Properties of Ethoxylate Derivatives of Nonrandom Alkylphenols[1]

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Abstract

Performance evaluation data for highly biodegradable C_8-C_{18} nonrandom linear alkylphenol ethoxylates and ethoxysulfates are presented for typical heavy- and light-duty detergent formulations. The effect of the derivatives' molecular weight on performance characteristics is discussed, including variations in the hydrophobic and hydrophilic parts of the molecule.

Introduction

IT HAS BEEN ESTABLISHED that the position of phenol attachment in linear alkylphenols affects the biodegradability of the resultant ethoxylate derivative (1). Optimum biodegradability is obtained when the phenol is attached near the end of the alkyl side chain (Table I, Fig. 1). A predominantly 2-isomer alkylphenol can be made in a commercially practical process. In this paper we show what effect variations in the hydrophobic and hydrophilic portions of ethoxylate derivatives of such C_8-C_{18} nonrandom linear alkylphenols (NRLAP) have on their physical characteristics and performance evaluations.

We have compared the detergency performance of the NRLAP ethoxylate derivatives to that of the ethoxylate derivatives of primary and secondary alcohols. Two recent publications (2,3) reported detergency evaluations using a variety of synthetic soils and implied that the results based on a single soil may be unreliable. Trowbridge and Rubinfeld (4) suggest using a natural skin sebum soil in a laboratory detergency test. We have used this soil in our evaluations because we consider it to be an important natural soil. Other publications (5–7) concerning the performance evaluation of alcohol nonionics have reported results using the synthetic U.S. Testing soil. We have included this soil in our evaluations in order to aid cross-comparisons.

Experimental

Preparation of Materials

The C_8-C_{18} carbon NRLAP's were prepared using Humphrey Chemical Company pure grade 1-olefins and nonstabilized Chevron Phenol (Chevron Chemical Company) in a Chevron Research Company process (8). The C_9-C_{10} NRLAP was prepared using C_9-C_{10} Chevron Alpha Olefins.

The heart cuts were dried for 16 hr in a 60–80C vacuum oven and ethoxylated using the method of Mansfield and Locke (9). Polyethylene glycol contents were determined by the ethyl acetate-5 N sodium chloride extraction technique of Weibull (10). Cloud points were determined on 0.5% solutions of the NRLAP nonionic. Hydroxyl numbers were determined by the uncatalyzed acetic anhydride procedure of Ogg, Porter and Willits (11). The ethoxysulfates were prepared by reacting the dried NRLAP ethoxylates with a 10% mole excess of sulfamic acid for 16 hr at 90–110C (see Ref. 12).

TABLE I
Effect of Phenol Attachment on Biodegradability of Linear Nonyl Phenol Ethoxy Sulfates

	Percent degraded	
	Mild[a] die-away test	Strong[b] die-away test
Ortho-(2-nonyl) phenol	90	>90
Ortho-(5-nonyl) phenol	0	0
Para-(5-nonyl) phenol	0	60

[a] 90/10 tap water/bacterial medium.
[b] 90/10 tap water/Lodi activated sludge effluent.

Performance Testing

Detergency performance was measured for the NRLAP nonionics in a low foaming formulation by washing natural skin sebum-soiled cotton swatches (13) in a Terg-O-Tometer (Model BD-101, U.S. Testing Company). Soil removal was measured in the usual way by reflectance (Photovolt Model 610 reflection meter with an external, high sensitivity galvanometer, Chevron Research Company Electronics Laboratory). The sebum soil test results were normalized after three soil/wash cycles by the use of two controls, one of which is picked to give good cleaning (6 in relative detergency rating scale) and the other poor cleaning (2 on the scale). Using these internal standards, many random fluctuations in soil removal results are overcome. U.S. Testing soil data are averages of duplicate washings.

Washing machine foamability for the NRLAP nonionics was obtained by measuring the foam height in a Westinghouse washing machine containing 6 lb of clean shop towels and ten 16-in. × 30-in. × 3-ml polyethylene sheets in 26 liters of water containing 40 ppm lard oil.

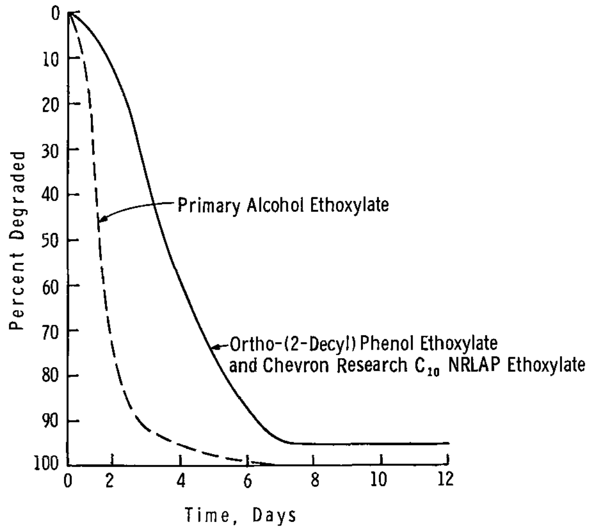

FIG. 1. Chevron Research die-away test.

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[3] Primary and secondary alcohol ethoxylates and ethoxysulfates used in the performance evaluations are commercial products available from the Continental Oil Company, Shell Chemical Company or the Union Carbide Corporation.

TABLE II
Analysis of Nonrandom Linear Alkylphenol Nonionics

Alkyl-phenol	Hydroxyl Number mg KOH/g	Number E.O. Groups: Calculated from E.O. uptake	Number E.O. Groups: Calculated from OH No.	Average Molecular weight	Average weight percent E.O.	Cloud point °F
C_8	90	8.3	9.4	596	65.4	80
C_8	87	10.6	9.8	659	68.7	141
C_{10}	79	10.1	10.8	691	66.1	126
C_{12}	88	8.5	8.5	636	58.8	57
C_{12}	76	11.2	10.8	747	64.9	118
C_{12}	65	12.5	13.5	836	68.7	164
C_{14}	67	12.1	12.4	824	64.8	128
C_{16}	72	10.5	10.5	778	59.1	87
C_{16}	65	13.7	13.1	889	64.2	148
C_{18}	61	13.7	13.3	933	62.9	147
C_9-C_{10}	86	10.6	9.6	667	65.5	124

The ethoxysulfates were evaluated in the Purex Dishwashing Foam Test (14). This test measures the foam generated in a detergent solution by beating the solution with a Kitchen-Aid mixer (Model K4-13) after addition of a grease-carbohydrate soil load. The results are expressed as the number of soil loads added until the foam height is less than 3 mm. Surface tensions were measured on pure solutions of NRLAP nonionics or ethoxysulfates using a du Nouy Tensiometer.

Results and Discussion

Physical Properties

Gas chromatographic analyses of the NRLAP's produced by the Chevron Research Company process show that the resultant alkylphenols have 80–90% 2-alkyl attachment and about 95% ortho attachment (15).

Analyses and properties for nonionics and ethoxysulfate precursors of the NRLAP's are presented in Tables II and III. The molecular weights and weight percent ethylene oxide are the average of values calculated from ethylene oxide uptake and hydroxyl number. The polyethylene glycol contents in the NRLAP nonionics are less than 3%. Cloud points for NRLAP's with the same hydrophobic group increase linearly with ethylene oxide content.

All sulfamic acid sulfations of the 40–50% ethoxylates gave greater than 96% yield of active by methylene blue-Hyamine 1622 titration.

du Nouy surface tension measurements for 63–68% ethylene oxide content nonionics and 40–50% ethylene

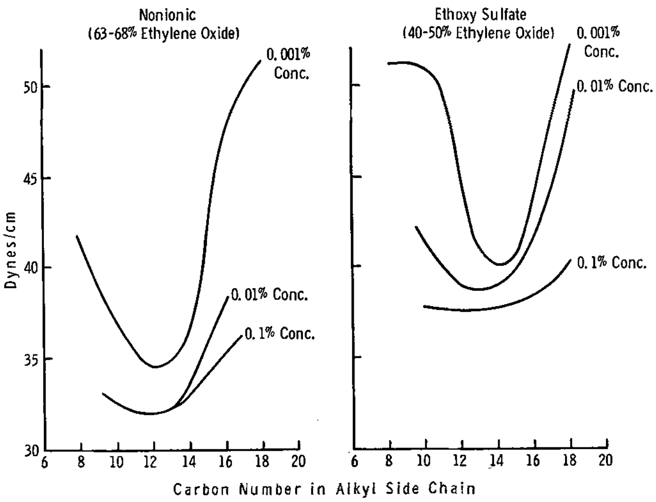

FIG. 2. Surface tensions of nonrandom linear alkylphenol ethoxylates (measured by the du Nouy Ring Method at room temperature).

TABLE III
Analysis of Nonrandom Linear Alkylphenol Ethoxylates Precursors to the Ethoxy Sulfates

Alkyl-phenal	Hydroxyl number mg KOH/g	Number E.O. Groups: Calculated from E.O. Uptake	Number E.O. Groups: Calculated from OH No.	Average Molecular weight	Average weight percent E.O.
C_8	155	3.1	3.5	352	41.5
C_{10}	118	4.8	5.5	459	49.0
C_{12}	117	4.9	4.9	479	45.3
C_{14}	101	6.0	6.0	554	47.6
C_{16}	87	6.7	7.4	629	49.4
C_{18}	84	7.4	7.6	675	48.7
C_9-C_{10}	136	3.9	4.1	409	43.8

oxide content ethoxysulfates (Fig. 2) show minima in surface tensions for NRLAP nonionics and ethoxysulfates with side chain lengths of C_{12} to C_{14}.

Performance Evaluation—Nonionics

Typical Terg-O-Tometer cotton detergency evaluations using the natural skin sebum soil are presented in Table IV; these data are illustrated in a relative detergency isogram (Fig. 3).

The formulation used in these evaluations (Table V) is an example of a low foam, heavy-duty formula and is not suggested as being an optimum formulation.

The performance results are presented as relative detergency values (Table IV) and as contour lines of equal relative detergency values (Fig. 3). In this series of tests the good standard, given a relative value of 6, has an average reflectance of 72%; the bad standard, relative value of 2, 62%; the new unsoiled cotton swatch, 80%; and the soiled swatches averaged 56%. A difference of 1 relative detergency value is considered significant at about a 75% confidence level.

At 50 ppm water hardness and a "home use" concentration of 0.2%, all of the nonionics perform well. Variations in performance under these conditions are

TABLE IV
Terg-O-Tometer[a] Performance Evaluations Natural Skin Sebum Soil

Hydrophobe No. of carbons in side chain	Hydrophile No. of E.O. groups in molecule	Relative detergency units[b] at 0.2% concentration: 50 ppm	Relative detergency units[b] at 0.2% concentration: 180 ppm
C_8	8.9	6.2	6.1
C_8	10.3	6.4	4.7
C_{10}	10.4	6.5	7.2
C_{12}	8.5	6.4	6.1
C_{12}	11.0	6.6	7.0
C_{12}	13.0	6.8	6.7
C_{14}	12.1	6.4	5.7
C_{16}	10.5	5.9	3.6
C_{16}	13.0	6.1	4.9
C_{18}	13.3	5.3	3.7
~1/3 C_9-2/3 C_{10}	10.1	6.4,6.4	6.4,6.7

[a] Washed at 120F.
[b] Standard deviation 0.4 relative detergency units (95% confidence interval 1.4 R.D.U.).

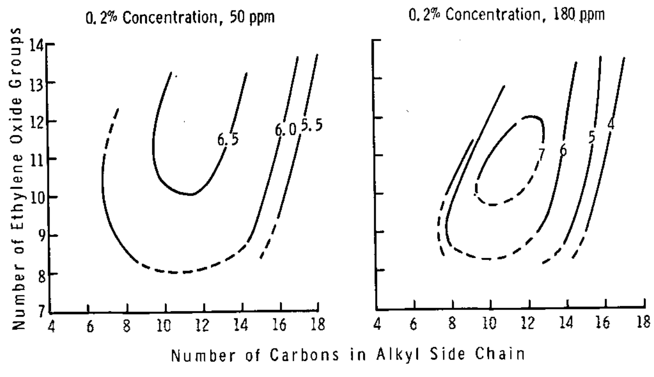

FIG. 3. Relative detergency isogram natural sebum soil (measured at 120F).

TABLE V
Low Foaming Heavy Duty Formulation

10% Nonionic Active
40% Sodium Tripolyphosphate
7% Silicate (3.22/1 SiO_2/Na_2O)
1% CMC
32% Sodium Sulfate
10% Water

probably insignificant, except for the small drop in detergency of the octadecylphenol derivative. In 180 ppm water, NRLAP nonionics with alkyl side chains of C_8-C_{12} and polyether lengths of 8 to 14 ethylene oxide groups perform as well as or better than the good standard. There is a significant drop-off in detergency as the alkyl side chain increases from C_{14} to C_{18}. These data also show that optimum soft and hard water performance is obtained with ethylene oxide content of between 63% and 68%.

We find that there are no significant differences between the performance of C_9-C_{10} NRLAP nonionics and commercial samples of primary or secondary alcohol ethoxylates[3] in either 50 ppm or 180 ppm water using the natural sebum soil (Table VI). In this test all performed well and were better than the good standard.

Alkylphenol nonionics are primarily used in low foaming formulations, and accordingly their sudsing level is an important property. The NRLAP nonionics used in the above formulation were compared to commercial low foaming formulations in a Westinghouse washing machine foam test and were found to have essentially the same level of foaming as the commercial products.

Detergency evaluations using U.S. Testing soil are presented in Table VII.

The NRLAP nonionic data in the 10% active formulation are presented as percent soil removal calculated from reflectance differences. The results are compared to good and bad standards. These standards are chosen on the basis of their ability to show a large visible difference in soil removal when used in our natural soil white shirt test. With the

TABLE VI
Comparison of Detergency Performance[a] Natural Sebum Soil

Active	Relative detergency units[b] at 0.2% concentration 50 ppm	180 ppm
C_9-C_{10} NRLAP 65% E.O.	7.2	6.3
C_{10}/C_{12} Primary Alcohol 60% E.O.	6.9	6.4
C_{12}-C_{18} Primary Alcohol 60% E.O.	6.9	6.6
C_{11}-C_{15} Secondary Alcohol 67% E.O.	6.9	6.4

[a] Washed in a Terg-O-Tometer at 120F.
[b] Standard deviation 0.4 relative detergency units (95% confidence interval 1.4 R.D.U.).

TABLE VII
Terg-O-Tometer[a] Performance Evaluation, U.S. Testing Soil

Alkylphenol nonionic: Alkyl side chain	No. of E.O. groups	Percent soil removal at 0.2% conc.: 50 ppm	180 ppm
C_8	8.9	25.6	26.6
C_8	10.3	27.0	26.0
C_{10}	10.4	26.8	28.1
C_{12}	8.5	31.7	30.6
C_{12}	11.0	28.3	28.0
C_{12}	13.0	28.4	28.0
C_{14}	12.1	31.6	31.9
C_{16}	10.5	32.8	30.6
C_{16}	13.0	23.4	22.2
C_{18}	13.3	31.9	32.5
C_9-C_{10}	10.1	27.4	27.2
Good standard		26.4	
Bad standard		20.5	

[a] Washed at 130F.
[b] Standard deviation 1.2% soil removal (95% confidence interval 4.8%).

TABLE VIII
Light Duty Formulation

15% Oronite alkane 1056 sodium sulfonate
3% Oronite alkane 1060 sodium sulfonate
10% Ethoxy sulfate
2% Lauric diethanol amide
10% Alcohol
Q.S. Water

natural skin sebum soil, we get a good differentiation between these standards. With U.S. Testing soil, the difference between good and bad standards is 6% soil removal (i.e., a difference of 3 reflection units). This difference is small and barely within the 95% confidence level for distinguishing a difference between two samples. Despite the uncertainties in these data, the area of good NRLAP nonionic detergency is similar to that obtained in the natural skin sebum test.

Thus, our performance results as well as field information concerning hard surface detergency, viscosity, and freeze-thaw stability indicate that the optimum for NRLAP nonionics and ethoxysulfates is in the C_{10} range when both industrial and household uses are considered. Also because of similarities in structure their use as a replacement for branched alkylphenols would not require expensive reformulation.

Performance Evaluation—Ethoxysulfates

The NRLAP ethoxysulfates were formulated in a lightduty liquid detergent (Table VIII) and evaluated in the Purex Dishwashing Foam Test. The liquid detergent formula used in this test is representative of many on the market today but is not suggested as necessarily being an optimum formulation for these products. The results from this test, presented in Table IX, show that there is a slight performance maximum in soft and hard water for NRLAP ethoxysulfates with alkyl side chain lengths of around C_{10}. C_{10} and C_9-C_{10} NRLAP Ethoxysulfates perform as well as primary or secondary alcohol ethoxysulfates in this test and formulation.

Conclusions

Our data indicate that the preferred range for the NRLAP nonionic alkyl side chain is between C_9-C_{14}. Above C_{14} the hard water performance falls off. The preferred ethylene oxide content is in the 63–68% range. These conclusions are based on the Terg-O-Tometer detergency test using the natural skin sebum soil. The Purex Dishwashing Foam Test shows a slight maximum in performance for C_{10} NRLAP ethoxysulfate. We have not determined if this apparent optimum will exist for ethoxysulfates with

TABLE IX
Light-Duty Liquid Detergent Performance, Purex Dishwashing Foam Test

NRLAP ethoxy sulfates: Alkyl side chain	E.O. groups	Number of soil loads: 0.14%, O ppm	0.20%, 300 ppm
C_8	3.3	11	7
C_{10}	5.1	16	11
C_{12}	4.9	14	8
C_{14}	6.0	13	4
C_{16}	7.0	11	3
C_{18}	7.5	9	4
C_9-C_{10}	4.0	16	10
C_{12}-C_{15} Primary Alcohol (40% E.O.) Ethoxy Sulfate		14	8
C_{11}-C_{15} Secondary Alcohol (40% E.O.) Ethoxy Sulfate		15	10

Standard deviation 1 soil load (95% confidence interval 4 soil loads).

ethylene oxide contents other than the 40–50% we have used in these evaluations.

A C_{10} NRLAP gives excellent performance for both nonionics and ethoxysulfates. Both the NRLAP nonionics and ethoxysulfates perform as well as the commercial primary alcohol and secondary alcohol products in our formulations and performance tests.

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