Ester Alkoxylation Technology[1]
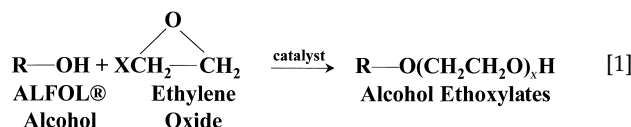
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ABSTRACT: Conventional ethyoxylation technologies, when used on fatty methyl esters, produce poor yields as well as flat ethoxymer distributions. Peaking ethoxylation catalysts have been successful in efficient conversion of methyl esters into the ethoxylates possessing peaked ethoxymer distribution. Surfactant performance of methyl ester ethoxylates was evaluated. Results generally show these to behave similarly to alcohol ethoxylates, with the exception of exhibiting a lower foam profile. This ester ethoxylation technology has been successful in ethoxylating esters of varying steric environments. Triglyceride ethoxylates have been partially saponified as well as glucaminolyzed to produce mild surfactant blends.

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KEY WORDS: Detergency, fatty glucamide, foaming, hard surface cleaning, methyl ester ethoxylates, mild surfactant blend, partially saponified triglyceride ethoxylates, peaked ethoxylation, triglyceride ethoxylates.

The development of ester ethoxylation technology received a boost from the peaked alcohol ethoxylation technology developed in the mid-1980s. As is well known, alcohol ethoxylates are produced by the reaction between an alcohol and ethylene oxide (EO) in the presence of a catalyst (1) (Eq. 1).

$$R\text{—}OH + XCH_2\text{—}CH_2 \xrightarrow{catalyst} R\text{—}O(CH_2CH_2O)_xH \quad [1]$$

ALFOL®   Ethylene   Alcohol Ethoxylates
Alcohol   Oxide

The catalyst types are strong bases such as NaOH, KOH (conventional), Lewis acids such as $SbCl_5$, $SnCl_4$, and other categories such as Peaking Catalysts and the NOVEL® II catalyst (2). The EO distribution of the alcohol ethoxylate is dependent on the type of catalyst employed. The most widely used conventional catalysts are NaOH and KOH.

They give rise to a broad EO distribution in the ethoxylate product. Lewis acids are also used as catalysts to produce highly peaked low-EO ethoxylates.

As a result of the nature of these acid catalysts, these processes produce some undesirable by-products along the way (1). A third type of catalyst called a peaking catalyst leading to peaking technology was under development in the mid-1980s. Peaked ethoxylates were produced in the presence of a catalyst known as NOVEL® II catalyst (2).

The NOVEL® II catalyst is a Ca and Al alkoxide-type catalyst, partially neutralized and dispersed in an Alfonic® C10–12-2.5 EO alcohol ethoxylate. The calcium/aluminum ratio in the catalyst is 5:1. The alcohol ethoxylate itself makes up about 90% of the catalyst.

The significance of peaking is shown by the EO distribution curves for the two types of ethoxylates; one produced in the presence of conventional catalysts and the other produced using peaking or NOVEL® II catalysis are shown in Figure 1. The left-hand side of the curves shows that the residual alcohol level and the low-EO ethoxymer content are significantly reduced in favor of the peaked alcohol ethoxylate. Similarly, the right-hand side of the curves shows a significant reduction in the high-EO ethoxymer levels as a result of the peaking effect. Thus, in the peaked ethoxylate, most of the ethoxymers are concentrated in a desired narrow EO range (3,4).
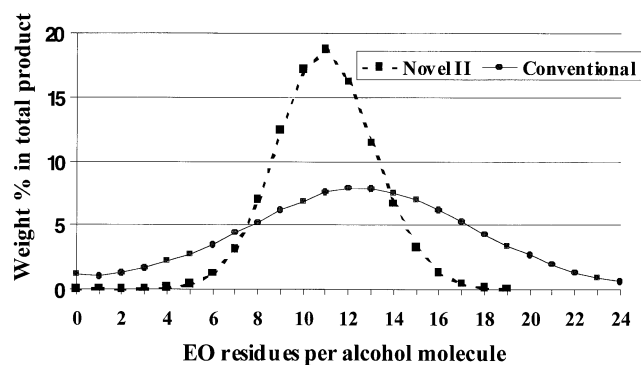

FIG. 1. Ethylene oxide (EO) distributions for NOVEL® II and conventional 1216-CO-10.5 alcohol ethoxylate.

Triglycerides $\xrightarrow[\text{H}_2\text{O}]{\text{fat splitting}}$ Fatty Acids + Glycerin

$\downarrow$ methanolysis $\downarrow$ hydrogenation

Methyl Esters $\xrightarrow{\text{hydrogenation}}$ Oleochemical-Based
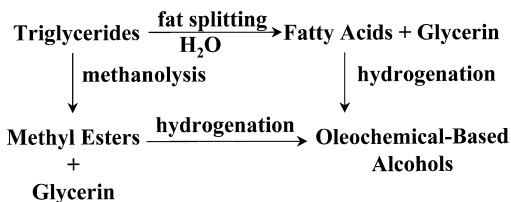+   Alcohols
Glycerin

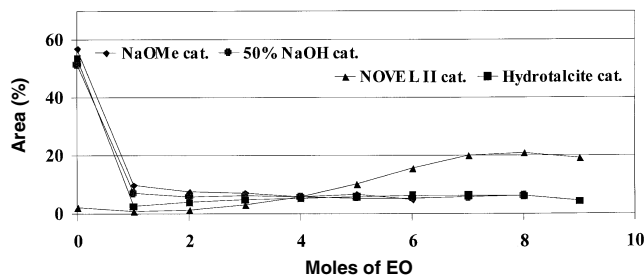**FIG. 2.** Major oleochemical routes for making alcohols.

FIG. 3. EO distributions of high-mole ethoxylates made from methyl myristate (60% w/w EO). See Figure 1 for abbreviation.

DEVELOPMENT OF METHYL ESTER ETHOXYLATION TECHNOLOGY

While the peaked ethoxylation technology was being commercially developed, two literature processes appeared in the late 1980s for producing methyl ester ethoxylates (MEE) from oleochemicals. These two processes involved the use of sodium hydroxide (5) and calcined hydrotalcite (6), respectively, as catalysts. Figure 2 shows the major oleochemical production routes to detergent alcohols. One process involves fat splitting of triglycerides such as coconut oil or palm kernel oil to produce fatty acids, which are then hydrogenated to produce oleochemical-based al-

cohols. The more commonly used process is the methanolysis of triglycerides to produce methyl esters, followed by hydrogenation to produce the alcohols (7). MEE could therefore have a significant production cost advantage over oleochemical-based alcohol ethoxylates.

In the processes cited in the literature for producing MEE using either sodium hydroxide (and also sodium methoxide) or calcined hydrotalcite as the catalyst, the ester ethoxylation reactions do not proceed smoothly. The reaction product contains very high levels of starting methyl ester, and the EO distribution curves are quite flat. With the peaking catalyst, the reaction proceeds smoothly, the conversion of methyl ester into the desired product is very high, and the EO distribution curves show peaking. These results are shown by the partial EO distribution curves obtained using gas chromatographic analytical data in Figure 3 (8).

Figure 4 outlines a postulated mechanism for explaining this facile ester ethoxylation reaction. Herein is invoked a transesterification/ethoxylation or ethoxylation/transesterification process involving the catalyst, EO, and methyl ester. This process continues to proceed until all of the methyl ester is consumed and the product is formed (3,4).

Figures 5 and 6 show complete EO distribution curves for methyl ester ethoxylates produced using NaOH and NOVEL® II catalyst, respectively, obtained using supercritical fluid chromatography. The curve in Figure 5 applies to the sodium hydroxide-catalyzed process for producing MEE and shows a large peak for the starting material and a flat EO distribution. The EO distribution curve obtained for the NOVEL® II-catalyzed ethoxylation of the methyl ester (Fig. 6) shows a small starting material peak and a peaked EO distribution. A side-by-side comparison of the two curves (Fig. 7) shows a marked difference in the two technologies, which is much larger than that for the corresponding alcohol ethoxylate cases (7).
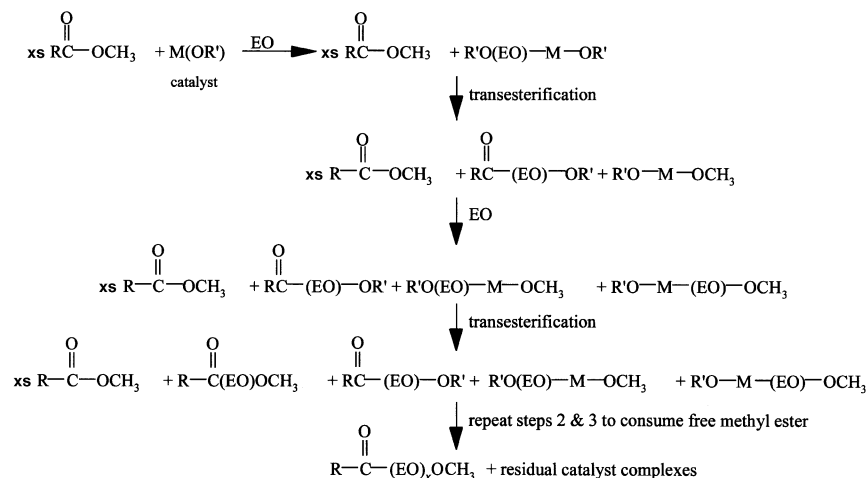

FIG. 4. Proposed mechanism for ethoxylation of (MEE) methyl ester ethoxylate using NOVEL® II catalyst, where M = Ca or Al; x = moles of EO; xs = excess.
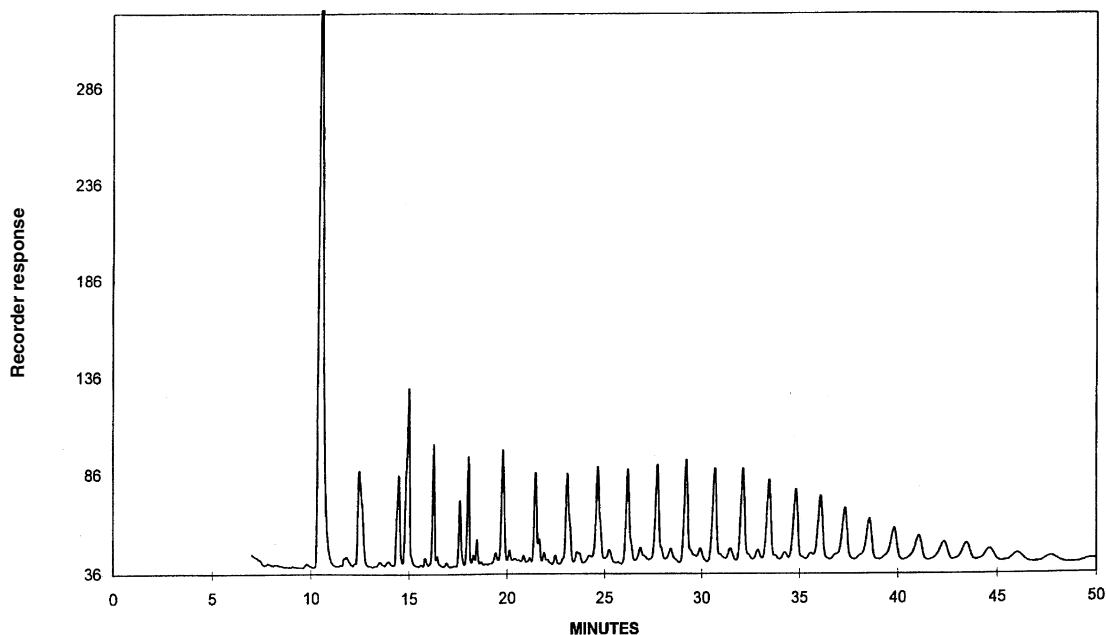
FIG. 5. EO distribution, obtained using supercritical fluid chromatography, of MEE (C_{14}-60% EO) obtained with conventional (NaOH) catalyst. See Figure 1 for abbreviation.

PERFORMANCE OF MEE

The detergency of MEE compares favorably with commercial surfactants. Figure 8 shows the results of studies on detergency of MEE vs. a variety of commercially available surfactants, such as alcohol ether sulfate (AES), alcohol sulfate (AS), alcohol ethoxylate from oxo-alcohol (C1215 7-mol AE), linear alkylbenzenesulfonate (LAS), and a variety of Ziegler alcohol-based ethoxylates (AE). MEE perform at least as well as the commercially available surfactants on sebum/cotton, sebum/permanent press, and red mineral oil/permanent press (3,4,7).

The length of the hydrophobe chain as well as the EO content affects detergency. Figure 9 shows that short-chain hydrophobes lead to inferior detergency. The coco-range MEE with an adequate EO level provide good detergency.
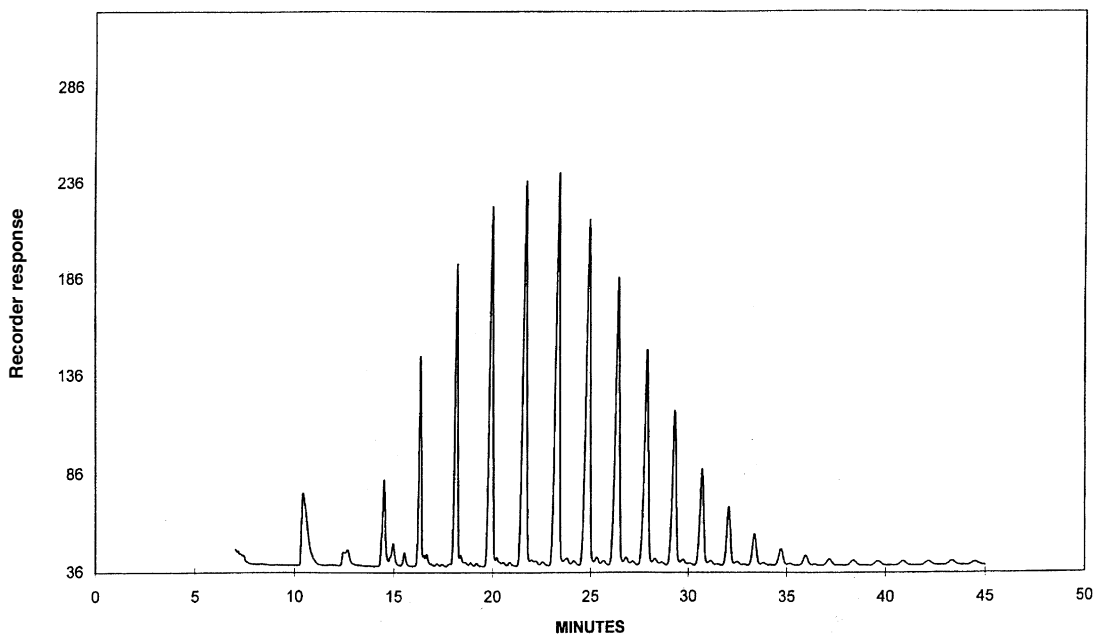

FIG. 6. EO distribution, obtained using supercritical fluid chromatography, of MEE (C14-60% EO) obtained with NOVEL® II catalyst. See Figure 1 for abbreviation.
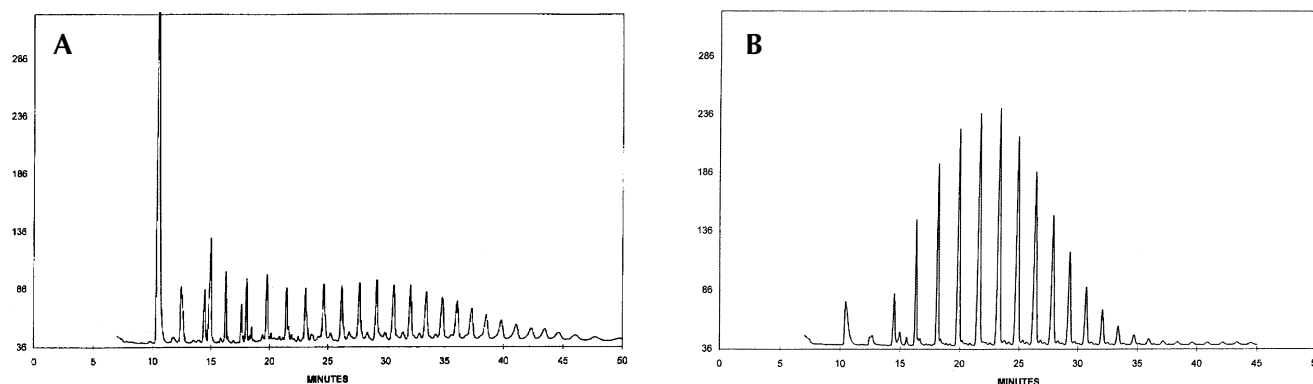
FIG. 7. EO distribution of MEE (by supercritical fluid chromatography) obtained with (A) conventional (NaOH) and (B) NOVEL® II catalysts. See Figure 1 for abbreviation.

Surprisingly, the tallow-range methyl esters with high EO content also showed very high detergency.

Compared to industry standards such as alcohol ethoxylates and nonylphenol ethoxylates, shorter-chain MEE at lower EO levels provide superior hard-surface cleaning performance on graphite, wax, and grease soil (3,4,7). Figure 10 summarizes hard-surface cleaning performance data obtained with MEE compared to some commercial ethoxylates.

Disregarding the ester linkage, MEE may be viewed as a methyl-capped alcohol ethoxylate, and as such, should be expected to produce low levels of foam. Indeed this is observed in practice (Fig. 11). Compared to a variety of commercially available surfactants, MEE produce the least

amount of foam with or without the soil being present. This may be an advantage in detergency and industrial applications where low foam is desired (3,4,7).

Thus, it appears that the MEE generated using peaked ethoxylation technology exhibit useful and attractive surfactant properties. Not surprisingly, therefore, numerous companies are actively studying and developing MEE: CONDEA Vista Company, Hoechst, Henkel, Lion, Kao, LG Chemical (S. Korea), and BASF.

CONDEA Vista Company (Houston, TX). The catalyst system used is a calcium/aluminum oxide complex (8). A description of the catalyst was given earlier in the text. The EO distribution of MEE is peaked, and the products exhibit good surfactant properties (3,4,7). This technology was de-
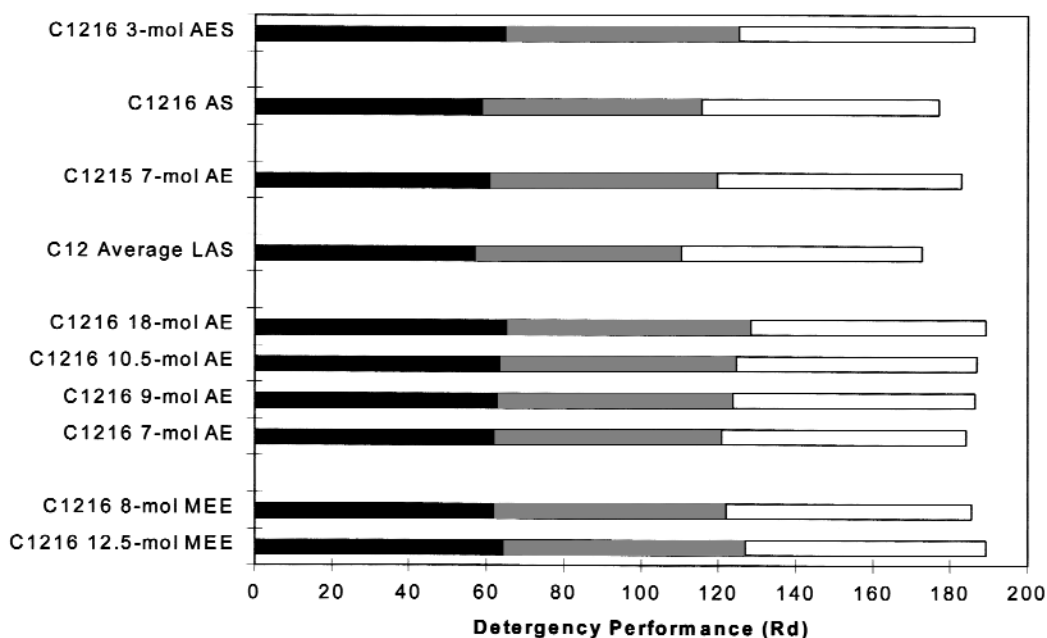

FIG. 8. Fabric detergency performance (measured as reflectance of light from cloth) of methyl ester ethoxylate (MEE) vs. conventional surfactants. (closed box), Sebum/cotton; (shaded box), sebum/permanent press; (open box), red mineral oil/permanent press. AES, alcohol ether sulfate; AS, alcohol sulfate; AE, Ziegler alcohol-based ethoxylates; LAS, linear alkylbenzenesulfonate.
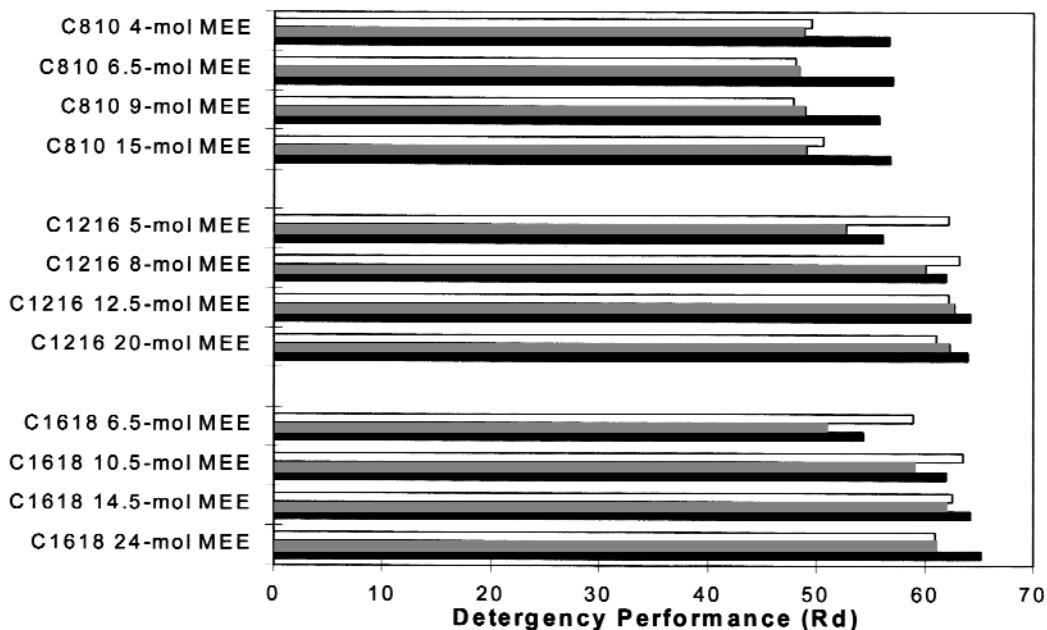
FIG. 9. Fabric detergency performance of MEE. See Figure 8 for abbreviation. (closed box), Sebum/Cotton; (shaded box) sebum/permanent press; (open box), red mineral oil/permanent press.

veloped by Vista Chemical Company (now CONDEA Vista Company) (Austin, TX) in 1990.

Hoechst AG (Frankfort, Germany). A 1989 Hoechst publication (5) disclosed the use of NaOH and NaOCH$_3$ as catalysts for the ethoxylation of methyl esters to produce MEE. The ethoxylates produced therein showed poor conversion of the starting methyl ester into products. Moreover, the EO distributions were flat (3,4). In 1999, Clariant (Frankfort, Germany) (formerly Hoechst Celanese) presented a paper (9) describing the use of a calcium-based peaking catalyst to produce peaked MEE that show good surfactant properties.

Henkel KGaA (Dusseldorf, Germany). In 1990, a Henkel publication (6) disclosed the use of calcined hydrotalcite as a catalyst to produce MEE. The ethoxylates thus produced

FIG. 10. Hard-surface cleaning performance of MEE. NPE, nonylphenol ethoxylate. See Figure 8 for other abbreviations.

showed high levels of starting methyl ester as well as a flat EO distribution (7,8). In 1997, Henkel demonstrated that acceptable reactivities and conversions can be achieved with calcined hydrotalcites when co-catalysts such as ethylene glycol, fatty acids, alkali catalysts, etc. are used (10,11).

Lion Corporation (Tokyo, Japan). A 1994 U.S. patent to Lion discloses the use of magnesium oxide-based catalyst to perform effective ethoxylation of methyl esters (12). These ethoxylates exhibit high conversion of the starting methyl ester, peaked EO distributions, and good surface chemical properties (12–18).

Kao Corporation (Tokyo, Japan). In 1997, Kao disclosed the use of magnesium-aluminum oxide (KYOWAAD) type catalyst for the production of peaked MEE (19,20).

LG Chemical (Tasjou, S. Korea). In 1998, LG Chemical disclosed the production of methyl esters using a solid metal oxide catalyst (W-7) (2). The EO distributions appear to be peaked.

BASF Corporation (Ludwigshafen, Germany). In 1999, BASF disclosed the use of hydrophobicized hydrotalcites as catalysts for the production of MEE (22).

DEVELOPMENT OF METHYL ESTER PROPOXYLATION TECHNOLOGY

The propoxylation of alcohols, with a conventional catalyst such as potassium hydroxide or the NOVEL® II catalyst, always proceeds through the 1-PO (propylene oxide) adduct (Fig. 12). Addition of one mol of PO to an alcohol produces the 1-PO adduct with a secondary terminal hydroxyl group. Further propoxylation results in an alcohol propoxylate with a PO distribution (23).
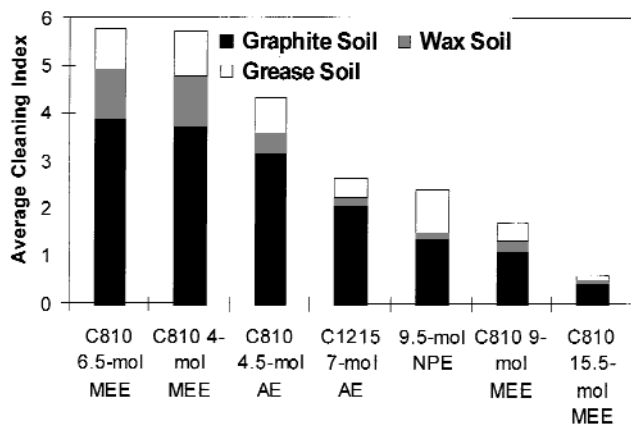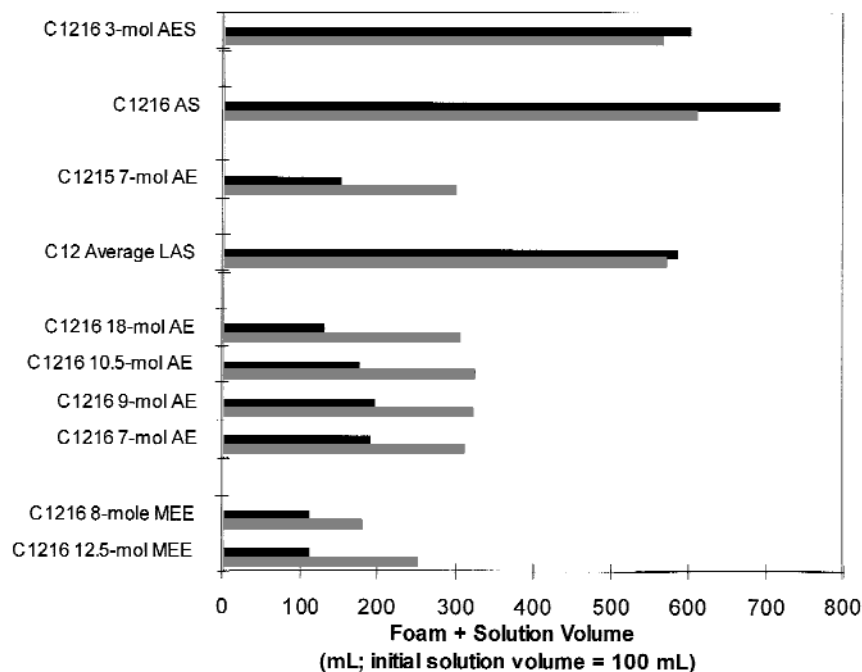
FIG. 11. Foam performance evaluation of methyl ester ethoxylates. See Figure 8 for abbreviations. (shaded box), No soil; (closed box), with soil.

Figure 13 shows the results of the propoxylation when methyl ester was propoxylated using NOVEL® II catalyst.

The starting material is shown in Figure 13A. Figure 13B shows the PO distribution of a 1-PO adduct of methyl ester. The 2-PO distribution is shown in 13C, and 13D shows the 3-PO distribution. In terms of the PO distribution, the propoxylation of methyl esters is seen to be quite different from that of alcohols wherein the alcohol is first converted almost completely to the 1-PO adduct before higher propoxymers get formed.

Figure 14 gives the postulated reaction mechanisms for the ester propoxylation reaction in analogy to that given in Figure 4 (24).

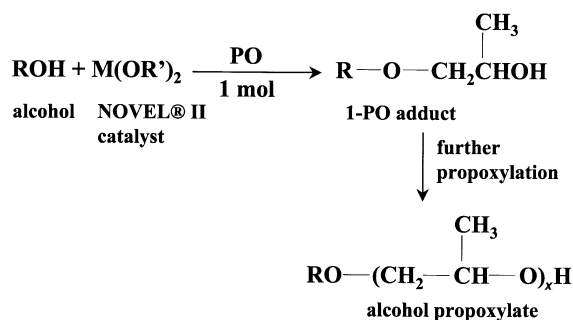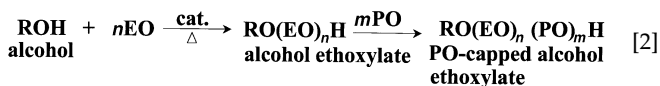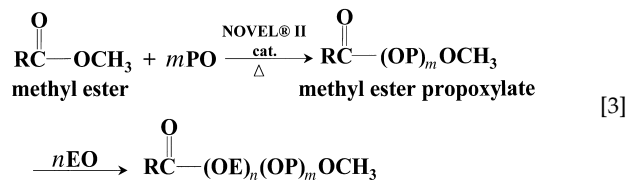A common application of propoxylation is the produc-

tion of PO-capped alcohol ethoxylates, which yields ultra low-foaming nonionics. The reaction involves first the ethoxylation of the alcohol using a conventional catalyst such as KOH, followed by propoxylation (Eq. 2). In the

$$\underset{\text{alcohol}}{\text{ROH}} + n\text{EO} \xrightarrow[\triangle]{\text{cat.}} \underset{\text{alcohol ethoxylate}}{\text{RO(EO)}_n\text{H}} \xrightarrow{m\text{PO}} \underset{\substack{\text{PO-capped alcohol}\\\text{ethoxylate}}}{\text{RO(EO)}_n(\text{PO})_m\text{H}} \quad [2]$$

production of PO-capped methyl ester ethoxylate, the order of addition of PO and EO has to be reversed. First, the methyl ester is propoxylated using the NOVEL® II catalyst to produce methyl ester propoxylate, which is next ethoxylated to yield the PO-capped MEE (Eq. 3). This

$$\underset{\text{methyl ester}}{\overset{O}{R\overset{\|}{C}}-\text{OCH}_3} + m\text{PO} \xrightarrow[\triangle]{\underset{\text{cat.}}{\text{NOVEL® II}}} \underset{\text{methyl ester propoxylate}}{\overset{O}{R\overset{\|}{C}}-(\text{OP})_m\text{OCH}_3}$$

$$\xrightarrow{n\text{EO}} \overset{O}{R\overset{\|}{C}}-(\text{OE})_n(\text{OP})_m\text{OCH}_3 \qquad\qquad [3]$$

difference can be easily ascertained on the basis of reaction mechanisms involved in the alkoxylation of the two hydrophobes (Fig. 4).

PO-capping of MEE results in drastically reduced foam levels. Table 1 shows foaming behavior of PO-capped MEE compared to that of MEE and alcohol ethoxylates (24).
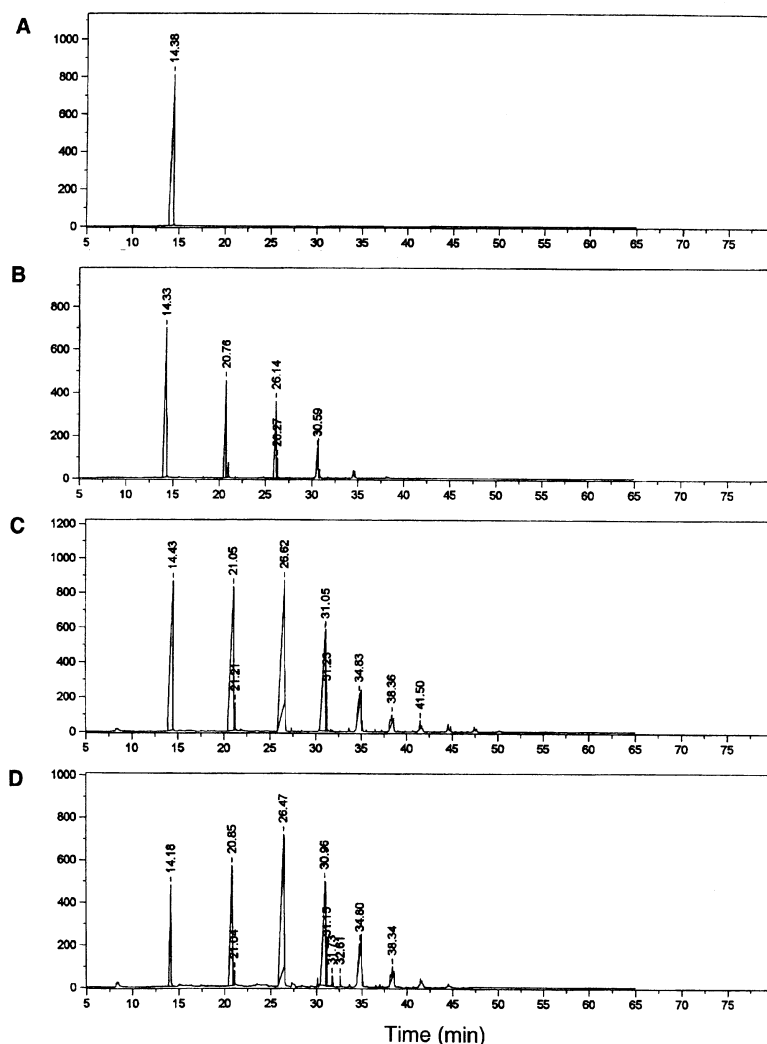
$$\underset{\substack{\text{alcohol}\quad\text{NOVEL® II}\\\text{catalyst}}}{\text{ROH} + \text{M(OR')}_2} \xrightarrow[\text{1 mol}]{\text{PO}} \underset{\text{1-PO adduct}}{R-O-\overset{\overset{\displaystyle\text{CH}_3}{|}}{\text{CH}_2\text{CHOH}}}$$

further propoxylation ↓

$$\underset{\text{alcohol propoxylate}}{\text{RO}-(\text{CH}_2-\overset{\overset{\displaystyle\text{CH}_3}{|}}{\text{CH}}-\text{O})_x\text{H}}$$

FIG. 12. Propoxylation of linear alcohols, where M = Ca or Al; x = mol of propylene oxide (PO).

FIG. 13. Methyl ester propoxylates. Distribution of propoxymers (detector response vs. time) for lauric acid methyl ester 1-, 2-, and 3-mol (avg.) propoxylates (*via* gas chromatography). (A) Lauric acid methyl ester; (B) lauric acid methyl ester 1-mol (avg.) propoxylate; (C) lauric acid methyl ester 2-mol (avg.) propoxylate; (D) lauric acid methyl ester 3-mol (avg.) propoxylate.
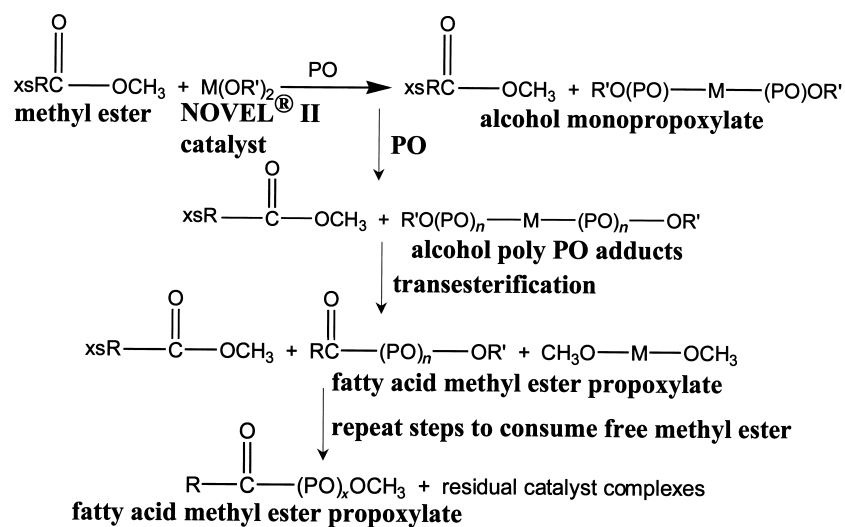

FIG. 14. Propoxylation of methyl esters, where M = Ca or Al; x = mol of PO; xs = excess.

TABLE 1
Impact of Propoxylation on Methyl Ester (ME) Ethoxylate Foaming

		Volume of foam (+ solution) generated[a] (mL)		
Feedstock	PO (mol)	w/o Soil	w Soil[b]	Std. dev.
C_{12} alcohol 9 EO	0	580	580	10
C_{12} ME 9 EO	0	520	450	7.5
C_{12} ME 9 EO + 2 PO	2	120	110	7.5
C_{12} ME 9 EO + 3 PO	3	110	110	12.5
C_{12} alcohol 12 EO	0	650	625	10
C_{12} ME 12 EO	0	560	460	12.5
C_{12} ME 12 EO + 2 PO	2	130	120	12.5
C_{12} ME 12 EO + 3 PO	3	120	110	10
C_{12} alcohol 15 EO	0	550	550	10
C_{12} ME 15 EO	0	580	580	10
C_{12} ME 15 EO + 2 PO	2	180	120	7.5
C_{12} ME 15 EO + 3 PO	3	130	110	5.7

[a]Initial volume of test solution [1% (w/w) surfactant] = 100 mL; number of test strokes of Schlag = 80.
[b]Soil (0.01 g) made up of 30% homogenized milk, 25% water, 15% Crisco[TM] vegetable shortening, 15% olive oil, and 15% instant mashed potato flakes; soil is placed on top of a 2.3-g sugar cube, and the cube is added to the test solution. PO, propylene oxide; EO, ethylene oxide.
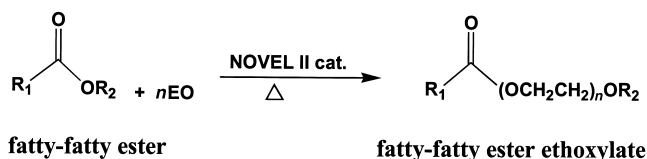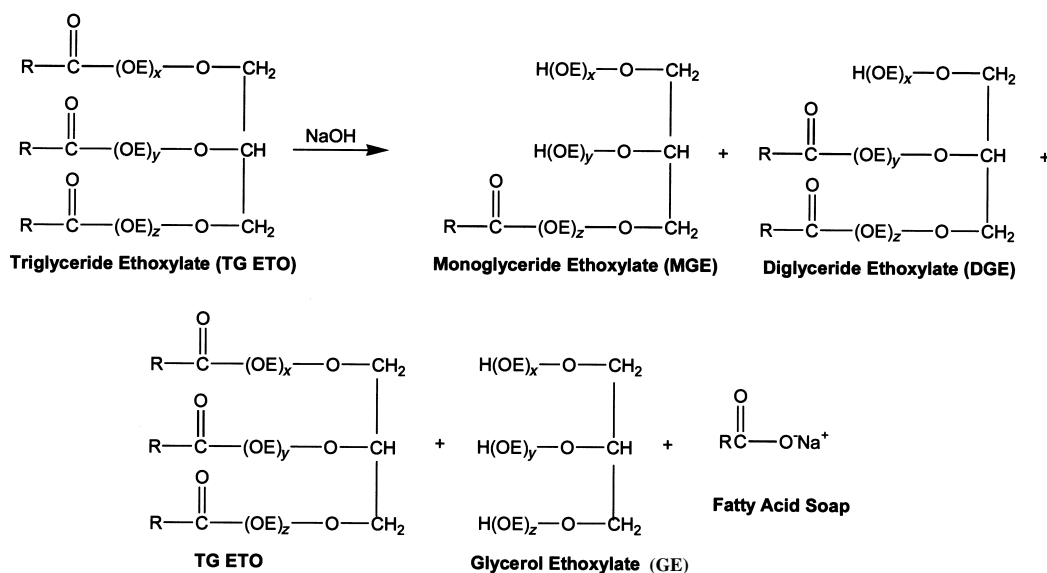

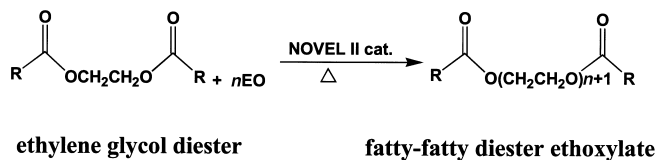**FIG. 15.** Fatty-fatty ester ethoxylate. See Figure 1 for abbreviation.

FIG. 16. Fatty-fatty diester ethoxylate. See Figure 1 for abbreviation.
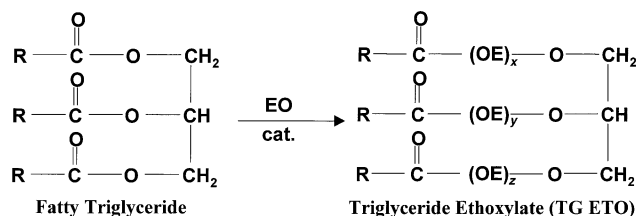

FIG. 17. Fatty triglyceride ethoxylate. OE (oxyethylene) is synonymous with EO (ethylene oxide or ethoxy) (25).

EXTENSIONS OF TECHNOLOGY

The ethoxylation technology has been extended to materials other than methyl esters such as fatty-fatty esters, fatty-fatty diesters, and hindered substrates, (Figs. 15–17). In Figure 15, a fatty-fatty ester is ethoxylated to produce fatty-fatty ester ethoxylates. Figure 16 shows the facile ethoxylation of a fatty-fatty diester to produce a fatty-fatty diester ethoxylate.

Figure 17 shows the case of ethoxylating a highly sterically hindered substrate. The ester is a fatty triglyceride such as coconut oil, palm kernel oil, or tallow. Thus, the NOVEL® II technology is able to ethoxylate esters of varying steric bias.
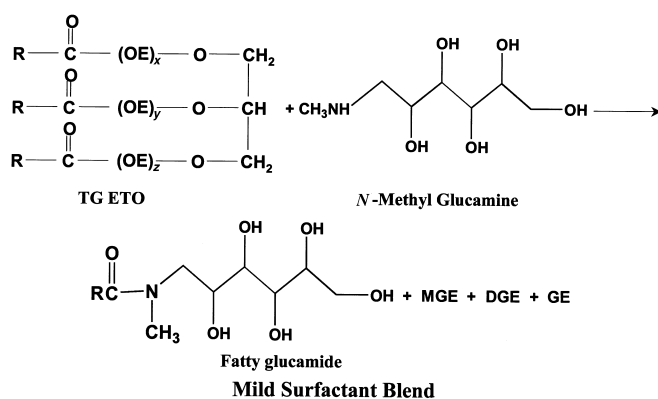

Mild Surfactant Blend
FIG. 18. Partially saponified triglyceride ethoxylates.

FIG. 19. Glucaminolized triglyceride ethoxylates (TG ETO). See Figures 17 and 18 for other abbreviations.

DERIVATIZATION OF ESTER ETHOXYLATES

Ester ethoxylates were derivatized to produce useful surfactant blends. The first example (Fig. 18) is a partially saponified triglyceride ethoxylate. Partial saponification of the triglyceride ethoxylate leads to a blend of surfactants composed of monoglyceride ethoxylate, diglyceride ethoxylate, unreacted triglyceride ethoxylate accompanied by glycerol ethoxylate, in addition to fatty acid soap. While fatty acid soaps are known to be harsh to the human skin, the entire product blend was reported to be very mild to skin (26,27).

Triglyceride ethoxylates were also derivatized by reaction with *N*-methyl-glucamine (Fig. 19) to produce a mixture of fatty glucamide, monoglyceride ethoxylate, diglyceride ethoxylate, and glycerol ethoxylates. All of these components are known to be mildness-imparting agents, and, as such, the product mixture is presumed to be a mild surfactant blend (28).

Peaked ethoxylation technology developed for producing narrow-range alcohol ethoxylates offers a powerful methodology for alkoxylating esters of various steric bias. Some of these ester ethoxylates can be derivatized to produce useful surfactant blends. Thus, this ester ethoxylation technology may offer a commercially viable route toward the production of low-cost surfactants.

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