MODIFIED OXO ALCOHOL DERIVATIVES FOR PERSONAL CARE

CA Burnley[1], JE Carty[1], LL Garza, KH Raney[1], WW Schmidt[1], PL Tortorici[1], RJ Wiersma[2]

ABSTRACT
Personal care products have traditionally been formulated with linear C_{1214} alcohol derivatives. Alcohol derivatives based on modified-Oxo technology and having at least 20% 2-alkyl branching with odd and even carbon chains, have demonstrated comparable results for key performance criteria. Modified-Oxo alcohols are also very effective in a variety of body wash products. The sulfate and ethoxysulfate derivatives of modified-Oxo alcohols are easily formulated in body wash products like shampoos, liquid hand-soaps and shower gel formulations. Fundamental surfactant physical properties including formula appearance, solution times and hard-water stability are reported. Additionally, the hardness tolerance, foam profiles, freeze/thaw stability and viscosity measurements of prototype shampoos and hand-soaps formulated with modified Oxo alcohol derivatives were determined and perform well. Earlier work using an *in vitro* technique to rank order eye irritation of selected Oxo- and coco alcohol derivatives showed that shampoos containing both products are ranked as "mild." Also, there was no significant difference between the oral and dermal toxicity data for coco alcohol- or modified Oxo alcohol-based derivatives. In conclusion, modified Oxo alcohols and their derivatives, which serve as key components in detergent products, are also good functional equivalents to the linear C_{1214} alcohol derived products being used today in many body wash formulations.

INTRODUCTION

Oleochemical and petrochemical alcohol derivatives are very well suited for use in a variety of personal care products. In some instances, alcohol derivatives obtained via modified Oxo process have demonstrated inherent technical performance advantages due to their excellent surface-active properties. These properties support their efficacy in body wash and skin cleansing products.

The aqueous body wash and shampoo formulations were selected primarily to leverage the ability of the surfactant to perform at the skin interface, removing residual dirt, bacteria or soil by dispersion, solubilization and/or emulsification processes. For the purposes of this work, we focused on oily soils primarily because the cleansing action occurs on the skin's permeable lipid interface.

OBJECTIVE

The objective of this work was to verify the flexibility of modified Oxo alcohol derivatives as efficient functional replacements for oleo alcohol derivatives in body wash and skin cleansing products, like shampoos and liquid hand-soaps; and to evaluate the efficacy of modified Oxo mono-methyl (MO MM) branched alcohols in moisturizers and lotions.

This work will show the suitability of a biodegradable modified Oxo mono-methyl branched alcohol as an exceptional emollient/moisturizer with desirable handling properties when compared to oleo linear alcohols of comparable molecular weight. Additionally, this work verifies that modified Oxo alcohol derivatives are not expected to be skin sensitizers based on results obtained from the Human Repeat Insult Patch Test (HRIPT).

This discussion will comprise of the following major points:

- The significant differences between oleo- and petrochemical alcohol hydrophobes. The physical and surface-active properties of select derivatives targeted for personal care product formulations will also be shared;

[1] Shell Chemical LP, Houston, USA
[2] Shell International Company, Amsterdam, Netherlands

- Data featuring the surfactant solution properties, i.e. calcium tolerance, foam volume, density and flash foam profile in soft and hard water and calcium salt tolerance;
- Comparison of prototype liquid hand soap, shampoo and bubble bath formulation properties; including viscosity, foam volume, density, flash foam generation and decay in soft and hard water and hard-water containing a hydrophilic oily soil;
- The results of a HRIPT test from a skin patch test containing a use level of 0.5%w fatty alcohol administered following typical HRIPT test protocols.

EXPERIMENTAL

Formulation appearance: The prototype formulation was blended and the physical appearance of the formulation was recorded at room temperature (25°C).

pH: The pH for surfactants and prototype formulations were measured neat and at 1.0% in d.i. water.

Freeze/Thaw testing: Phase stability was observed using approximately 30 ml of a prototype formulation. After preparation, the samples were then cooled until solid for 24 hrs. Upon removal they were allowed to equilibrate to room temperature when the appearance of the formulation was recorded. This process was repeated for three 24hr. freeze/thaw cycles.

Clear point: Approximately 30 ml of the prototype formulation was cooled in an ice water-bath until cloudy. The sample was warmed gently using a heat gun. The clear point temperature was recorded as the temperature at which the formulation became clear/translucent.

Foaming Properties

1. SEN Foam Profiles

Foam Height: A 0.01%w surfactant, prototype formulation or commercial product was prepared in the SEN foam tester. The circulating pump was turned on for 30 seconds to ensure proper mixing before the air valve was opened to begin circulating air through the surfactant solution. The time required for the foam height to reach 20 cm was recorded.

Foam Decay: Using the same solution, and after reaching the 20 cm height, the pump was turned off. The foam decay was measured immediately after shut off for a specified time interval.

Foam Density: The foam density was determined qualitatively; ie by observing bubble size (large/small), and foam volume (closely/tightly packed/loose).

Influence of Hardness and Soil Addition: Hardness ions (calcium and magnesium chloride in a 3/2 ratio) was added to the desired level. Additionally, a 4:1 mixture of hexadecane/oleic acid was incorporated in the test sample. The Foam decay and foam density method were recorded.

This procedure of adding subsequent amounts of hardness and soil to the surfactant solution determines a foam profile of foaming characteristics of surfactant/formulation under specific conditions.

2. Waring Blender Lather Test

0.2%w of each additive ingredient, except Polyquaternium-10 was dosed in a solution containing 200 ppm hardness (PQ-10 was dosed at 0.1%w). No salt was added to the formulations. The solution was added to a Waring blender and blended at high speed for 10 sec at room temperature then transferred to a 1000 ml graduated cylinder. The flash foam volume was measured and the foam stability was measured after the solution had equilibrated for 2 minutes.

Salt Tolerance

This test determines the amount of calcium chloride that can be added to a surfactant solution until the solution becomes cloudy and precipitates. A 0.06%w solution of the surfactant was prepared. Small increments of 10%w calcium chloride solution was added and the mixture was heated slowly overnight in

a laboratory oven until the solution turned cloudy, indicating that the surfactant had precipitated out of solution.

RESULTS AND DISCUSSION

Alcohol Hydrophobe Structure

Oleochemical alcohols derived from palm kernel, coconut oils and tallow fatty acids have 100 % linear alkyl hydrophobes. Ziegler, Conventional- and Modified-Oxo (MO) technologies that yield alcohols from olefins are well documented in the literature.[1] The data in Table 1 shows that the process technology utilized in the alcohol synthesis determines the relative degree of 2-alkyl hydrophobe branching. [1,2]

TABLE 1: Alcohol Branching and Carbon Number Type

Process Technology	Carbon No. Type	2-Alkyl Branching (%)
Oleochemical	Even	0
Ziegler	Even	1
Conventional Oxo	Odd & Even	54
Modified Oxo	Odd & Even	20

Table 2 lists the physical properties and hard water tolerance of alcohol sulfates and ethoxysulfates typically used in personal cleansing products. As expected, alcohol sulfates are more sensitive to water hardness.

TABLE 2: Physical Properties of Anionics Typically Used in Personal Cleansing Products

Chemical Description	Producer	pH (1.0%)	cmc (ppm)	Surface tension (dynes/cm)	Krafft Temp., °C	Calcium Tolerance (ppm)
Modified Oxo Sodium Salt C_{1213}-2S	Shell	7.5	0.015	27	0	> 2000
Modified Oxo Sodium Salt C_{1115} -2S	Shell	8.5	0.0050	33	0	> 2000
Laureth-Sulfate-2S	Stepan	7.0	0.030	31	0	> 2000
Modified Oxo Sodium Salt C_{1213} –S	Shell	8.5	0.078	23	32	180
Modified Oxo Sodium Salt C_{1115}-S	Shell	7.0	0.11	25	36	440
Sodium Laurylsulfate	Stepan	7.0	0.14	36	16	400

Surface-active Properties

Sodium lauryl alcohol anionics are commonly used alone or as blends in a variety of personal cleansing products. Table 2 shows that the surface-active properties of MO anionics are competitive with oleo anionics; eg the critical micelle concentration (cmc's) were all approximately 0.01 ppm. This suggests that these anionics would be equally efficient at reducing the skin-soil-water interface to facilitate the cleansing process. The MO C_{1213}-S, –2S and C_{1115}-S derivatives demonstrate the lowest equilibrium surface tension and the MO ether sulfates Krafft temperature data suggests they are readily miscible with water and well suited for formulation into pearlescent cleansing products.

PROTOTYPE PERSONAL CLEANSING FORMULATION PROPERTIES

I. Liquid Hand-Soaps

Liquid hand soaps are convenient, moderately viscous liquid cleansing products that are generally stored in attractive, decorative plastic squeeze bottles or pump containers. They are generally fragrant and may contain additive ingredients that support label claims. They may be used for washing hands and face in the kitchen or bathroom sink. Table 3 lists the raw materials and their relative composition used in the hand-soap formulations.

TABLE 3: Prototype Liquid Hand-soap Formula Composition

Component	% w
Water	84.9
Alcohol ethoxysulfate	5.4
Alcohol Sulfate	6.2
LMMEA	1.0
Cocoamidopropyl betaine	1.2
Sodium chloride	1.5

Liquid Hand-Soap Formulation Viscosity

Figures 1 – 2 show the effect of equilibrium solution viscosity as a function of salt (NaCl) added and additive ingredient effects respectively, for prototype liquid soaps containing blends of MO alcohol (ether) sulfate relative to oleo anionics.

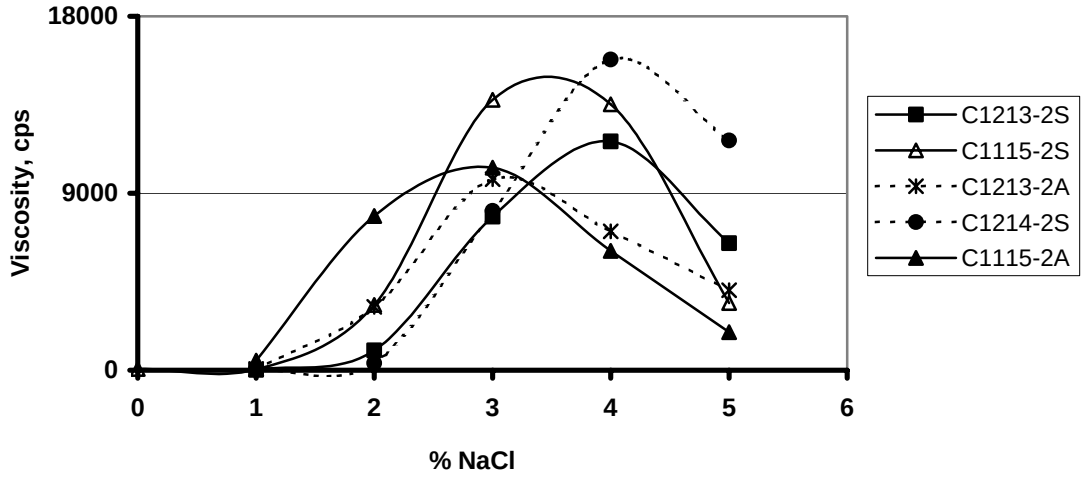


FIGURE 1: Viscosity of Prototype Hand Soaps as a Function of Sodium Chloride

The data in Figure 1 compares the rheology of hand-soap formulations containing blends of MO C_{12}-C_{13} alcohol sulfate/alcohol ether sulfates relative sodium lauryl alcohol sulfate (SLS)/sodium laureth-2 (SLES-2S) as the major surfactants. It is important to note that the level of sodium chloride was incrementally varied in each formula prototypes.

Additive ingredients are typically incorporated to enhance skin conditioning or softening effects. Figure 2 shows the impact of some common formula additives on the viscosity of the liquid soap.

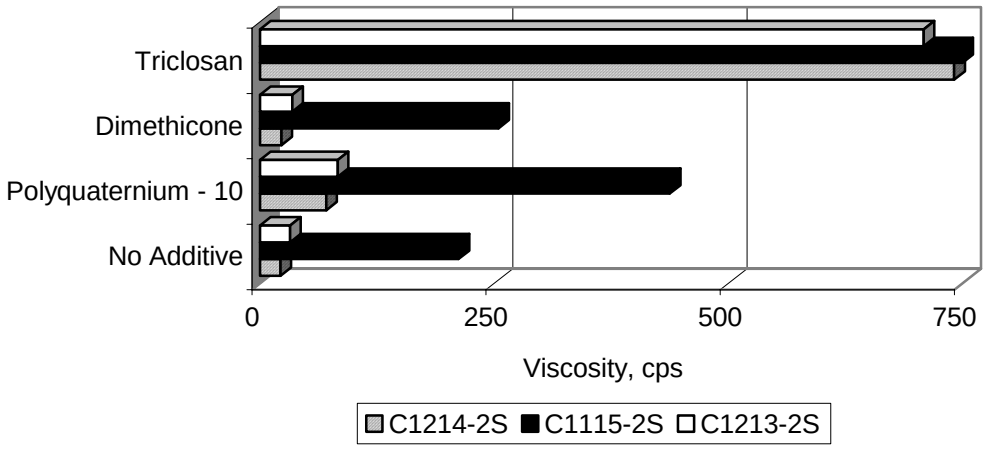


FIGURE 2: Effect of Additives on Formula Viscosity

Interestingly, trichlosan, an antibacterial agent, generates a dramatic increase in formula viscosity when it is incorporated into liquid soap prototypes containing alcohol sulfates/ether sulfate blends irrespective of the alcohol source.

Figure 2 also shows that liquid soaps containing MO C_{1115} -2S show a significantly higher solution viscosity compared to oleo anionics. These prototypes had considerable body and product texture, presenting a significant formulation optimization opportunity. The formulator has the capability to incorporate other sensorial ingredients or milder co-surfactants and still reach a target formula viscosity. Thus, MO ether sulfates are excellent choices for compounding a moderately viscous cleansing product, like liquid hand soaps.

Foaming Properties of Prototype Liquid Hand Soaps

Among oleochemical alcohols, lauryl alcohol sulfates are predominantly used for body wash products since the longer hydrophobes, like cetyl/cetearyl sulfates would be less water-soluble and, hence produce less copious foam. Alcohol sulfates are seldom used as the sole surfactant for personal cleansing and are often blended with fatty acid ethanolamides or other suds-stabilizing materials to compensate for the foam volume deficiency. These ingredients also have the added advantage of improving the mildness or skin feel. Figure 3 and 4 indicate that MO C_{1213}-2S and C_{1115}-2S MO are compatible with oleo alcohol sulfates and maintain foam stability in the presence of hard water and/or oily soil.

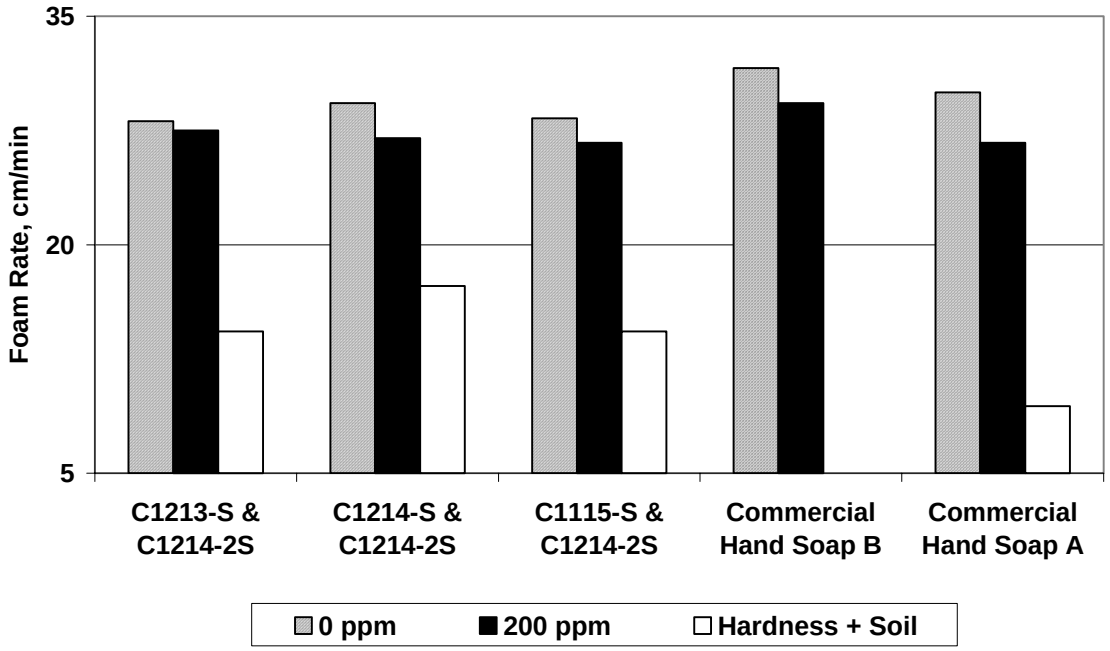
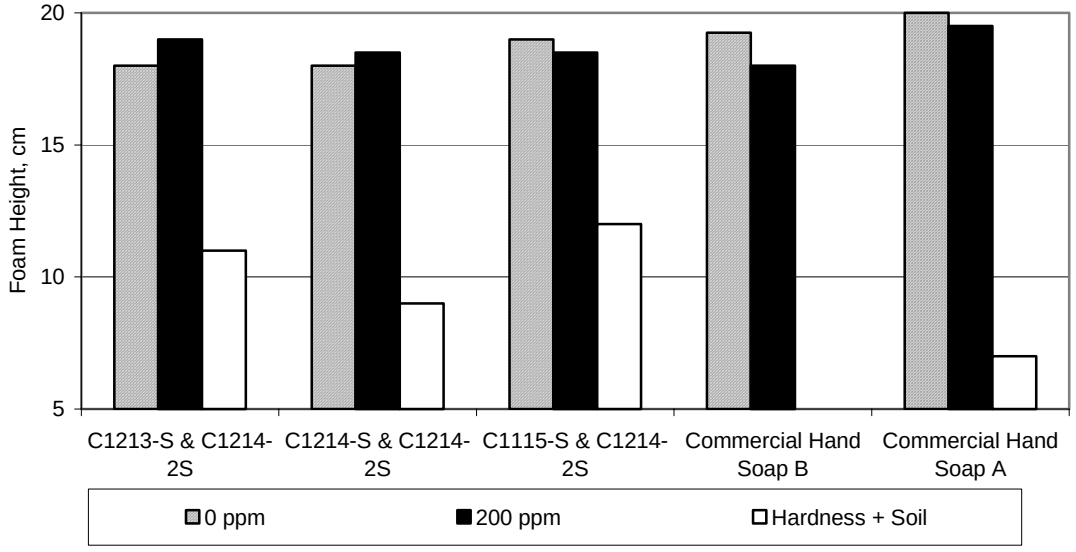


FIGURE 3: Foam Rate of Prototype Liquid Soaps



(58 ppm Surfactant Active, 3 min)

FIGURE 4: Foam Stability of Prototype Liquid Soaps

In summary, prototype liquid soaps containing MO alcohol ethoxysulfates demonstrate flash foam and foam stability that is comparable to oleo anionic blends. The data suggests that the MO ether sulfates are excellent functional replacements for laurylether sulfates. Additionally, liquid soaps containing MO C_{1115}-2S, foam well and respond well to thickening with salt and maintain formula thickness, body and foaming in the presence of other additive ingredients like trichlosan, dimethicone and Polyquaternium-10. Thus, these anionics provide unique formulation optimization potential.

II. Shampoo Formulations

A simple, alcohol ether sulfate based, non-acid formulation was selected and prototypes prepared as indicated in Table 4. The foam and viscosity properties were measured.

TABLE 4: Prototype Shampoo Formula Composition

Component	%wt
Alcohol (ethoxy) sulfate	10.5
Propylene Glycol	1.0
Cocoamidopropyl betaine	3.6
LMMEA	2.2
Ammonium chloride	1.5
Water	79.2

Prototype Shampoo Formulation Viscosity

Figure 5 indicates that the shampoo formulations based on MO C_{1115}-2S can produce prototype shampoos with acceptable viscosities.

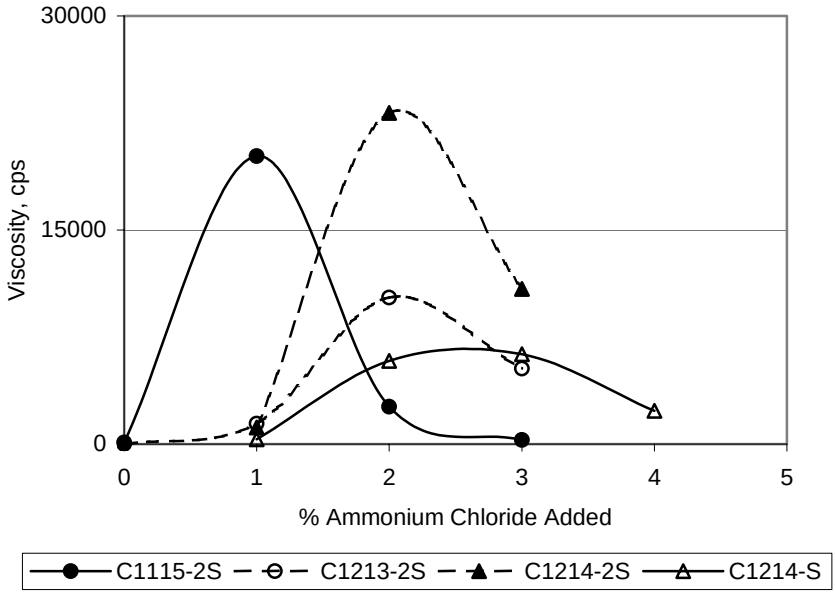


FIGURE 5: Impact of Salt on Shampoo Viscosity

Relative to oleo laureth-2S, the data in Figure 5 also shows that shampoo prototypes containing MO C_{1115}-2S, compared to laureth-2S, require less ammonium chloride salt to build solution viscosity.

Foam Properties of Prototype Shampoo Formulations

MO C1115-2S and MO C1213-2S demonstrate good foam height and foam drainage. The time to generate a constant foam height in soft water, hard water and in hard water containing oily soil was recorded for prototype shampoos. The data in Figure 6 indicates that the foam profile of MO C_{1115} -2S and MO C_{1213} -2S are competitive with laureth-2S and the commercial brand. This trend was also consistent for the foam decay rates.

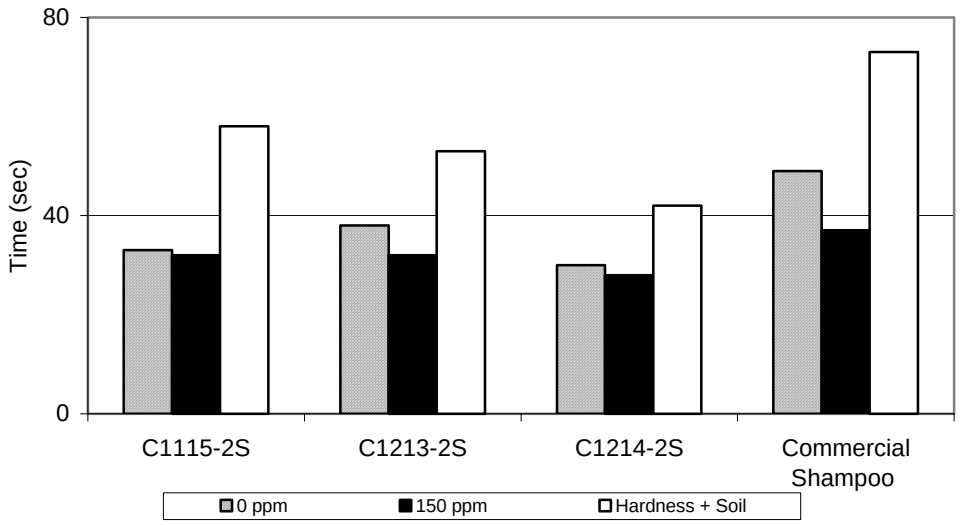


FIGURE 6: Foaming of Prototype Shampoo Formulations

Dimethicone, a silicone-conditioning agent, is routinely added to shampoo products. Hence, the lather-ability of the prototypes were measured in presence of 0.01%w dimethicone, 0.4%w ether sulfate, 200 ppm water hardness.

Figure 7 shows that MO C_{1213} -2S formula is very efficient relative to C_{1214} - 2S in its capability to generate lather in the presence of dimethicone. Interestingly, both MO C_{1115} -2S and MO C_{1213} -2S demonstrate significantly better foam drainage when compared to prototypes based on C_{1214}-2S.

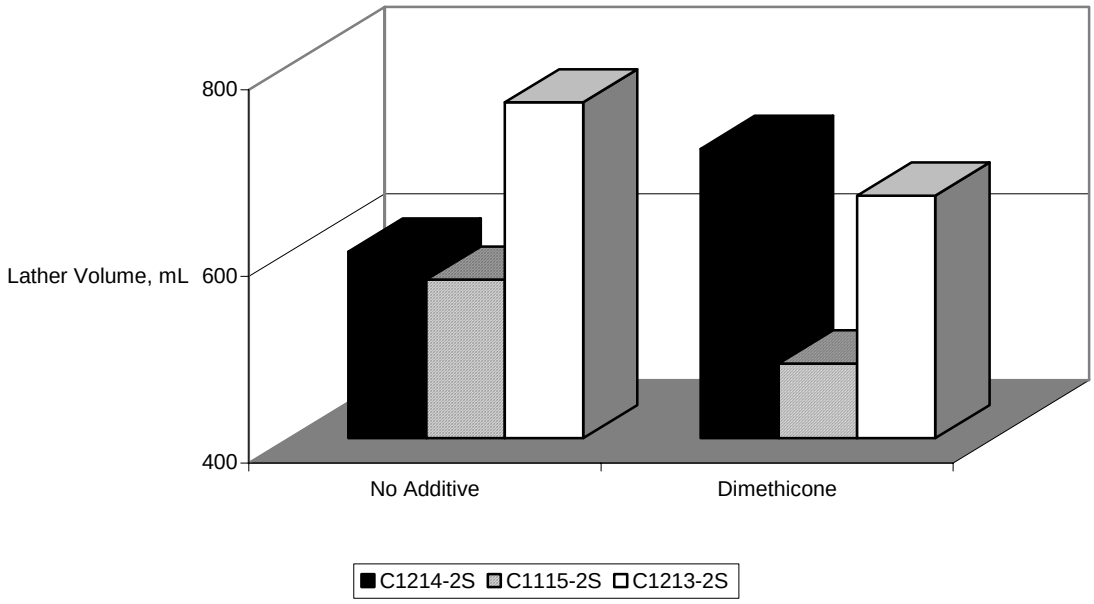


FIGURE 7: Effect of Dimethicone Conditioning Agent on Shampoo Lather

Therefore, Figures 7 and 8 suggest that MO anionics have the capability to generate considerable lather, which subsequently drains rapidly. This presents an advantage to the formulator allowing for efficient deposition of conditioning and other actives to hair tresses.

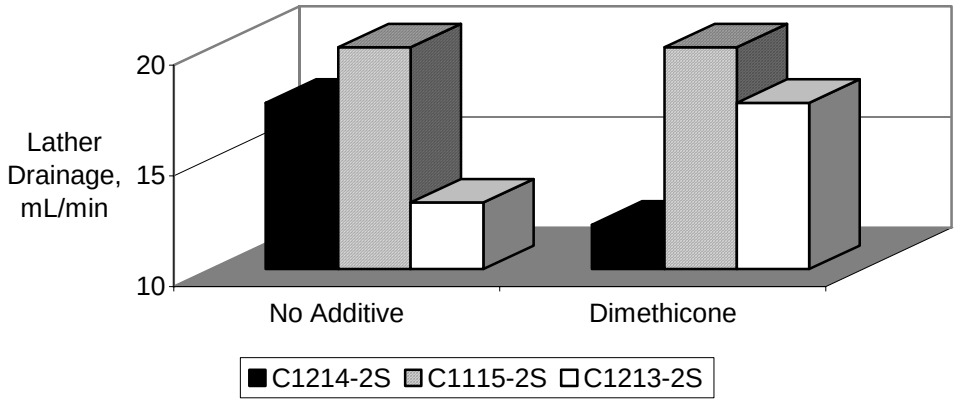


FIGURE 8: Effect Dimethicone Conditioning Agent on Lather Drainage

In summary, MO anionics are competitive with oleo anionics in shampoo formulations. The formula viscosity response to salt added, as well as lather and foam stability; suggest the MO anionics are very well suited for shampoo preparations. They exhibit exceptional capability to maintain excellent lather in the presence of conditioning agents and drain rapidly so that conditioning actives are deposited to hair tresses and not washed away with the surfactant.

III. Bubble Baths

Table 5 lists the relative composition of the prototype bubble bath formula evaluated.

TABLE 5: Prototype Bubble Bath Formula Composition

Component	% w
Water	75
Alcohol ethoxysulfate	14
Myrisyl isoproanolamide Coco MIPA	5
Cocamidopropyl betaine	5
Sodium Chloride	1

Like oleo ether sulfates, MO anionics are efficient foaming agents in the formula indicated in Table 5. Figure 9 shows that at 125 ppm anionic active, both oleo and MO ether sulfates demonstrate equivalent capability to maintain stable foam after 10 mins in hard water containing oily soil. Thus, they are excellent surfactant choices for bubble baths formulated for use with bath salts or oils.

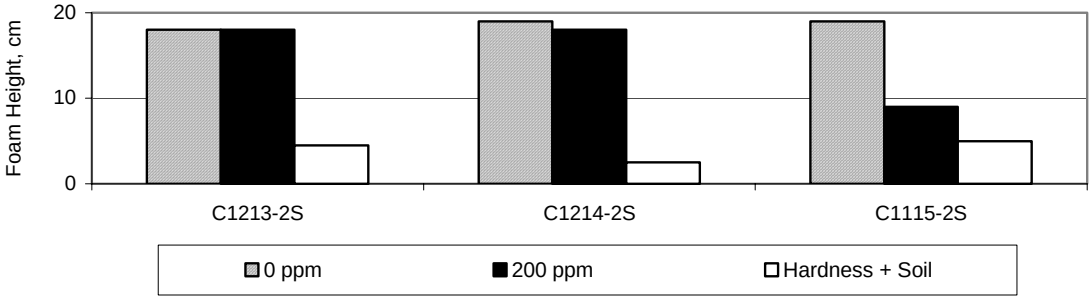


Figure 9: Foam Stability of Prototype Bubble Baths after 10 min

Bubble baths formulated with MO and oleo anionics were equivalent at dispersing lime-scale salts. Figure 10 suggests bubble baths formulated these raw materials may be easily washed down the drain with little soap scum or scale left behind.

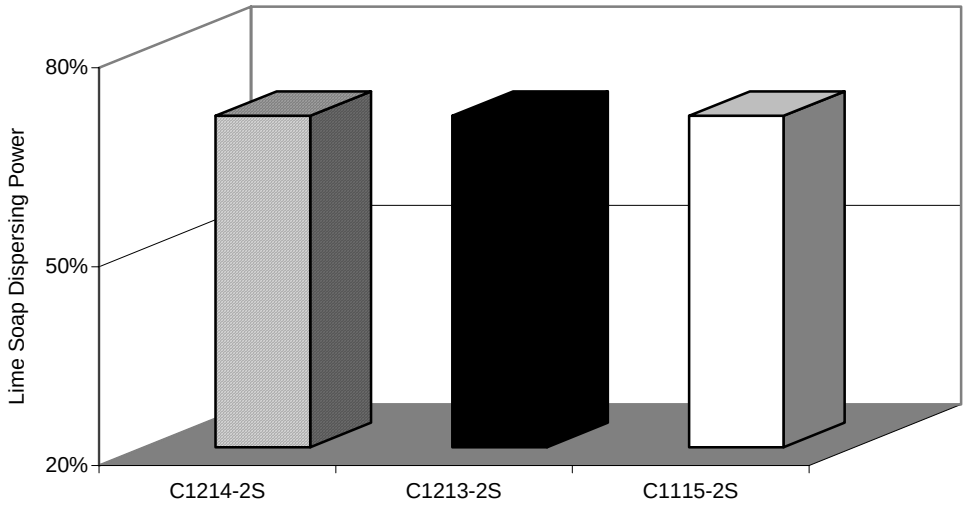


FIGURE 10: Lime-Soap Dispersability for Bubble Baths

IV. Mono Methyl Branched Modified OXO Alcohol as an Emollient

MO C_{1617} mono-methyl branched primary alcohol was formulated in a water-in-oil night cream and an oil-in-water moisturizer formula as indicated in Tables 6 and 8 respectively. The viscosity and formula properties of the MO methyl-branched primary alcohol were evaluated relative to a branched C_{18} emollient alcohol and the data is indicated in Tables 7 and 9 respectively.

TABLE 6: Water-in-Oil Night Cream Formula Composition

Phase	Ingredient	%w
A	Cetyldimethicone Copolyol	5.0
A	PEG-30 (dipolyhydroxystearate)	1.0
A	Par. Hydrogenated Castor Oil	2.5
A	Octyl Palmitate	5.0
A	Fatty Alcohol	15.0
A	Vitamin E Acetate	0.1
B	Propylene Glycol	2.5
B	Hydroxyethyl cellulose	0.8
B	Sodium Chloride	0.8
C	DMDM Hydantoin	0.2
D	Water	69.1

TABLE 7: Water-in-Oil Night Cream Formula Properties

Fatty Alcohol	**Viscosity, cps**	Freeze-Thaw (3 cycles)	Oven Stability
MO MM Branched C1617	10,400	Pass	Pass
Octyldodecanol	7,600	Pass	Pass

TABLE 8: Oil-in-Water Moisturizer Formula Composition

Phase	Ingredient	%w
A	Water	63.6
A	EDTA	0.1
A	Glycerin	2.5
A	Poly acrylic copolymer (2.5%)	15.0
B	Fatty Alcohol	10.0
B	Glyceryl Stearate, PEG-100 Stearate	2.5
B	Stearic Acid	2.5
B	Cetearyl Alcohol	1.0
B	Dimethicone DC 200-50	1.0
C	20% NaOH	0.8
D	Propylene Glycol, Diazolidinyl Urea	1.0

TABLE 9: Oil-in-Water Night Cream Formula Properties

Fatty Alcohol	Viscosity, cps	Freeze-Thaw (3 cycles)	Oven Stability
MO MM Branched C1617	35,600	Pass	Pass
Octyldodecanol	11,300	Pass	Pass

Compared to oleo alcohol emollients, like cetyl/cetearyl alcohols and branched guerbet alcohols typically used as emollients in moisturizers and night-creams, MO C_{1617} alcohol has exceptional handling and viscosity-building properties. In a water-in-oil emulsion product, the MO C_{1617} night cream had excellent slip characteristics, good product texture with a non-oily skin after-feel. Similarly, in an oil-in-water moisturizer, the MO C_{1617} product demonstrated good rub-in characteristics with a good matte skin after-feel.

V. Skin/Eye Irritancy of Detergent Range Alcohol Derivatives

A consumer's perception of skin irritation attributed to personal care product generally involves an itching and/or burning sensation, which may involve dryness and scaling. Additive ingredients or co-surfactants, like betaines, are added to improve skin mildness. Earlier published work sponsored by Shell utilized an

Eye Irritation Scoring method to correlate the DRAIZE Scale with the *in vitro* EYETEX® assay.[3,4] The results of this work indicated that shampoos formulated with 18%w MO and oleo ether sulfates, respectively, alone and with 8%w betaine, were all ranked as "minimally irritating". [5]

Recent data developed on an oil-in-water moisturizer formulation containing 0.5%w MO MM branched alcohol was evaluated for skin irritation potential in a Human Repeat Insult Patch test. The moisturizer was administered in three twenty-four hour applications to thirty test subjects following typical HRIPT test protocols. The results of this test indicated that skin-care lotions or moisturizers formulated with MO MM branched alcohol are essentially non-irritating and non-sensitizing.

Consequently, results from the primary irritation potential and HRIPT data for oleo and petrochemically-derived alcohols and derivatives are similar.

CONCLUSIONS

Modified Oxo alcohols are unique in that they are essentially linear alcohols, which contain both odd and even carbon chains. Modified Oxo alcohol anionic derivatives have good surface-active properties that are competitive with oleo anionics, thus making them suitable alternatives for many personal cleansing end-uses including shampoos, liquid hand soaps and bubble baths.

The MO ether sulfates are very compatible with oleo alcohol sulfates and may be used as blends to generate copious and stable foam under adverse conditions. Whether they are used in blends or alone, they respond well to formula viscosity thickening with relatively small amounts of electrolyte. MO anionics are also compatible with many formulation additives, thereby allowing the formulator flexibility to attribute sensorial effects, mildness and/or performance claims to their personal cleansing product.

Mono-methyl branched C_{1617} modified Oxo alcohol has particularly unique and interesting properties as a moisturizer. It is a fluid high molecular weight alcohol with excellent emolliency and moisturization characteristics. Additionally, recent HRIPT data has indicated that anionic derivatives of oleo or modified Oxo alcohols are not expected to be skin sensitizers.

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