigned to Shell Oil Company.
3. Fabry, B., Mild Surfactants—“Smooth” Chemistry Taken Word-for-Word, translated from *Seifen-Öle-Fette-Wachse 117*:3–7 (1991).
4. Borghetty, H.C., and C.A. Bergman, Synthetic Detergents in the Soap Industry, *J. Am. Oil Chem. Soc. 27*:88–90 (1950).
5. Linfield, W.M., Lime Soap Dispersants, in *Detergency Theory and Technology*, edited by W.G. Cutler and E. Kissa, Vol. 20, Marcel Dekker, Inc., New York, 1987, pp. 1–10.
6. Merrill, C.L., and D.L. Wood, U.S. Patent 5,034,158, July 23, 1991, assigned to Shell Oil Company.
7. Schmidt, W., NEODOL® Alcohols and Derivatives in Shampoos, *Shell Chemical Technical Bulletin 1346-92*, Shell Chemical Company, Houston, TX.
8. Raney, K.H., and H.L. Benson, The Effect of Polar Soil Components on the Phase Inversion Temperature and Optimum Detergency Conditions, *J. Am. Oil Chem. Soc. 67*:722–725 (1990).
9. Merrill, C.L., and D.L. Wood, U.S. Patent 5,035,838, July 30, 1991, assigned to Shell Oil Company.
10. Schmidt, W., W. Lilienthal, K.H. Raney, and S.T. Dubey, A Novel Dianionic Surfactant from the Reaction of C_{14}-Alkenylsuccinic Anhydride with Sodium Isethionate, *J. Am. Oil Chem. Soc. 71*:695–703 (1994).
11. Olsen, D.K., and C.B. Josephson, Carboxymethylated Ethoxylated Surfactants, Department of Energy National Institute for Petroleum and Energy Research, Report No. 228, Bartlesville, OK, 1987, pp. 11–14.
12. Schultz, K., Fettalkoholoxäthylacetate (Fatty Alcohol Ethylacetate), translated from *Seifen-Öle-Fette-Wachse 101*:37–41 (1975).
13. Van Paasen, N.A.I., Alkylethercarboxylate: Hautfreundliche Rohstoffe für Kosmetische Anwendungen (Alkyl ethercarboxylate: A Raw Material with Skin Mildness for Cosmetic Applications), translated from *Seifen-Öle-Fette-Wachse 109*:353–355 (1983).
14. Schafer, D., and R. Schafer, U.S. Patent 4,808,239, Feb. 28, 1989, assigned to Alcon, Inc.
15. Harbell, J.W., K.A. Wallace, F. Marchesani, R. Stahl, P.B. Nyberg, E.V. Buehler, and R.D. Curren, The Use of Excised Corneas from Slaughterhouse Animals to Assess Potential Ocular Irritation from Consumer Products and Related Raw Materials, presented at the Congress on Cell and Tissue Culture, San Diego, CA, June 1993; abstract published in In Vitro *Cellular and Developmental Biology 28*:97A (1993).
16. Southee, J., L.K. Hall, and J.W. Harbell, Ocular Irritation Potential of Complex Surfactant Mixtures Evaluated *In Vitro* Using the Bovine Corneal Opacity and Permeability Assay, *Proceedings, International Federation of the Societies of Cosmetic Chemists, Between Congress Conference*, 1995, pp. 433–440.
17. Harbell, J.W., J.A. Southee, C.L. Cannon, P.J. Neal, J. Kubilius, and M. Klausner, Inter- and Intralaboratory Reproducibility of a Three Dimensional Human Epidermal Model—EpiDerm™, *The Toxicologist 14*:108 (1994).
18. Gautheron, P., M. Dukic, D. Alix, and J.F. Sina, Bovine Corneal Opacity and Permeability Test: An *In vitro* Assay of Ocular Irritancy, *Fundam. Appl. Toxicol. 18*:442–449 (1992).
19. Sandopan® Carboxylated Surfactants...Worlds of Formulating Possibilities, *Product Bulletin 7-025/93*, Sandoz Chemicals Corporation, Charlotte, 1993, pp. 2–3.

[Received March 4, 1996; accepted September 15, 1996]