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S. Holt, J. Velasquez, S. Muresan, O. Forsberg

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Introduction

The consumer attitude toward household cleaning products is changing. No longer are cost and performance the only considerations. The consumer is increasingly aware that they need to make careful selection of products, tending towards selection of natural, preferably vegetable-based ingredients that are sustainably sourced and which are mild in the environment once released post-use.

In this paper we will explore an example of how it is possible to increase the bio-based content of a class of specialty surfactants – narrow range ethoxylates, which have historically been of synthetic origin. By switching to a natural, vegetable-based hydrophobe, sourced via a sustainable supply chain (RSPO), we can better meet customer expectation, and will demonstrate that the same high performance of the cleaning ingredient can be fully maintained. In so doing, we provide formulators the option to develop more bio-based, high-performance cleaning formulations, with ingredients that also qualify as EU Ecolabel.

Consumer Drive for more Sustainable Cleaning – Supported by Third Party Certifiers

Consumers are increasingly aware of their personal responsibility in selecting the right cleaner for use in their homes. That selection is no longer exclusively based on cost and performance. An increasingly nuanced approach is being taken, based on an awareness of the greater impact of the cleaning formulation on the user, the home and the environment. Guidance in the decision-making process can come from multiple sources. It can be from producers, who sometimes provide statements of ingredient origin or environmental performance on their labels, but more typically comes from third-party certifiers (such as EU Ecolabel, Blauer Engel, Nordic Swan etc.) who provide overall assessments of the cradle to grave aspects of the formulation which is shared with consumers through use of certifying trademarks on product labels. Information on the sustainable sourcing of ingredients is also available from third-party supply chain certifiers such as Roundtable on Sustainable Palm Oil (RSPO), Eco-Cert etc. As such, consumers today are empowered with decision-making information that allows selection of more sustainable cleaning products at point of sale. Retailers are also reacting to the trend by clustering greener cleaning solutions together to further aid enlightened consumer choice. The net result is a greater diversity of bio-based cleaning products available to the consumer, who is actively choosing such products to buy, and where growth is now significantly outperforming that of the overall cleaning sector. Objective assessment of the performance and environmental elements of products is also provided by Stiftung Warentest, which offers an added insight to a consumer, with its excellent reputation for independent and comparative product assessment.

A current trend is to transition formulations from ingredients originating from synthetic sources toward natural ones, preferably ones originating from sustainably-sourced, natural vegetable origins. This is evidenced by the continuing adoption of EU Ecolabel products and services from 2010 to 2019 as illustrated in **Fig. 1**. Note that such data was not collected prior to 2010, data per latest March 2019 release.

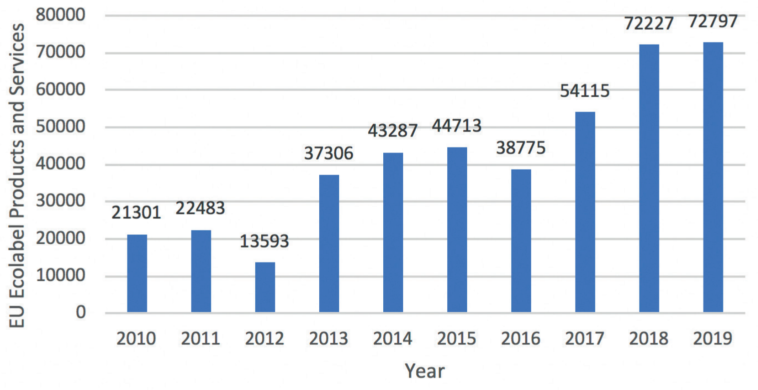

Fig. 1 Growth in EU Ecolabel certified products and services across all categories – 2010-2019

Non-detergent Specialty Alcohol Ethoxylates – Historically from Synthetic Sources

Mid-cut, C12-C14 alcohols (and derivatives) are used extensively in detergent manufacture in Europe today and are derived largely from natural raw material feedstocks according to the newest IHS Markit report on Detergent Alcohols (https://ihsmarkit.com/products/detergent-alcohols-chemical-economics-handbook.html – September 2016) – although synthetics still dominate in North America, Africa and elsewhere.

For the lower cut alcohols (C6-10) however, synthetic sources have historically been favored. The demand for lower chain lengths is driven by enhanced performance-in-use, particularly for degreasing in hard surface cleaning applications, although the overall demand is small in proportion of that of the mid-cuts. The reason for the preference for synthetically-derived hydrophobes has been the historically broader availability of the synthetic alcohols, the ability to build specialty hydrophobes (i.e. with branching) and the relatively stable and historically lower price point for synthetics derived from the enhanced economics of integrated petrochemical producers that are basic in ethylene.

Commercial natural sources of these alcohols are limited today to coconut and palm kernel oils (PKO), and these have only low yields of these lower cut fractions – for example, a typical composition of coconut oil is 6.5% C10, 5.8% C8 and only trace amounts of C6, with the remainder C12 and above (according to Acme-Hardesty Oleochemicals "Typical Composition of Natural Oils and Fats)). PKO low cut yields are lower again. Further, the price that can be achieved for the low-cut fractions once separated had to be competitive with ethylene-derivatives, thus making the complexity and expense of separation of the low cuts from the natural oils often not worth the effort, particularly for a relatively limited market demand.

As natural oil production has grown in recent years (particularly for PKO), the availability and price point of natural oils has reduced (somewhat correspondingly for low-cut fractions), complementing a limited but growing consumer-led demand for natural surfactants. This is influencing the entire supply chain from grower through ingredient producer to formulator and beyond. And with a higher availability, and the optional extra of more sustainably sourced raw materials (i.e. RSPO-certified), the ability to source natural low-cut raw materials for surfactant manufacture is greater and more competitive now than it ever has been.

Narrow Range Ethoxylation – Providing Consumer and Formulator Advantage

Conventional base-catalyzed fatty alcohol ethoxylates are used in many detergent cleaning formulations today. In certain circumstances they provide fit-for-purpose performance. However, in high performance cleaning applications, the use of an advanced narrow-range ethoxylation process can provide significant benefit to both the consumer and the formulator.

In **Fig. 2** we show the typical degree of ethylene oxide polymerization of three alcohols reacted with an average 5 moles of ethylene oxide:

- In orange – a C9-11 synthetic alcohol ethoxylated using a narrow range process
- In grey – a C9-11 synthetic alcohol ethoxylated with a conventional base-catalyzed process
- In blue – a nonyl-phenol synthetic alcohol ethoxylated with a conventional base-catalyzed process

5EO was chosen as a benchmark as it is at around this degree of ethoxylation that the performance of the surfactant molecule as a degreaser is optimal i.e. the hydrophilic/lipophilic balance (HLB) is ideal. Thus, a maximum yield of the 5EO surfactant is most desirable with the area given a green background for contrast. In low (<2 EO), and especially no ethoxylation of the fatty alcohol is undesirable (poor solubility and degreaser performance – with any unreacted alcohol giving the product odor). Similarly, an excessive ethoxylation adds components with undesired functionality, diluting the optimized degreasing function at 5EO, and adding issues with product viscosity and foaming tendency. The less desirable portions of the surfactant distribution have a grey background in **Fig. 2**. The impact of these issues will be exemplified below.

The nonyl phenol ethoxylate (NPE) is included as a benchmark only, as its use is now banned in European detergent applications, but as can be seen, it forms a tightly peaked distribution with a high percentage in the target 5EO range.

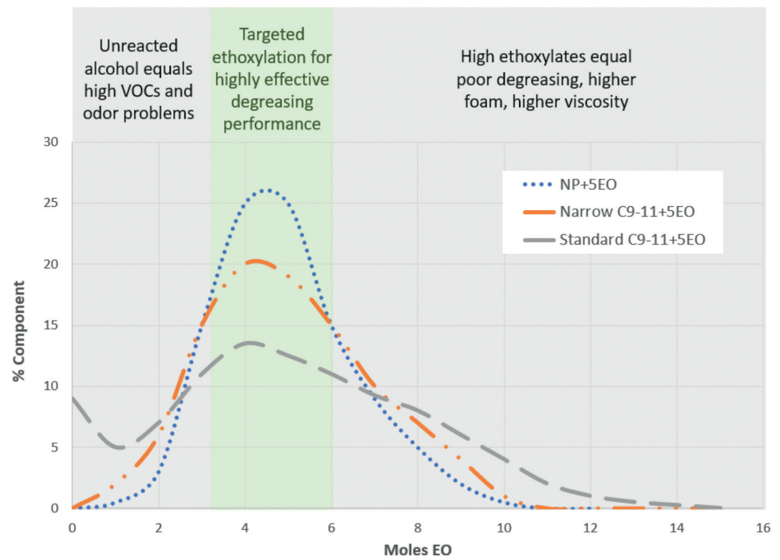

Fig. 2 Molecular distribution of various alcohols ethoxylated to provide an average 5EO via standard and narrow range processes.

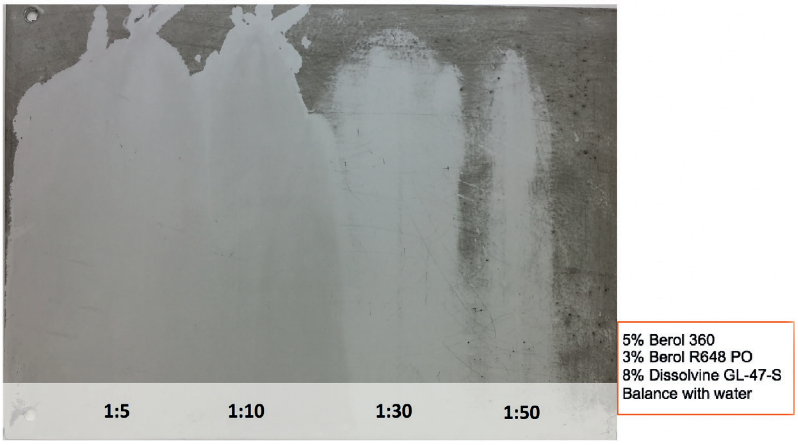

Fig. 3 Black box performance of various dilutions of a simple cleaning formulation on a coated metallic white tile treated with engine oil and aged for 12 hours at room temperature.

Introducing NRE's with Natural Hydrophobes – RSPO-certified

For all their advantages, narrow range ethoxylates have traditionally only been offered to the market using synthetic raw materials, particularly the C9-11 hydrophobe, as exemplified in **Fig. 2**, the hydrophobe of which is petroleum-derived. With the evolution of consumer needs, there is now a strong desire for the use of natural hydrophobes in such surfactants. Nouryon has undertaken extensive research work to develop narrow range ethoxylates based on natural hydrophobes which have equivalent performance and function to the petroleum derived variants. Two products are commercially available:

- Berol 360 – a C10 4EO primary NRE surfactant targeted for more extreme industrial and institutional degreasing applications
- Berol 366 – a C10 5.5EO primary NRE surfactant targeted for household degreasing challenges

It is this peaked distribution that provided the excellent performance characteristics that made NPE usage so ubiquitous in the past, and which made its replacement so challenging to achieve.

As can be seen, the narrow-range ethoxylates (NRE's) most closely match the peaked distribution of the NPE's, without, of course, the major environmental and toxicity burden. Narrow range ethoxylates are readily biodegradable and low toxicity. Narrow range ethoxylates have a strong peak around the target 5EO with very low residual alcohol and smaller amounts of high ethoxylates. Because the average MW of the molecules is smaller than the standard ethoxylates, the rate of diffusion is faster, promoting faster spreading and wetting, and giving the water-free product as-sold, a much lower viscosity.

The standard process ethoxylates have a very different, and much broader profile than the other processes exemplified, with a much wider molecular distribution. On the low MW end, a significant amount of starting alcohol remains unreacted. This alcohol is volatile and leads to odor in the final product, detectable by consumers in the final formulation. The yield of optimized 5EO product is also much lower with the profile skewed to the higher degree of ethoxylation. The higher molecular weight fractions have far less degreasing power than the optimized 5EO polymers (poor HLB), contributing mostly to undesirable characteristics in the finished product, such as viscosity and foaminess. These negative characteristics are exemplified in **Fig. 4** and **Fig. 5** respectively.

Fig. 4 Comparison of the viscosity at 0°C of standard ethoxylates and comparable NRE products.

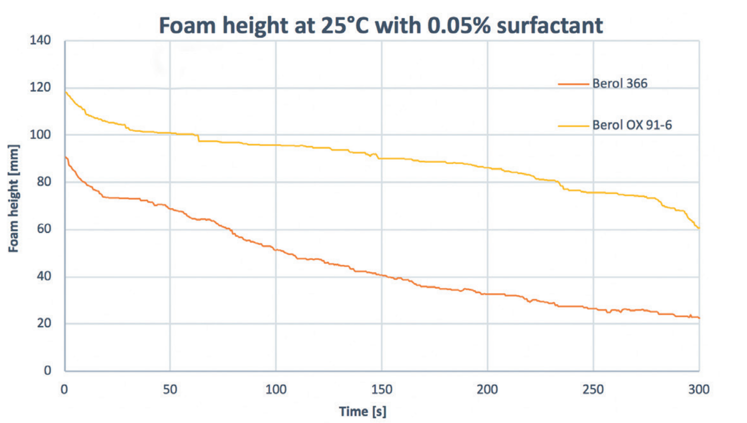

Fig. 5 Comparison of Ross-Miles foaming performance of a standard process ethoxylate (Berol OX 91-6) with a comparable NRE (Berol 366) at 25°C with 0.05% surfactant present.

Both these products are made from RSPO mass balance (MB) raw materials and come with the relevant RSPO certification of origin.
In the following figures we will demonstrate some of the advantage of narrow range ethoxylates in comparison to ethoxylates produced using the standard process (Berol OX 91-4 and Berol OX 91-6). Firstly, we will demonstrate the excellent degreasing performance, even at low concentration (**Fig. 3**). We illustrate the lowering of product viscosity (**Fig. 4**) and improved foam characteristics (**Fig. 5**) in comparison with synthetic C9-11 fatty alcohol ethoxylates produced via a standard ethoxylation process. In **Fig. 6**, we also demonstrate how the NRE primary surfactant performance can be further optimized through synergy with secondary ingredients in simulated cleaning product application scenarios.
In **Fig. 3**, the cleaning performance of the primary surfactant, Berol 360 is clearly demonstrated in a simulated industrial degreasing situation. Even at low concentration, the powerful degreasing function of the NRE continues to show, making for a very efficient formulation.
In **Fig. 4**, the two NRE products (to right) are readily flowable at 0°C. The two standard ethoxylates (to left) are highly viscous or semi-solid. As a rule, the higher the degree of ethoxylation, the more the viscosity is negatively affected, due to the higher average MW of the molecules. This is reflected in the above examples.
In **Fig. 5**, the NRE shows much lower foaming, with a more rapid foam instability with time when compared with the equivalent standard ethoxylate. The impact of unwanted foam is most challenging at lower temperatures, such as this room temperature study. This is due to the slower dynamics of foam decay at these temperatures.
In **Fig. 6**, we show that NRE's offer great performance in a simple framework formulation (**Formulation 1**) using conventional hydrotropes. The test is a conventional black box test for a ceramic tile soiled with used cooking grease and aged for 20 hours at room temperature. However, the functionality of the primary surfactant is synergistic with high-performance hydrotropes (such as Berol R648 PO – also RSPO-certified) – which is shown with **Formulation 2**.
In summary, NRE's provide both the formulator and consumer with the following benefits:

Advantages for the formulator:

- Maximum concentration as-sold - 100% active
- Low viscosity, especially for lower temperature handling
- VOC-free, low odor
- Low foaminess during formulation preparation
- Optimized performance providing low effective dose and/or high dilution performance
- Easy formulation – rapid dissolution times, and compatible with other surfactants, including anionic, cationic and other nonionic ingredients
- Strong synergies with performance hydrotropes

Advantages for the customer:

- Excellent degreasing performance
- Low foam
- Fast wetting and spreading
- Low odor
- Good environmental characteristics

And where these products utilize RSPO-certified raw materials (as with Berol 360 and Berol 366) the consumer can also realize the following benefits:

- Vegetable-based
- RSPO-certified
- EU Ecolabel compliant

Comparison of Synthetic vs. Natural NRE's – like-for-like Performance

One of the main aims of developing vegetable-based NRE's was to give the formulator the choice of switching to an NRE containing a natural hydrophobe from one containing a petroleum-based hydrophobe used today. There is an assumption amongst some in the cleaning community that switching from a synthetic to a natural raw material source will come at a cost to performance, but we will demonstrate that is not the case here.
In an ideal world, a formulator would want to be able to swap out any synthetic components in a formulation for natural ones, without the need to spend time and effort on reformulating. In such a case, the physicochemical properties of the finished product need to be very similar, so too the performance-in-use characteristics.

Formulation 1	
5.0%	Berol 360
6.5%	SCS (40%)
5.0%	Dissolvine GL-47-S
Balance	water

Formulation 2	
5.0%	Berol 360
4.5%	Berol R648 PO
5.0%	Dissolvine GL-47-S
Balance	water

Fig. 6 Optimization of NRE performance by using advanced hydrotropes for all-purpose cleaning.

The three following data sets will show that this is achievable. We will look at NRE's containing the natural hydrophobe and the equivalent slightly-branched hydrophobe of synthetic origin – the latter being widely used in the market today.
We will investigate the surface tension/critical micelle concentration (CMC), the hydrotroping demand and look at the performance-in-use in a typical household cleaning test. Berol 366 is used as the natural NRE benchmark in this case alongside its synthetic counterpart – Berol 266. Both have similar physicochemical properties and technical sales specifications.
As can be seen in **Fig. 7**, the movement from synthetic to natural hydrophobe had little discernible impact on the interfacial tension of the NRE. As might be expected for a primary surfactant, the CMC is quite low, 90 mg/L (Berol 266) and 100 mg/L (Berol 366). The surface tension at CMC is about 25mN/m and 28 mN/m, respectively.
Fig. 8 again shows that there is almost now difference in demand for hydrotrope to get both synthetic and natural NRE formulations to a cloud point of 45°C. When no caustic soda is added, the hydrotrope demand is 2% Berol R648 PO. A slight difference between the two ingredients performance is observed when 2% NaOH is added, but the hydrotrope demand is consistent, in the range 4 to 4.2% Berol R648 PO to achieve a cloud point of 45°C. A higher hydrotrope demand is anticipated for high alkalinity solutions due to the primary surfactant "salting-out" effect of the electrolyte.
Fig. 9 shows that using a simple alkaline household cleaning formulation and including the NRE non-ionic primary surfactant at 5%, almost no discernible difference is observed when comparing the degreasing performance of both the natural and synthetic hydrophobes. Both degrease well, with performance equivalence seen in two dilutions of the base formulation – 1:10 (effective cleaning) and 1:40 (suboptimal cleaning).
Fig. 7 to **9** demonstrate an interchangeability of narrow range ethoxylate products made with either natural (C10) or synthetically derived (C9-11) hydrophobes in

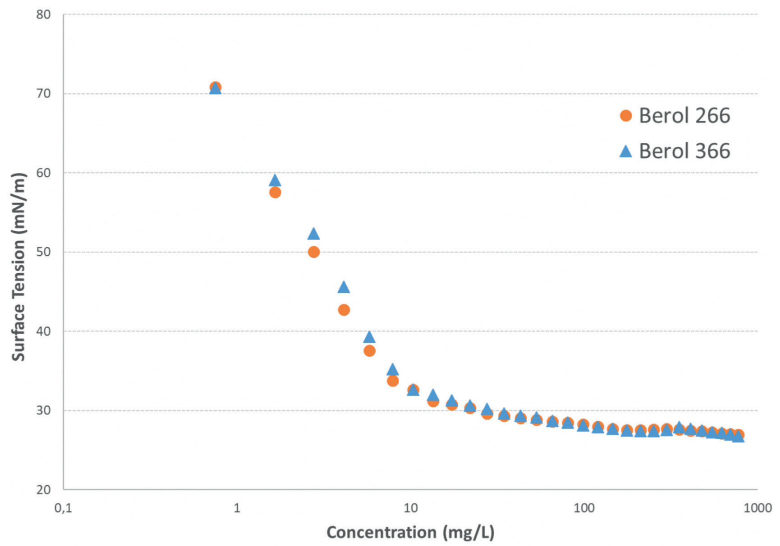

Fig. 7 Interfacial tension measurement of a natural (Berol 366) vs. a synthetic (Berol 266) NRE.

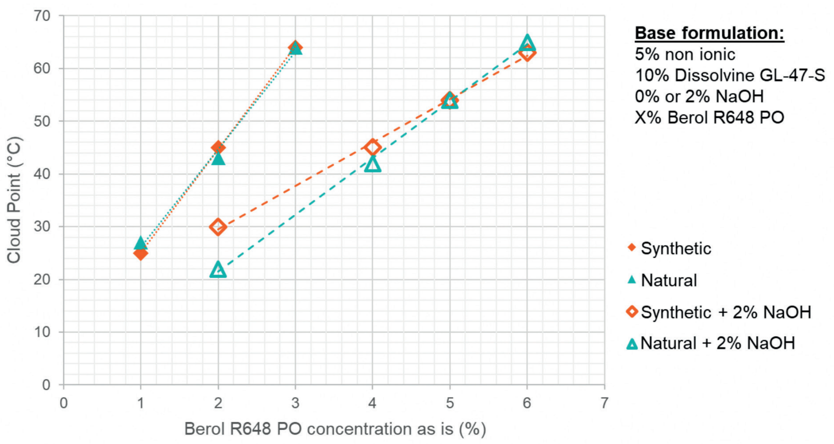

Fig. 8 Hydrotrope demand to achieve a base formulation cloud point of 45°C for a framework cleaning formulation – with and without 2% NaOH.

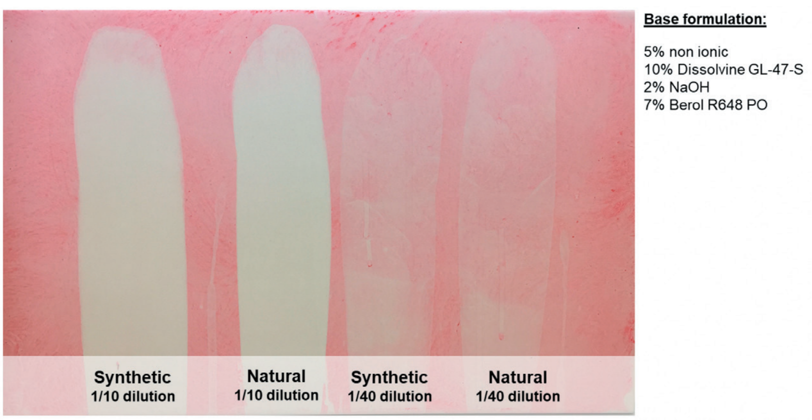

Fig. 9 Black box test on a ceramic tile soiled with colored used cooking grease and aged for 5 hours at 60°C.

typical hard surface cleaning applications. Given that the physicochemical specifications of these finished products are similar, this evidence suggests that the natural products can be dropped into existing formulations without the need to reformulate. However, it is recommended that some performance-in-use validation work should be done to confirm.
The new Berol 360 and Berol 366 natural narrow-range ethoxylate ingredients offer both industrial and institutional (I&I) as well as household customers the ability to incorporate natural, sustainable, vegetable-based content into their high-performance cleaning formulations.

Conclusions

Narrow range ethoxylates provide a variety of favorable performance characteristics that make them desirable to both formulators and end consumers, particularly in tough degreasing applications. The use of RSPO-certified hydrophobes increases the bio-based content of these ingredients, making them compliant with newest EU Ecolabel requirements – the cobranding of which helps customers select greener cleaning formulations for use in their home or business. The demand for such solutions continues to grow; with green cleaners outperforming the overall cleaning market as consumer attitudes have evolved to favor such materials.
As an industry, the more we can do to "green" our products the better it will be for producers, formulators, consumers and the environment. Providing lower environmental impact in use, using raw materials from sustainable vegetable-based supply routes whilst maintaining the expected consumer-anticipated performance cleaning is a critical part of this industry's evolution. Nouryon continues to work towards this aim, and these new ingredients are evidence of such a commitment.

contact

Stuart Holt
Global Technical Marketing Manager – Cleaning

Nouryon Surface Chemistry LLC
525 West Van Buren Street
60607 Chicago | USA

https://surfacechemistry.nouryon.com/markets/cleaning/