SURFACTANT PERFORMANCE AS A FUNCTION OF HYDROPHOBE BRANCHING

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Abstract

Surfactant properties and end-use performance parameters of a variety of alcohol sulfates have been evaluated. A range of hydrophobes was selected to document both the overall effect of hydrophobe branching, as well as the effect of the position of branching. Foaming, surface tension reduction, and calcium tolerance were among the surfactant properties evaluated. Prototype formulations were employed to evaluate both light duty dishwashing solutions and fabric detergency. Detergent alcohols ranging from 99 % linear to 99 % branched have been evaluated. Hydrophobe branching dramatically affects foaming, leading to reduced performance in dishwashing as branching increases. Prototype laundry liquid evaluations showed no statistically significant effect for hydrophobe branching. Laundry powder detergency was heavily influenced by alcohol sulfate molecular weight, but, at constant molecular weight, detergency was diminished by hydrophobe branching.

Introduction

The structure and molecular weight of detergent range alcohols varies widely as a function of both raw materials and process. Alcohols derived from palm or coconut oil are essentially entirely linear, and similar alcohols are made *via* the Ziegler Process from ethylene[1]. Further, there are several variations of the OXO Process. When based on linear olefins, the OXO process yields alcohols with a range of 50 to 80 % linearity[2]. All of these alcohols as nonionic surfactants have been documented to biodegrade readily[3]. Further, the evidence for the acceptability of the anionic derivatives has been collected[4]. A systematic study of some of the physical chemistry of these alcohols and derivatives has been completed. Further, the practical application of alcohol sulfates and ethoxysulfates of varying degrees of branching to light duty dishwashing has been examined[7]. This research has extended the study of branching effects to fabric detergency

Experimental

The samples used in this work were all commercial products, and are identified in Table 1 by name, acronym, and supplier. The samples identified, in Table 2, as linear and branched modified-OXO are the separated components of commercial synthetic alcohols. The fractions were separated in the laboratory by molecular sieves. All alcohols were characterized by gas chromatography, gc/ms, and by both proton and carbon NMR.

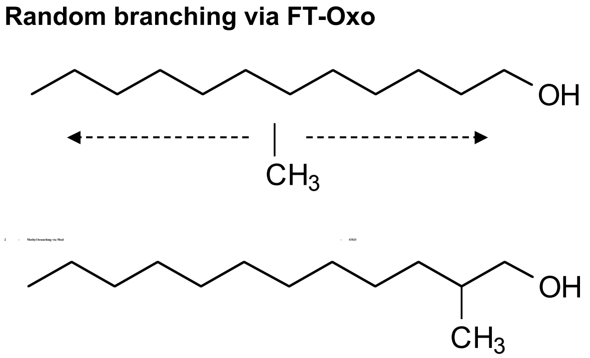
Trade Name	**Chemical Description**	**Acronym**	**Supplier**
NEODOL® 23	C_{12}, C_{13} – Modified OXO	Mod-OXO-23	Shell Chemical
NEODOL® 45	C_{14}, C_{15} – Modified OXO	Mod-OXO-45	Shell Chemical
SAFOL® 23	C12, C13 – Fischer-Tropsh	FT-OXO	Sasol (South Africa)
Lial® 23	C_{12}, C_{13} – OXO	OXO-23	Sasol (Italy)
Steol	Oleochemical	C-12,14	Stepan

Table 1. The commercial products examined in this work are listed along with common acronym and supplier.

Acronym	**% Branching**	**Branch Position**	**Branch Type**
Mod-OXO-23	20	2	Methyl, Ethyl, etc.
L-Mod-OXO-23	< 1	2	Methyl, Ethyl, etc.
B-Mod-OXO-23	99	2	Methyl, Ethyl, etc.
Mod-OXO-45	20	2	Methyl, Ethyl, etc.
L-Mod-OXO-45	< 1	2	Methyl, Ethyl, etc.
B-Mod-OXO-45	99	2	Methyl, Ethyl, etc.
FT-OXO	50	random	Methyl, Ethyl, Unidentified
C12,14	< 1	random	Methyl

Table 2. Branching pattern and the types of branching in various detergent alcohols.

Figure 1 illustrates the different positions of branching in FT-OXO alcohols, as compared to the exclusive 2-alkyl branching in Mod-OXO alcohols.


Random branching via FT-Oxo

2 - Methyl branching via Mod - OXO

Figure 1. Typical branching type and position in OXO-alcohols.

The detergent alcohols were converted to sulfates by reaction of the organic substrate with SO_3 in a laboratory falling film device, and neutralization was with NaOH. The resulting sodium salts of alcohol sulfates were characterized by active matter titration, ion chromatography, and ion exchange separation (for unsulfated organic material, UOM). All anionic surfactants had UOM content below 2%, and the residual Na_2SO_4 content was below 1.5%.

Critical micelle concentration (cmc) was determined with an automated Lauda instrument.

Krafft temperatures were determined by heating or cooling aqueous 1% solutions. The temperature reported corresponds to complete surfactant dissolution.

The calcium ion tolerance was determined by titration with $CaCl_2$, as previously reported[5].

Foaming of surfactants was determined at room temperature with the Sen Foaming Test device. Foaming was determined at 0.01 weight % concentration for each surfactant in 150 ppm hardness water (3/2 Ca/Mg ratio). Additional measurements were conducted at the same conditions with added 4:1 hexadecane:oleic acid at 1-1 soil-to-surfactant weight ratio.

The predicted performance of a formulated light duty dish product (LDL) was determined with the published soil titration procedure[6]. The foam booster used in this work was a dodecyl dimethyl amine oxide.

Detergency evaluations were conducted using the previously published radiotracer procedure[5]. The soil used exclusively in this research was a synthetic multisebum. Detergency testing was done in a laboratory Terg-o-tometer with the following prototype formulations: laundry powders, 0.2 g/L alcohol sulfate, 0.34 g/L zeolite, and 0.2 g/l of Na_2CO_3; and, laundry liquids, 0.1 g/L of nonionic (C12,15-7EO), 0.1 g/L alcohol sulfate, 0.01g/L triethanol amine.

All dishwashing and detergency experiments were conducted in duplicate, and the mean value has been reported. A LSD_{95} was calculated for each set of experiments (LSD_{95} is the least significant difference between any two mean values at the 95% confidence level).

Background

In a previous publication, the diminished foaming with FT-OXO branching was established. As shown in Figure 2, the foaming in a prototype LDL formulation was compared as a function of alcohol structure.

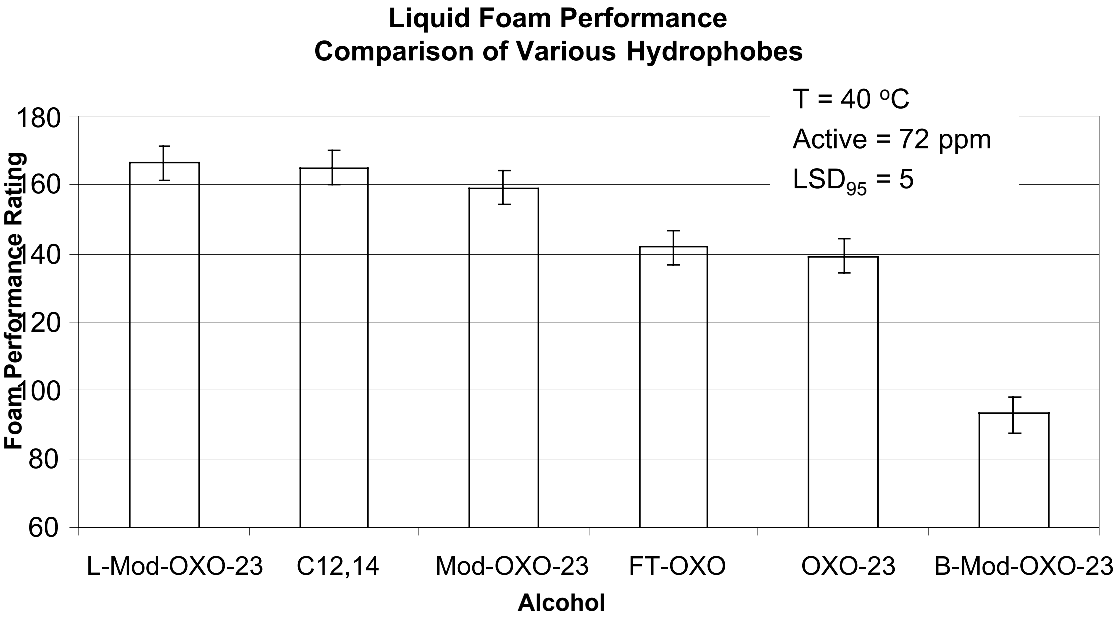


Figure 2. Prototype light duty dishwash product foaming comparison.

The highest level for foaming performance was observed for the most linear hydrophobes, although the performance of the MOD-OXO-23 was statistically equivalent. The foaming of the FT-OXO hydrophobe was substantially poorer than MOD-OXO-23, the linear fraction of MOD-OXO-23, and the essentially linear C-12,C-14.

In order to establish conclusively the performance difference (in LDLs) between MOD-OXO and FT-OXO, the foaming was compared over a range of concentrations, Figure 3.

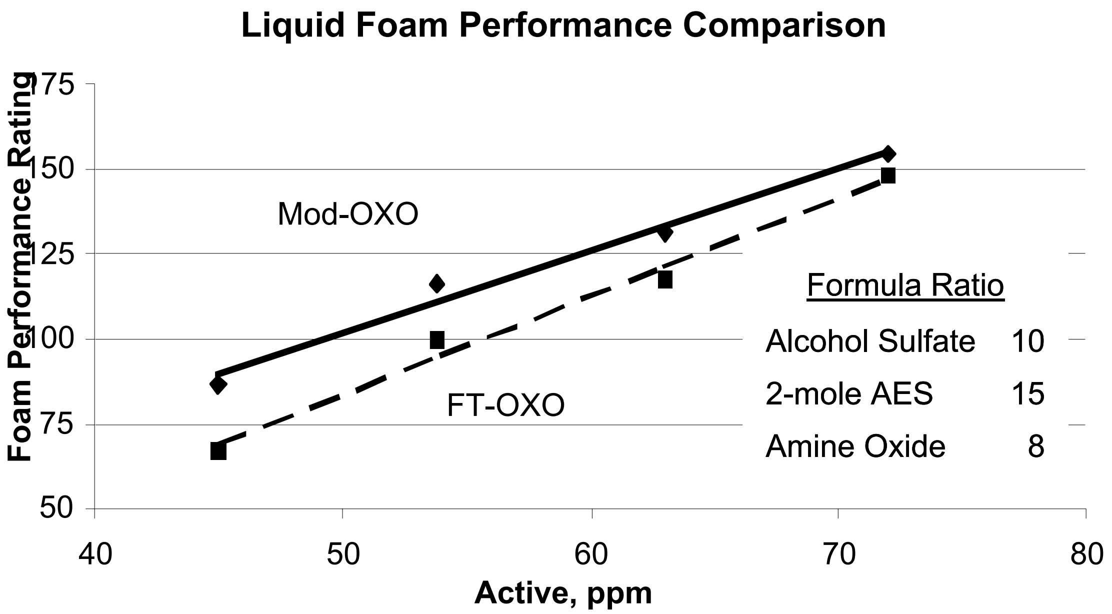


Figure 3. The concentration dependence of light duty dishwash prototype products.

As shown, the MOD-OXO was superior to FT-OXO over the concentration range from 45 to 80 ppm of prototype LDL. The performance deficiency of the FT-OXO alcohol has been attributed to the, as yet, unidentified isomeric alcohols in this mixture. These homologs have a saturated five- or six-membered ring, but the precise structure has not been determined.

The comparison of MOD-OXO to FT-OXO has now been extended to higher molecular weight MOD-OXO alcohols.

Discussion

Shown in Table 3 are some physical chemistry observations for the alcohol sulfates studied in this research.

Sulfate	CMC (ppm)	Krafft Temperature, °C	Hardness Tolerance (ppm Ca^{++})
Mod-OXO-23	623	32	150
L-Mod-OXO-23	922	32	170
B-Mod-OXO-23	1131	0	> 1,000
Mod-OXO-45	921	40	120
L-Mod-OXO-45	976	40	66
B-Mod-OXO-45	1155	0	500
FT-OXO	638	16	> 1,000
C12,14	848	14	180

Table 3: Physical Chemistry Properties of Alcohol Sulfates

The cmc values were representative of alcohol sulfates in this molecular weight range. The molecular weights were 194-200 for the C12,C13 and the C12,C14 alcohols. The molecular weight for the C14,C15 alcohol was 222. As expected, the Mod-OXO-45 alcohol sulfate had the highest Krafft temperature, but the Krafft temperature was dramatically reduced by branching. The improved hardness tolerance for the B-Mod-OXO-23 and FT-OXO derivatives resulted from the enhanced water solubility imparted by branching in the alcohols.

Figure 4 is a foaming comparison of the alcohol sulfate surfactants, while in Figure 5 the same foaming test has been conducted in the presence of a test soil. In both series, the FT-OXO alcohol sulfate foams at a somewhat slower rate. A similar comparison, using a different method of generating foam with alcohol ethoxylates, has previously been reported[8].

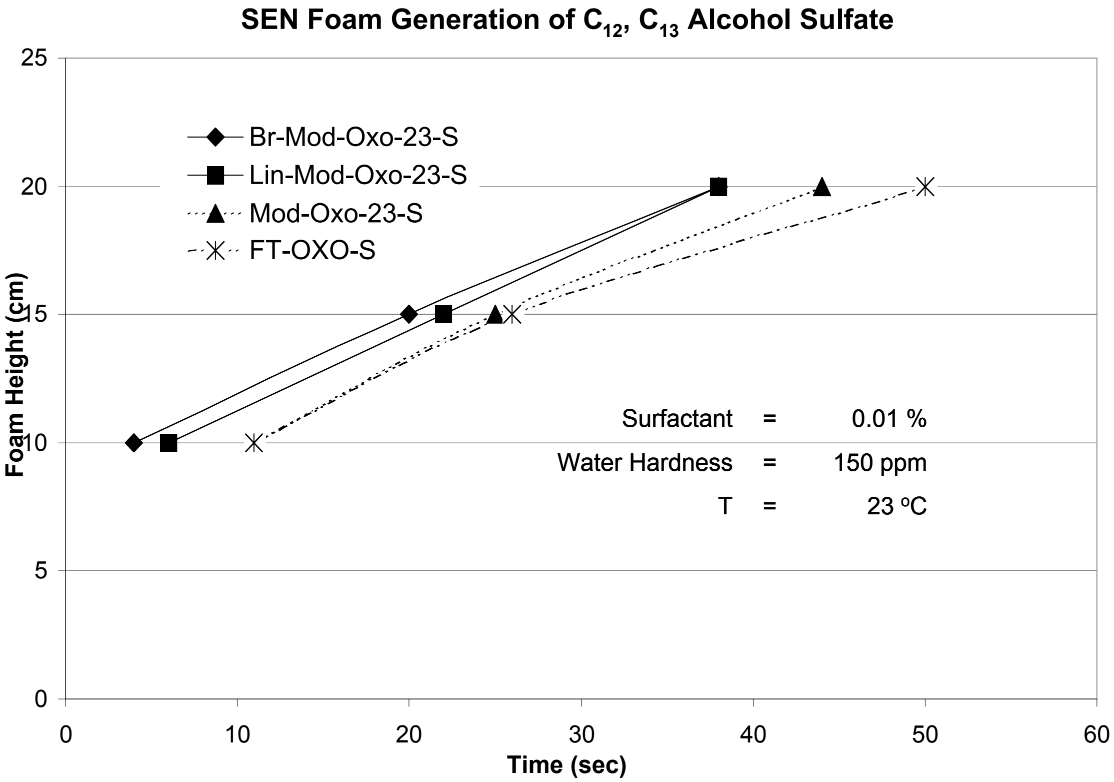


Figure 4. Foaming comparison of alcohol sulfates.

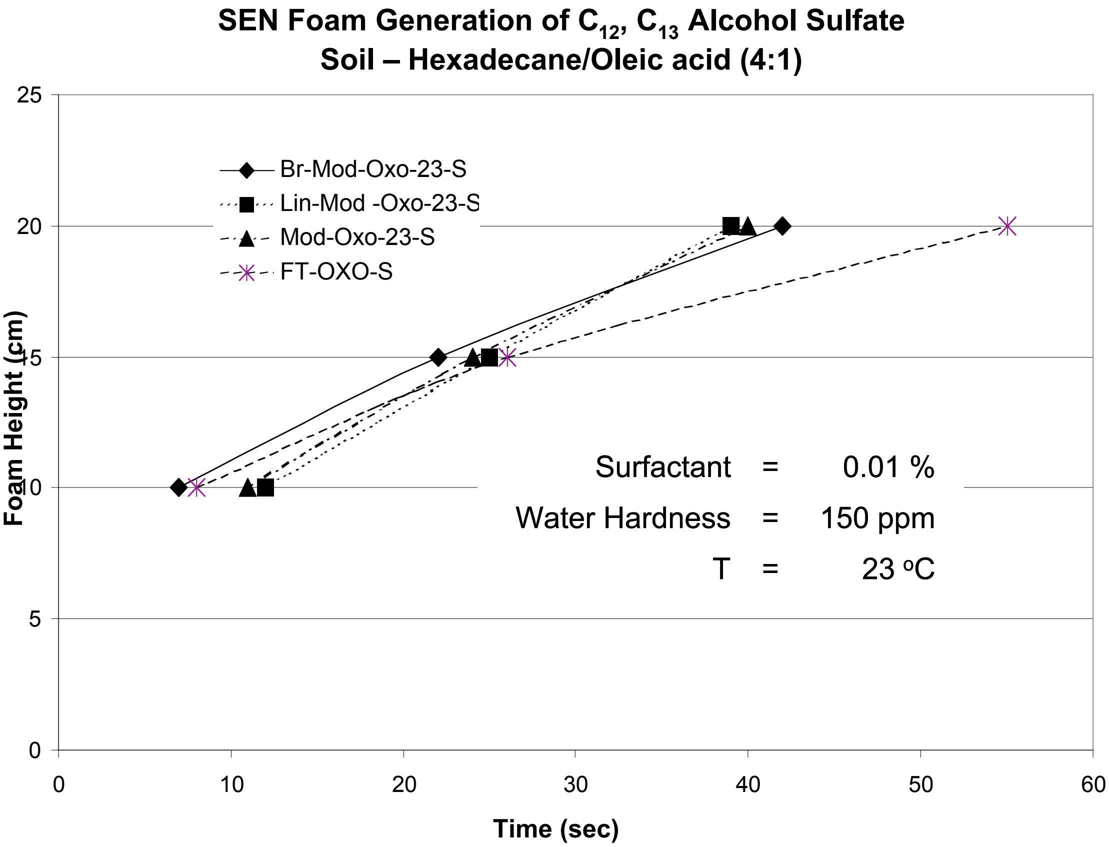


Figure 5. Foaming comparison of alcohol sulfates in the presence of soil.

Displayed in Figure 6 is a detergency comparison, using a prototype laundry liquid formulation.

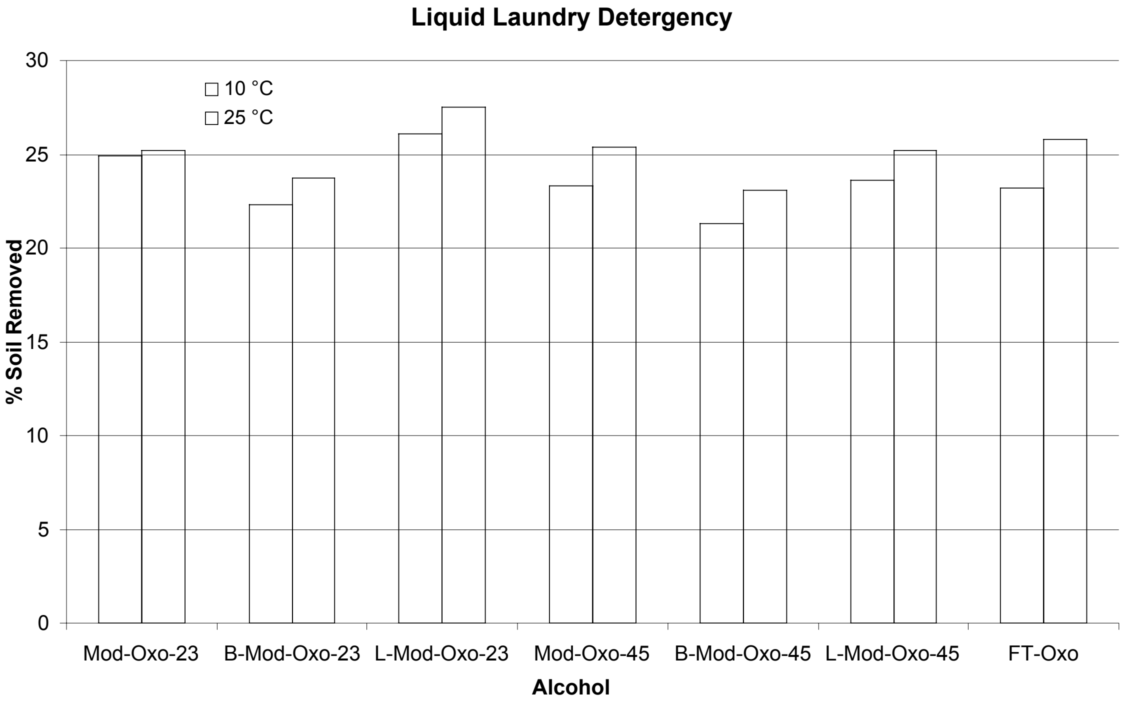


Figure 6. Prototype laundry liquid comparison of alcohol sulfates.

As shown, the comparison was done at two different temperatures (10 °C and 25 °C). In this evaluation, there was no statistically significant difference among the alcohols studied. For each alcohol sulfate, the detergency is slightly improved at 25 C, relative to 10 °C. It is notable that B-MOD-OXO-23 and B-MOD-OXO-45 were directionally the poorest performers in this group. This suggests that the improved solubility of these branched derivatives was detrimental in this evaluation. This most probably resulted from the increase in the cmc of these derivatives (relative to the more linear isomers).

Figure 7 presents prototype laundry powder detergency at 25 °C. The LSD_{95} in these experiments was 4.1. There was a directional advantage for Mod-OXO-23 over FT-OXO. The cleaning with the 99 % branched B-Mod-OXO-23 was equivalent to the soil removed by the 50% branching in FT-OXO. Clearly, the best alcohol for this detergency test was Mod-OXO-45. The relatively poor performance of B-Mod-OXO-45 indicated that, at this temperature and concentration, the greater solubility of the alcohol sulfate was not an improvement.

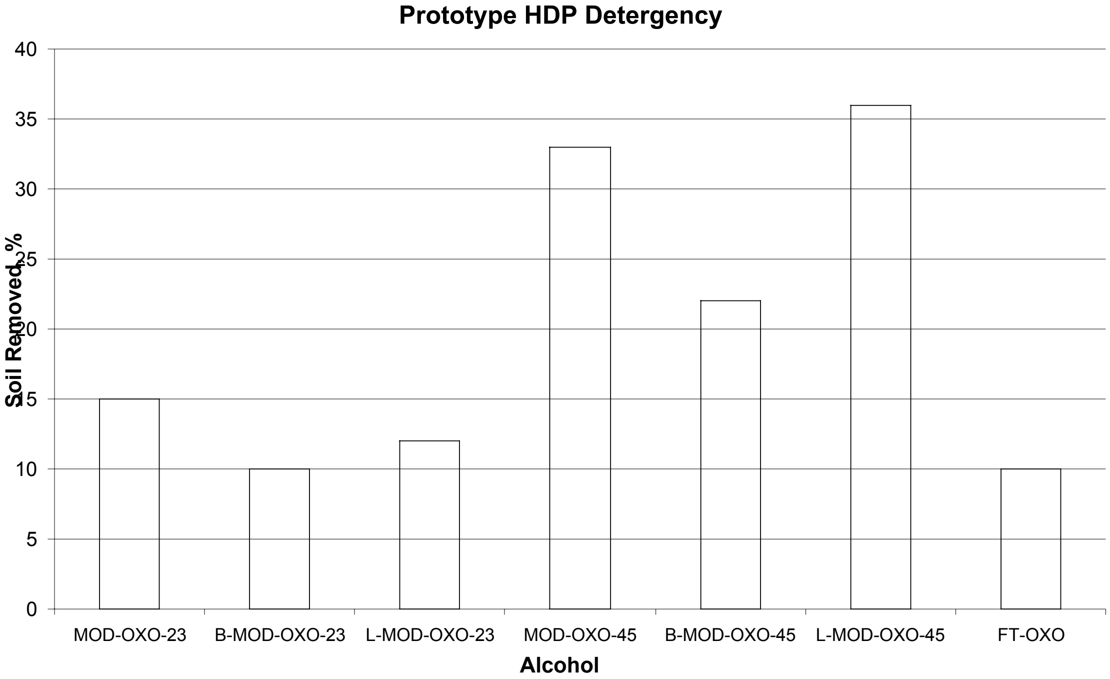


Figure 7. Prototype laundry powder evaluation of various alcohol sulfates.

Conclusions

The evaluation of the effect of branching on surfactant performance has been extended to detergency. Unlike the previous results with light duty dishwashing, branching was not detrimental in a prototype liquid laundry formulation. The prototype powder formulation selected for this research was sensitive to alcohol sulfate molecular weight, but less sensitive to the effects of branching.

Future work will extend these detergency evaluations to alcohol ethoxysulfates and to alcohol ethoxylates.

References

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