# Nonionic Detergent Degradation. I. Thin-Layer Chromatography and Foaming Properties of Alcohol Polyethoxylates

**STELLA J. PATTERSON, C. C. SCOTT, and K. B. E. TUCKER,**
**Laboratory of the Government Chemist, Cornwall House, London, England**

## Abstract

The thin-layer chromatographic method for determination of nonionic detergents has been used for the chemical assessment of alcohol polyethoxylates and material derived from them during degradation under simple laboratory conditions. Foaming capacity during degradation was also measured on a representative selection of the materials under test.

With one exception (a material with a highly branched alkyl chain) the disappearance of all the alcohol-ethoxylates tested was rapid; a small increase in time required for complete disappearance was observed with the more highly ethoxylated materials, and with the materials which had some slight branching in the alkyl chain. Residues of the polyethylene glycol type, which were generally more persistent than the original materials, were observed to build up as the original materials disappeared, increasing ethoxylation present in the original material giving rise to increasing quantities of residues.

The foaming capacity at every stage of the degradation, that is, foam formation alone or synergistic effect on foam formation because of other detergents, could be closely correlated with the results obtained by using the thin-layer chromatographic procedure.

## Introduction

Mills and Stack (1) in 1953 indicated that the ethylene oxide chain was not biodegradable, but two years later Bogan and Sawyer (2) suggested that the ethoxy ether linkage did not of itself resist biochemical oxidation although the nature of the groups attached to the polyoxyethylene chain, and the length of the chain itself, could exert a considerable influence on the rate of degradation of the various types of materials under study. Oldham (3) in 1958 stated that "Lissapol N", a typical branched-chain alkyl phenol polyethoxylate, could not be oxidized biochemically; then little progress appears to have been made until the degradation studies described in a series of papers (4–14), which have been published during the past three years. In the absence of a chemical test by which important breakdown products could be assessed as the degradation proceeded, the application of a variety of physical methods is described in these papers, such as surface-tension measurements (4,7), foaming (7,13), infrared and ultraviolet spectroscopy (10,14). Chemical assessment (5–9,11) has been almost entirely confined to the cobaltothiocyanate colorimetric method (15,16) although in one paper (13) there is a brief reference to the use of a potassium mercury iodide turbidity method (17).

The general conclusions that emerge from these papers may be summarized as follows: First, branched-chain alkyl phenol polyethoxylates are generally considered to be "hard" although some slow degradation has been observed in the majority of cases. Materials in which the hydrophobic group is a straight-chain, primary or secondary alcohol are generally considered to be "soft," *i.e.*, rapidly and completely degraded. Second, the rate of degradation varies, as might be expected, according to the procedure adopted for effecting the biochemical oxidation. Hence the conditions for a series of comparative tests should be maintained as uniform as possible. Third, the results of degradation tests which were followed by chemical means alone should be interpreted cautiously. Huddleston and Allred (12) recently reported that loss of cobaltothiocyanate sensitivity did not necessarily correlate with loss of foaming capacity and surface-tension properties of three typical alkyl phenol polyethoxylated nonionics.

The thin-layer chromatographic procedure (18,19,20), originally devised for the determination of small quantities of polyethoxylated nonionic detergents in sewage effluents, is particularly suitable for application to the study of biogradability since, in addition to providing a quantitative assessment of the amount of detergent material present, the behavior of ethoxylated degradation products containing three or more ethylene oxide groups in the chain can be observed at any stage during the degradation.

In this paper, degradation studies are described in which a variety of alcohol polyethoxylates supplied by several manufacturers were used. Excellent agreement was obtained in replicate tests with the same and different batches of activated sludge in the medium used for the simple laboratory die-away test conducted under standardized conditions. Many of the materials, representative of each type examined, were also subjected to the foaming test during the course of degradation.

## Experimental Procedure

### Thin-Layer Chromatographic Method

In outline the method (18,19,20) is as follows. First, 250 ml of the effluent are extracted four times with chloroform, using magnesium sulphate as the salting-out agent; the combined chloroform extracts are washed with acid, then with alkali, and evaporated just to dryness. The residue is dissolved in a small volume of chloroform (0.5 ml), and suitable aliquots, 10 μl and 20 μl, are applied to two silica-gel, thin-layer plates alongside a range of standards of a widely used type of nonionic detergent. Duplicate plates are prepared. One is run in a solvent mixture consisting of 40 parts of ethyl acetate, 30 parts of acetic acid, and 30 parts of water by volume, which isolates the nonionic material as a single spot for assessment of the quantity present; and the other is run in a second mixture consisting of 70 parts of ethyl acetate, 16 parts of acetic acid, and 15 parts of water by volume, which resolves the nonionic material into a

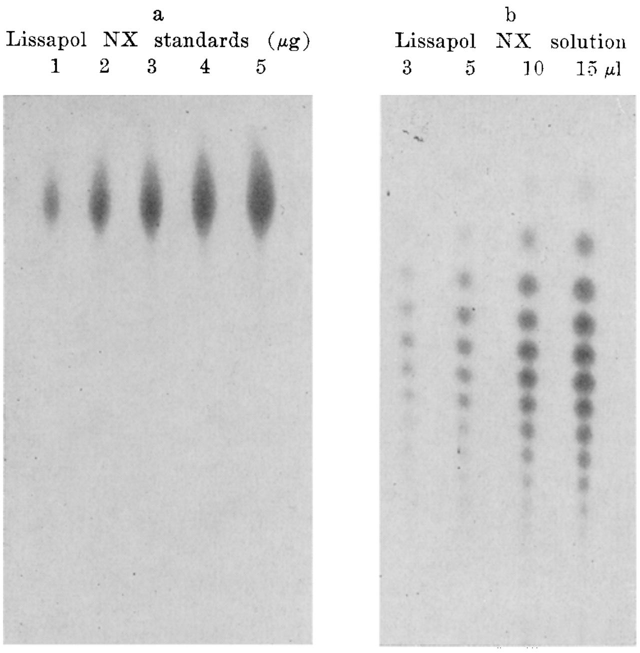


FIG. 1. Thin-layer plates, showing a range of standards of Lissapol NX. a) Run in the "single-spot" solvent: ethylacetate 40, acetic acid 30, water 30, parts by volume. b) Run in the "resolving solvent": ethyl acetate 70, acetic acid 16, water 15, parts by volume.

characteristic series of spots. The plates are sprayed with a modified Dragendorff reagent, then covered immediately with a clean glass plate; approximately 0.5 μg of nonionic material is the lower limit of detection on the single-spot, and 1 μg on the resolved, chromatograms. Figure 1 shows a range of standards of "Lissapol NX," a commercial 9-ethoxy nonionic run in a) the "single-spot" solvent and b) the "resolving" solvent.

In the routine degradation tests, the solutions contain very much less extraneous material than sewage effluents so it is possible to omit the acid and alkali washing of the chloroform extract; this also ensures that there is no loss of acid degradation products extracted into the chloroform. It is necessary however to introduce an additional stage into the procedure in order to extract any acid material that might be retained in the aqueous phase: after the "normal" chloroform extractions described above, the aqueous phase is acidified to approximately 2N with sulphuric acid and re-extracted three times with chloroform; this "acid" chloroform extract is evaporated just to dryness, dissolved in a small volume of chloroform, and separately chromatographed.

The polyglycol type of material is visible on the single-spot chromatograms as a streak of lower $R_F$ value than the principal spot of the nonionic detergent from which it is derived. It can be assessed visually against standards of the polyglycol nearest to it in position on the chromatogram, that is, the material derived from an alcohol 9-ethoxylate can be assessed against a range of standards of polyglycol of molecular weight 450. The $R_F$ value of polyglycols decreases as the molecular weight is increased.

### Biodegradation Test Method

The method used has been described in connection with the report on recent work on the biodegradation of anionic detergents in the Supplement to the Eighth Progress Report of the British Standing Technical Committee on Synthetic Detergents (21).

A steady stream of moist air is blown over a solution of the detergent in previously aerated dilution water of the type used in the BOD test (22), to which have been added 30 mg per liter of air-dried activated sludge. It is contained in a 1.5-liter flask darkened on the outside and maintained at a constant temperature of 20C. Aliquots of the solution are removed as required, at various stages of degradation, and examined by the thin-layer chromatographic method.

Several batches of dried sludge were used in the course of the experiments; they were all derived from the same sewage works and contained approximately 25 ppm of nonionic detergent, which was insufficient to interfere with the test method. No special acclimation of the solutions was undertaken prior to the introduction of the nonionic material under test. No detergent was detected in a "blank" test on the medium.

### Foaming Tests

The apparatus is adapted from the type described by Truesdale (23) and consists of a long glass tube 4 ft long and 3.75 in. in internal diameter, closed at the bottom by a rubber bung carrying an inlet tube that terminates in a No. 3 sintered glass disc and an outlet tube that ends in a tap for emptying.

Conditions were carefully controlled since slight variations were found to have considerable influence on the amount of foam produced, and the same tube and sinter were used throughout the work. The volume of liquid introduced into the tube was standardized at four liters, all dilutions were made with distilled water from the same glass still, the temperature was controlled at 22.5 ± 0.5C since temperature variations can have significant effects on the volume of foam produced, as shown in Table I, and air was forced through the sinter at a constant rate of 90 ml per minute. The material under test was foamed until the maximum foam height was observed (approximately 5 to 10 min but somewhat longer when anionic detergents were present); this was the stage at which the arrival of air bubbles at the surface of the liquid ceased to lead to the formation of stable foam bubbles. Slight cavities which developed at the surface were removed by releasing the tube from its clamp and rapidly swirling the solution, the layer

TABLE I
Variation in Foaming Capacity with Temperature[a]

| Material | Concn. | Foam Height, cm | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 15C | | 20C | | 25C | | 30C | |
| | | Initial | 2 min later | Initial | 2 min later | Initial | 2 min later | Initial | 2 min later |
| Nonionic | 1 mg per liter | 1.8 | 1.4 | 2.4 | 1.9 | 2.7 | 2.4 | 3.1 | 2.8 |
| Anionic | 1 mg per liter | 0.0 | | 0.1[b] | 0.1[b] | 0.3[b] | 0.1[b] | 1.0[b] | 0.7[b] |
| Nonionic + Anionic | 1 mg per liter + 1 mg per liter | 4.0 | 3.5 | 5.8 | 5.4 | 7.0 | 6.0 | 7.5 | 6.3 |

[a] The nonionic detergent is a soft alkyl 9-ethoxylate. The anionic detergent is a soft alkyl benzene sulphonate.
[b] Rim round outer edge of tube only.

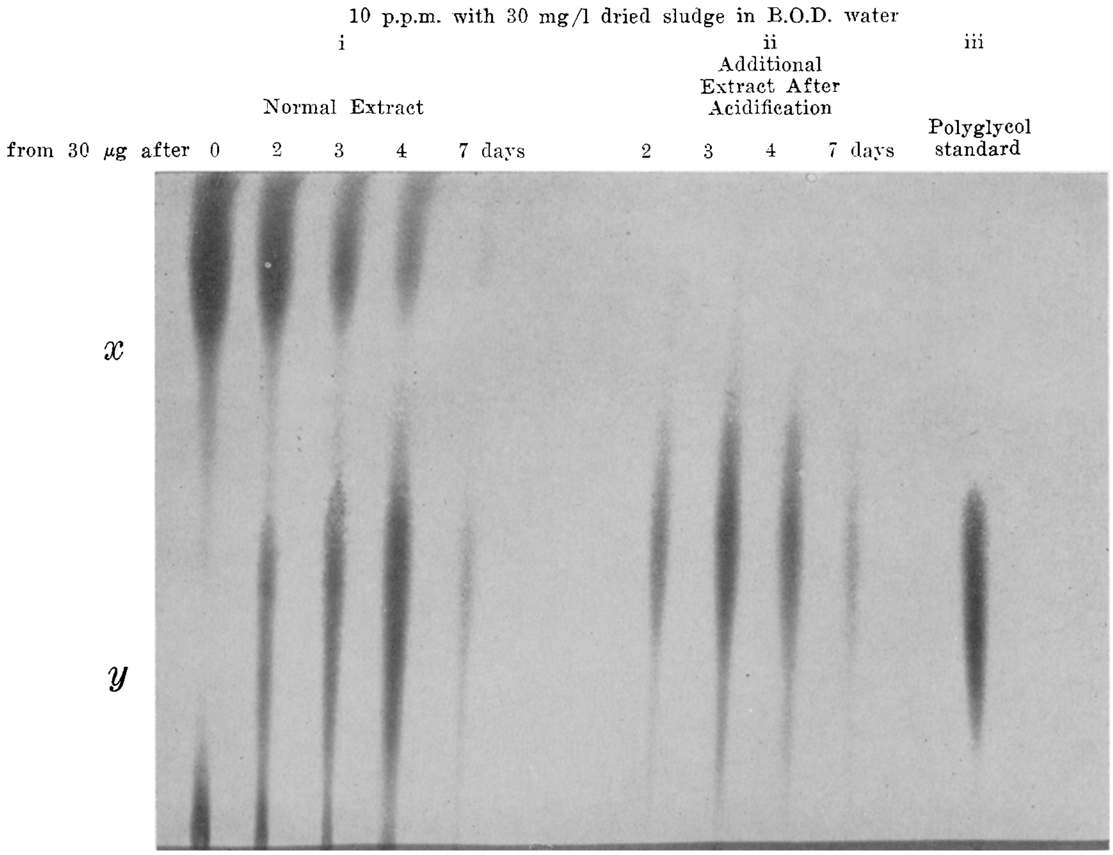


FIG. 2. Thin-layer plate, showing stages in the degradation of a linear alcohol 9-ethoxylate compound at 20C.

was then stabilized by a few seconds further bubbling, and its height was measured in centimeters. Exactly two minutes later the height was measured again; this second measurement served as a check on the stability of the foam. After each test the column was thoroughly washed out, and a blank check was done on four liters of distilled water. Checks on standard amounts of detergents were also run at frequent intervals, and after a little experience it was possible for an operator to obtain extremely consistent results.

## Results and Discussion

### Degradation

Figure 2 shows at i a chromatogram of the degradation of a straight-chain alcohol 9- ethoxylate. The disappearance of the original detergent, at position *x*, is accompanied by build-up of polyglycol-type material at position *y*, and the disappearance of this material is also shown. The chromatogram shows at ii the additional "acid extract" material obtained when the aqueous solution remaining after normal chloroform extraction was acidified and re-extracted with chloroform, and it will be seen that this material also disappears rapidly. A single spot of polyethylene glycol 450 has been added at iii in order to show its relative position.

A number of alcohol ethoxylates were selected so that they provided variety in the source of manufacture, in the alkyl group structure, and in the length of ethoxy chain; they were degraded by the standardized test procedure described above, using the same initial concentration of detergent, 10 mg per liter, in each experiment. The contents of nonionic detergent, polyglycol-type degradation product and "acid extract" degradation product were measured at frequent intervals, and the results are shown in Figures 3–9. Replicate results on individual samples were extremely consistent when the same conditions were maintained throughout the tests. Variation of the conditions, namely, an increase in the initial concentration of detergent or of activated sludge, led to differences in the rate of degradation and in the ratio of original to degraded material as degradation proceeded, but the types of degradation materials indicated on the thin-layer chromatogram were unchanged. In some duplicate experiments the BOD

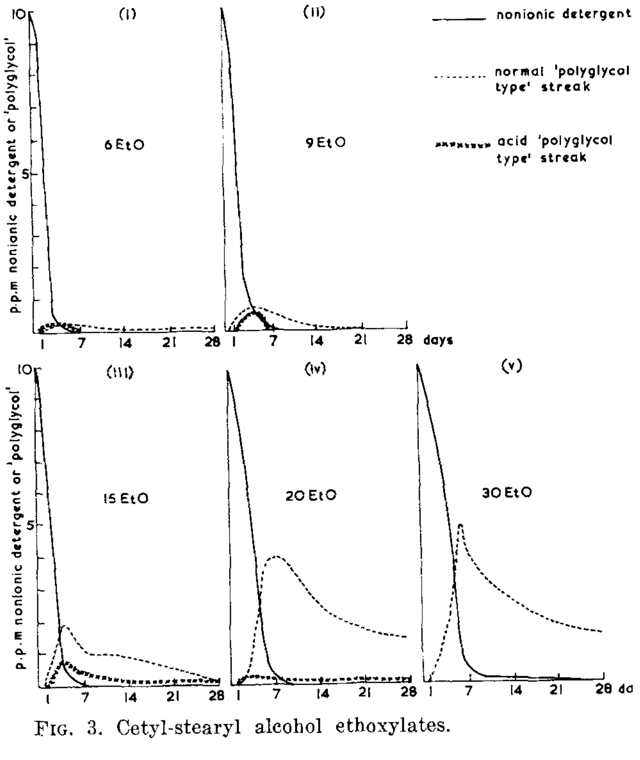


FIG. 3. Cetyl-stearyl alcohol ethoxylates.

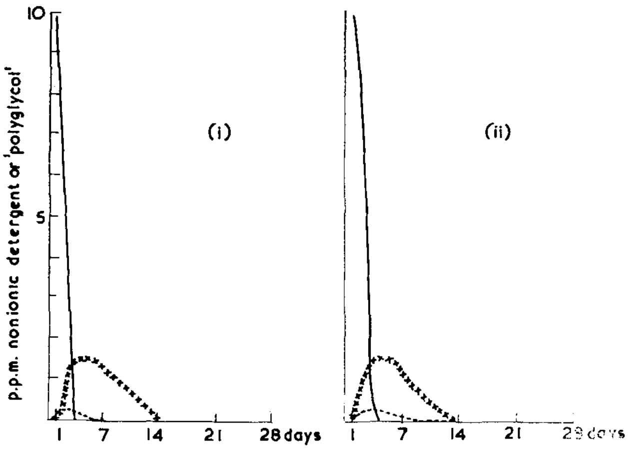


FIG. 4. Left, linear $C_{10}$-$C_{12}$ primary alcohol ethoxylate, approximately 58% EtO. Right, linear $C_{12}$-$C_{15}$ primary alcohol ethoxylate, approximately 62% EtO.

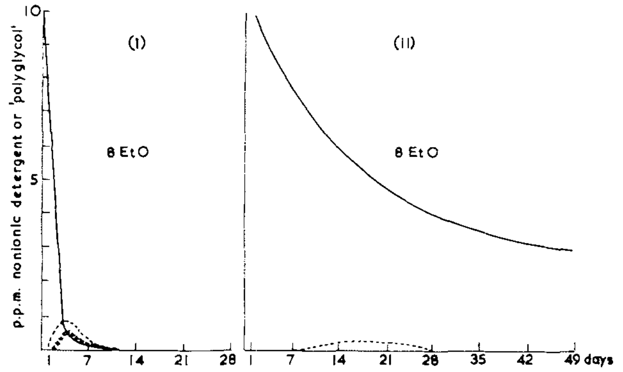


FIG. 6. Left, stearyl alcohol ethoxylate. Right, iso-tridecyl alcohol ethoxylate.

water containing activated sludge was filtered to remove all particles prior to the addition of the detergent; no significant differences were observed between the results obtained by using filtered or unfiltered solutions, hence there was no adsorption on particles in the unfiltered solutions.

In general, the longer the ethoxy chain of the original nonionic material, the more slowly it degrades and the greater the amount and persistence of the polyglycol type of material derived from it. The rate of disappearance of the nonionic material is also governed by the nature of the hydrophobic group. The influence of these factors is clearly illustrated in the graphs. Materials i to v of Figure 3, all from the same British source and with the same linear primary hydrophobic group, show a slight progressive reduction in the rate of degradation of the original nonionic material and an appreciable progressive increase in the quantity and persistence of the polyglycol type of material formed as the ethoxy chain length is increased. Figure 4 shows almost insignificant differences between the degradation rates of two products from the same German source, which differ in the length of the linear primary hydrophobic group, accompanied by a very slight change in the ethoxylate content. Figure 5 shows again the retardation in the degradation rate that occurs with the increasing length of ethoxy chain, demonstrated by the use of two linear secondary alcohol ethoxylates from an American source; it will also be observed that material i is degraded a little more slowly than a linear primary alcohol 9-ethoxylate. Figure 6 provides the most extreme example of the effect of branching in the alkyl chain: it shows two 8-ethoxylates from the same German source, material (i) is the normal straight chain 8-ethoxylate and behaves as expected whereas (ii), which is the highly branched iso-tridecyl 8-ethoxylate, degrades so slowly that it is doubtful whether this material can be regarded as "soft." Figure 7 shows a British material with a slightly branched primary alkyl chain, again a 9-ethoxylate, which is also degraded a little more slowly than corresponding straight-chain material. Figure 8 shows material from another British manufacturer, similar in composition and behavior to (iv) and (v) of Figure 3, inserted because it was utilized in the study of degradation mechanism to be described in Part III of this series. Figure 9 is inserted because it illustrates that this British material, which is widely used as a foam-booster in liquid detergents in the United Kingdom, degrades rapidly, leaving no residues which could cause any interference.

Figure 10 shows the degradation curves of polyglycols of different molecular weights when they were degraded under the same conditions as the nonionics discussed above. It illustrates that, although the simple lower-molecular-weight materials are rapidly degraded, the high-molecular-weight materials and copolymers can be very persistent.

### Foaming

In order to obtain sufficient material to provide four liters of solution of suitable concentration for

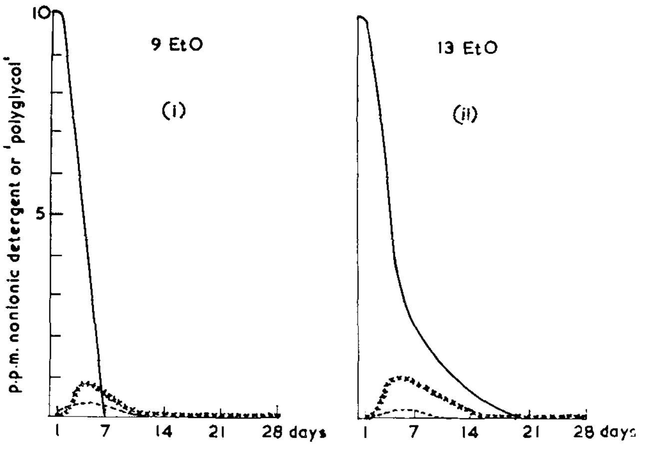
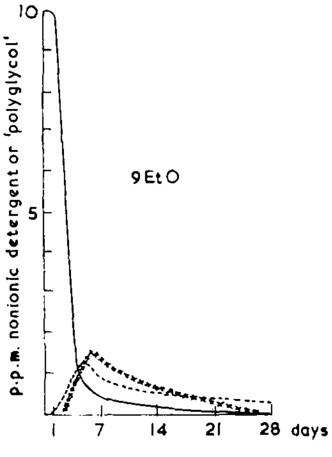


FIG. 5. Linear $C_{11}$-$C_{15}$ secondary alcohol ethoxylates.



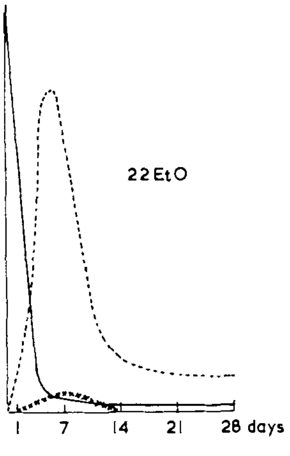


FIG. 7. Slightly branched $C_{12}$-$C_{15}$ primary alcohol ethoxylate.
FIG. 8. Right, linear $C_{16}$-$C_{18}$ alcohol ethoxylate.

the foaming experiments, it was necessary to start the degradations at a higher initial detergent concentration than in the experiments described above; a somewhat slower rate of degradation was also required so that the foaming properties could be examined at several stages during the degradation. These conditions were satisfied when 50 mg per liter of detergent were degraded at room temperature, using the usual quantity, 30 mg per liter, of dried sludge in the medium. The nonionic detergent content and the total, that is, "normal" plus "acid," polyglycol-type degradation products, were determined by the thin-layer chromatographic method prior to each foaming experiment. It was confirmed on a thin-layer chromatogram that the degradation products formed appeared to be of the same type as the degradation products formed in the experiments illustrated in Figures 3–9, where a lower initial concentration of detergent was involved but, since the degradations were not in this series of experiments conducted simultaneously and were not under controlled temperature conditions, the relative changes in rate of degradation corresponding to changes in composition of the detergents were less consistent than in the earlier series of experiments.

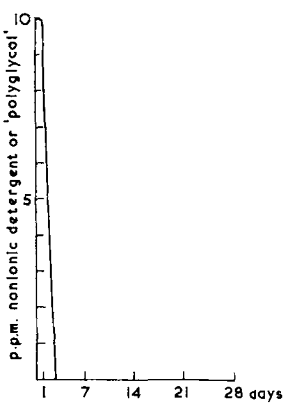
On the basis of the thin-layer chromatographic results a suitable dilution of the concentrated degrading solution was made to provide four liters of diluted solution containing 0.5 mg per liter of nonionic detergent; thus, as degradation proceeded, increasing quantities of the degrading solution were required. Whereas the nonionic detergent content was decreasing, the polyglycol type of material was increasing so that in the later stages of degradation some of the diluted solutions containing 0.5 mg per liter of nonionic detergent contained considerably

TABLE II

Soft Nonionic Detergents, Correlation of Foaming Capacity with Degradation[a]

| | Concentration, mg per liter | | | | Foam Height, cm | | | |
|---|---|---|---|---|---|---|---|---|
| Time | Total | | After dilution for foaming | | Alone | | +0.5 mg per liter anionic | |
| | N.I. det. | PEG | N.I. det. | PEG | Initial | 2 min later | Initial | 2 min later |
| *Linear $C_{16}$-$C_{18}$ Primary Alcohol Ethoxylate (9 EtO)* | | | | | | | | |
| Initially | 50 | 0[b] | 0.5 | 0 | 0.2 | 0.1 | 0.7 | 0.4 |
| after 2 days | 30 | < 2 | 0.5 | <0.03 | 0.3 | 0.2 | 0.8 | 0.5 |
| " 3 days | 20 | 6 | 0.5 | 0.2 | 0.2 | 0.1 | 0.7 | 0.4 |
| " 4 days | 12 | 6 | 0.5 | 0.3 | 0.2 | 0.1 | 0.8 | 0.5 |
| " 7 days | < 1 | 8 | <0.03 | 0.5 | 0.0 | | 0.0 | |
| " 4 wks | 0 | 2 | 0 | 0.5 | 0.0 | | 0.0 | |
| " 8 wks | 0 | < 0.5 | 0 | <0.5 | 0.0 | | 0.0 | |
| *Linear $C_{16}$-$C_{18}$ Primary Alcohol Ethoxylate (20 EtO)* | | | | | | | | |
| Initially | 50 | 0[c] | 0.5 | 0 | 0.5 | 0.3 | 1.1 | 1.0 |
| after 2 days | 20 | 15 | 0.5 | 0.4 | 1.2 | 0.9 | 2.4 | 2.0 |
| | | | | | *1.0* | *0.8* | *2.2* | *2.0* |
| " 3 days | 15 | 20 | 0.5 | 0.7 | 1.4 | 1.2 | 2.5 | 2.1 |
| | | | | | *1.3* | *1.1* | | |
| " 4 days | 12 | 30 | 0.5 | 1.3 | 1.3 | 1.0 | 2.7 | 2.3 |
| | | | | | *1.3* | *1.1* | *2.5* | *2.2* |
| " 7 days | < 1 | 40 | <0.03 | 0.5 | 0.3 | 0.1 | 1.3 | 1.1 |
| " 14 days | 0 | 30 | 0 | 0.5 | 0.1 | 0.0 | 1.0 | 0.6 |
| " 21 days | 0 | 15 | 0 | 0.5 | 0.1 | 0.0 | 1.0 | 0.6 |
| " 4 wks | 0 | 12 | 0 | 0.5 | 0.1 | 0.0 | 1.0 | 0.6 |
| " 8 wks | 0 | 6 | 0 | 0.5 | <0.1 | 0.0 | 0.7 | 0.4 |
| " 10 wks | 0 | 2 | 0 | 0.5 | <0.1 | 0.0 | 0.6 | 0.4 |
| *Linear $C_{16}$-$C_{18}$ Primary Alcohol Ethoxylate (30 EtO)* | | | | | | | | |
| Initially | 50 | 0[c] | 0.5 | 0 | 0.4 | 0.3 | 1.4 | 1.3 |
| after 2 days | 30 | 15 | 0.5 | 0.3 | 1.0 | 0.7 | 2.1 | 1.9 |
| | | | | | *1.1* | *0.9* | *2.3* | *2.1* |
| " 3 days | 25 | 20 | 0.5 | 0.4 | 1.5 | 1.3 | 3.5 | 3.2 |
| | | | | | *1.4* | *1.2* | *3.3* | *3.1* |
| " 4 days | 20 | 20 | 0.5 | 0.5 | 1.3 | 1.1 | 3.2 | 3.0 |
| | | | | | *1.4* | *1.2* | *3.3* | *3.1* |
| " 7 days | 10 | 20 | 0.5 | 1.0 | 2.3 | 1.6 | 4.0 | 3.5 |
| | | | | | *2.1* | *1.5* | *3.8* | *3.3* |
| " 14 days | < 1 | 30 | <0.03 | 0.5 | 0.3 | 0.2 | 1.8 | 1.5 |
| " 21 days | 0 | 20 | 0 | 0.5 | 0.3 | 0.2 | 1.7 | 1.5 |
| " 4 wks | 0 | 18 | 0 | 0.5 | 0.3 | 0.1 | 1.4 | 1.1 |
| " 8 wks | 0 | 12 | 0 | 0.5 | 0.2 | 0.1 | 1.1 | 0.8 |
| *Linear $C_{10}$–$C_{12}$ Primary Alcohol Ethoxylate (58% Eto)* | | | | | | | | |
| Initially | 50 | 0[b] | 0.5 | 0 | 0.4 | 0.3 | 1.4 | 1.1 |
| after 2 days | 40 | ≤ 2 | 0.5 | <0.03 | 0.4 | 0.3 | 1.5 | 1.1 |
| " 3 days | 35 | ≤ 2 | 0.5 | <0.03 | 0.4 | 0.3 | 1.5 | 1.1 |
| " 4 days | 25 | 5 | 0.5 | 0.1 | 0.3 | 0.2 | 1.4 | 1.1 |
| " 7 days | < 1 | 8 | <0.03 | 0.5 | 0.0 | | 0.0 | |
| " 3 wks | 0 | 4 | 0 | 0.5 | 0.0 | | 0.0 | |
| " 6 wks | 0 | 0 | 0 | 0 | 0.0 | | 0.0 | |
| *Linear $C_{11}$–$C_{15}$ Secondary Ethoxylate (9 EtO)* | | | | | | | | |
| Initially | 50 | 0[b] | 0.5 | 0 | 0.7 | 0.5 | 1.4 | 1.2 |
| after 2 days | 35 | < 2 | 0.5 | <0.03 | 0.7 | 0.6 | 1.5 | 1.3 |
| " 3 days | 30 | 6 | 0.5 | 0.1 | 0.6 | 0.4 | 1.4 | 1.2 |
| " 4 days | 20 | 9 | 0.5 | 0.2 | 0.7 | 0.5 | 1.5 | 1.3 |
| " 7 days | 6 | 10 | 0.5 | 0.8 | 0.6 | 0.5 | 1.5 | 1.3 |
| " 10 days | < 1 | 14 | <0.03 | 0.5 | 0.0 | | 0.0 | |
| " 6 wks | 0 | 4 | 0 | 0.5 | 0.0 | | 0.0 | |
| *Iso Tridecyl Alcohol Ethoxylate (8 EtO)* | | | | | | | | |
| Initially | 10[d] | 0 | 0.5 | 0 | 1.3 | 1.1 | 3.1 | 2.3 |
| after 7 days | 8 | 0 | 0.5 | 0 | 1.3 | 1.1 | 3.2 | 2.2 |
| " 14 days | 6 | 0.2 | 0.5 | <0.03 | 1.2 | 1.0 | 3.0 | 2.4 |
| " 21 days | 5 | 0.2 | 0.5 | <0.03 | 1.3 | 1.1 | 3.1 | 2.5 |
| " 28 days | 5 | 0 | 0.5 | 0 | 1.3 | 1.1 | 3.2 | 2.2 |

[a] The foam heights of mixtures of standard materials of corresponding composition are in italics.
[b] Expressed as PEG 450.
[c] Expressed as PEG 1000.
[d] Initial concentration of 10 mg per liter (at room temperature) appropriate for this material.



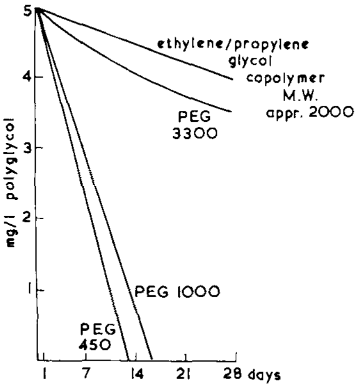


FIG. 9. Coconut monoethanolamide ethoxylate.
FIG. 10. Right, various polyglycols.

more than 0.5 mg per liter of polyglycol-type material. At this level a change in concentration of the nonionic detergent of ±20% produces significant differences in foam heights. When all the nonionic detergent had been degraded, foaming tests were continued, where appropriate, on four liters of solution diluted to contain 0.5 mg per liter of the residual polyglycol.

The results of foaming tests on several degrading nonionics, selected because they were representative of the types discussed earlier in this paper, are shown in Table II. The foam heights on the addition of 0.5 mg per liter of anionic detergent are also included because the synergistic effect between nonionic and anionic detergents (24) is significant and important. The foam heights of the solutions of standard materials of corresponding concentration are inserted in italics where appropriate. The standard polyglycols used for comparison with the degradation products were selected because they were nearest in position on the thin-layer chromatogram to the polyglycol type of streak derived from the degrading nonionics; thus PEG 450, which had negligible foaming capacity, was used for the 9-ethoxylates, and PEG 1000 was used for higher ethoxylates. It will be seen from the tables that PEG 1000, or the polyglycol-type material derived from the higher nonionics, had a considerable influence on foaming capacity but that the effect was practically independent of its concentration over the range studied. The foam formed by these materials also showed characteristic bubble formation: small, regular-sized, closely packed bubbles.

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