SurfaThix™ N: Rheology Modifier for Cleansing Systems

Dr. Martin Vethamuthu
Principal Scientist
A New Standard for Rinse-off Formulations

Manufacturers of hair and skin cleansers may now formulate clear systems with excellent rheology modification and sensory attributes using a single technology: SurfaThix™ N polymer.

An acrylate-based technology, SurfaThix -N polymer [INCI: Acrylates Copolymer, ACP] is broadly compatible in surfactant rich rinse-off formulations.

Appearance: Milky white liquid
Viscosity of 1% ACP Solution 25C, @pH 7 [Sp. 6, 20RPM]: 2000-6000 cp
Total Solids: 28.0 to 32.0 %
Use level (as is): 3.0-8.0%

pH: 2 – 3 (as is): Formulated at pH > 6
Limitations of current Rheology Modifiers

- Powder technology
- In use foam performance & visual impact could be improved
- Limited to batch processing
- Impacts coacervate region & performance of conditioning polymers
- Two step back acid thickening process
- Inferior in-use foam performance due to slower de-structuring profile

No current Rheology Modifier satisfies requirements for both Skin & Hair formulations without trade-offs
Innovation Toolbox - SKIN Cleansing/Moisturizing

Base / pH

Deposition & Luminosity

Mildness & Polymer Hydrodynamic Space filling Efficiency

Untreated

Leave -in

Treated - Wet

Treated – Dry (towel)
Fundamental Attributes of Rheology Modifier in Water & Surfactants

Zeta Potential Measurement: [LDM]  Particle Sizing Measurement:[DLS]

Henry’s Eqn: $\mu_e = \zeta 2 \varepsilon f(Ka) / 3 \eta$

<table>
<thead>
<tr>
<th>Water/pH 3</th>
<th>Avg. Zeta Potential / mv</th>
<th>Water/pH 3</th>
<th>Z-Avg(r.nm)</th>
<th>PD Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benchmark</td>
<td>-64.7</td>
<td>Benchmark</td>
<td>76.52</td>
<td>0.115</td>
</tr>
<tr>
<td>SurfaThix-N</td>
<td>-77.9, -41.5</td>
<td>SurfaThix-N</td>
<td>59.12</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Stokes-Einstein

$R_H = \frac{kT}{6\pi\eta D}$
Effect of pH (6.8) on Size & Zeta potential

Zeta potential: More negative at pH 6.8 so higher repulsion between similar charges distributed on polymeric chain

Chain uncoils & swells ~30 times and about 7% of chains are non-swollen ~78nm radius

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Avg.Zeta Potential / mv</th>
<th>Z-Avg (r.nm)</th>
<th>PD Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benchmark</td>
<td>-71</td>
<td>1593</td>
<td>0.99</td>
</tr>
<tr>
<td>SurfaThix-N</td>
<td>-82.7</td>
<td>1896</td>
<td>0.39</td>
</tr>
</tbody>
</table>
Effect of pH (8.5) on size & Zeta potential

Zeta potential: More negative than benchmark

Chain swells \(~36\) times and about 6% of chains are low-swollen \(~60\)nm radius

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Avg. Zeta Potential / mv</th>
<th>Z-Avg (r.nm)</th>
<th>PD Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benchmark</td>
<td>-102</td>
<td>1803</td>
<td>0.35</td>
</tr>
<tr>
<td>SurfaThix-N</td>
<td>-118</td>
<td>2020</td>
<td>0.67</td>
</tr>
</tbody>
</table>
SurfaThix-N apparent Hydrodynamic ‘space filling efficiency’ in water.

![Graph showing SurfaThix-N apparent Hydrodynamic 'space filling efficiency' in water.](image)

- **SurfaThix-N** apparent Hydrodynamic ‘space filling efficiency’ in water.
- **Sulfate Free Base**
- **Isethionate Base**
- **Glycinate Base**
- **Soap Base**

**Graph Details:**
- **x-axis:** pH (6.8, 7.05, 8.5)
- **y-axis:** Apparent Space Filling Efficiency

**Legend:**
- RH[UC]/RH[C] [Benchmark]
- RH[UC] /RH[C][SurfaThix-N]
### SurfaThix-N: Suspending rheology in water

**Good yield & flow profile compared to benchmark**

<table>
<thead>
<tr>
<th>pH</th>
<th>Viscosity (Pa·s) at 0.1 s⁻¹</th>
<th>Viscosity (Pa·s) at 10 s⁻¹</th>
<th>Oscillating Yield Stress (Pa)</th>
<th>Benchmark Yield Stress (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.8</td>
<td>32.6</td>
<td>0.98</td>
<td>3.0</td>
<td>2</td>
</tr>
<tr>
<td>7.0</td>
<td>33.1</td>
<td>0.99</td>
<td>3.0</td>
<td>2.5</td>
</tr>
<tr>
<td>8.5</td>
<td>20.3</td>
<td>0.79</td>
<td>2.9</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Onset point: Osc. stress: 2.917 Pa
G': 33.19 Pa
End condition: Finished normally

Straight line
a: y-intercept: 0.6139
b: slope: 0.1042
x-intercept: -5.895
regression: 0.99960
standard error: 6.736
End condition: Finished normally

1 s⁻¹ = 4.8 Pa·s
10 s⁻¹ = 0.9 Pa·s
SurfaThix-N: Suspending Rheology in Formulation

60 mm, 2° Titanium Cone and Plate Geometry

Rapid De-structuring:
Foam performance

Stability:

Flow profile:

Conditioning: 25° and 45 °C with 0.1 Pa (2 min)
Stepped stress ramp: 0.1-100 Pa (2 min/step)

<table>
<thead>
<tr>
<th>pH</th>
<th>2.1% SurfaThix-N In 9:3 Base SLES1EO: CAPB</th>
<th>0.1000</th>
<th>1.000</th>
<th>10.00</th>
<th>100.0</th>
<th>1000</th>
<th>10000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zero shear Viscosity (Pa·s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH – 6.8</td>
<td>2.1% SurfaThix-N 25C</td>
<td>3383</td>
<td>10</td>
<td>0.75</td>
<td>0.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH – 7.0</td>
<td>2.1% SurfaThix-N 45C</td>
<td>4313</td>
<td>12</td>
<td>1.03</td>
<td>0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Onset point</strong></td>
<td>shear stress: 0.7529 Pa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>viscosity:</strong> 3383 Pa.s</td>
<td>End condition: Finished normally</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Rapid De-structuring:

Foam performance

Conditioning: 25° and 45 °C with 0.1 Pa (2 min)
Stepped stress ramp: 0.1-100 Pa (2 min/step)
Clear Advantage with SurfaThix™ N polymer

Higher viscosity, better clarity in select formulations

At 2% concentration, formulations with SurfaThix N polymer are superior.
With Sulfates, SurfaThix™ N polymer Performs Better than Industry Benchmark

Higher viscosity, better clarity in select formulations

SurfaThix N polymer improves viscosity significantly and shows slightly better clarity with the inclusion of salt in formulation.
Rapid product de-structuring in-use provides better foam build-up
CONSUMER PANEL DATA: PRODUCT SENSORY EVALUATION [Paired Comparison]

KEY PRODUCT PARAMETERS:
- VISCOSITY
- TEXTURE
- CONSISTENCY
- RINSEABILITY

WET STAGE EVALUATION
- SMOOTH FEEL
- CLEAN FEEL

DURING APPLICATION
- OVERALL FOAM QUALITY
- FOAM DENSITY
- SMOOTH FEEL

DRY STAGE EVALUATION
- SMOOTH FEEL
- CLEAN FEEL
SurfaThix™ N polymer Delivers a Richer Experience in Body Wash Formulations

A thicker and creamier feel is achieved in testing with consumers

9/3 Sodium Laureth Sulfate/Cocamidopropyl Betaine
pH=6.7; 2.0% active thickener

Body wash containing SurfaThix N polymer was significantly thicker and creamier than industry benchmark.
SurfaThix™ N polymer Offers Foam Attributes Similar to Industry Benchmark

Density and smooth feel are similar in body wash testing

SurfaThix N polymer delivers foam density and smooth feel similar to industry benchmark.
SurfaThix™ N polymer Offers Foam Attributes Similar to Industry Benchmark

Directionally better smooth feel and similar clean feel in body wash testing

SurfaThix N polymer delivers dry smooth feel directionally better than the industry benchmark and has similar clean feel.
Clear Performance and Elegance in Body Wash

Formulate with better aesthetics and efficiency

SurfaThix™ N polymer offers:

- Clarity equal to or better than benchmark polymers in body wash formulations
- Better thickening than benchmark polymers in typical body wash systems
- Improved foam density (creamy lather)
- Smoother dry-feel in finished formulations
- Easy rinse

NEXT: HAIR FORMULATIONS
Coacervation (or Flocculation) is an important mechanism to deliver conditioning agents to hair fibres: No trade off from Rheology Modifier

Super Pearly Shampoo: 12:2 with 0.2% Mica, NO EGDS

Silicone Deposition from Shampoo

<table>
<thead>
<tr>
<th>Substance</th>
<th>Silicone deposited (lcp ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbomer 980</td>
<td>799</td>
</tr>
<tr>
<td>SurfaThix N</td>
<td>835</td>
</tr>
<tr>
<td>Benchmark</td>
<td>711</td>
</tr>
</tbody>
</table>
SurfaThix-N: Compatibility with Cationics

Aim: Minimize impact of two phase coacervate region by Rheology modifier

<table>
<thead>
<tr>
<th>Deionized Water</th>
<th>QS to 100</th>
<th>QS to 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Laureth Sulfate</td>
<td>11.00</td>
<td>11.00</td>
</tr>
<tr>
<td>Cocoamidopropyl Betaine</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>Polyaquaternium-7</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>SurfaThix™ N polymer</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Benchmark</td>
<td></td>
<td>1.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Deionized Water</th>
<th>QS to 100</th>
<th>QS to 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Laureth Sulfate</td>
<td>11.00</td>
<td>11.00</td>
</tr>
<tr>
<td>Cocoamidopropyl Betaine</td>
<td>4.00</td>
<td>4.00</td>
</tr>
<tr>
<td>Polyaquaternium-10 (medium charge, medium MW)</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Polyaquaternium-10 (high charge, medium MW)</td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>0.50</td>
<td>1.00</td>
</tr>
<tr>
<td>SurfaThix N polymer</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

| pH | 6.8 | 6.8 |
| Viscosity | 42300 | 34600 |
| Appearance | Clear | Slightly Hazy |
| Clarity (NTU) | 16.4 | 55 |

| pH | 6.8 | 6.8 |
| Viscosity | 21600 | 33000 |
| Appearance | Clear | V. slt haze |
| Clarity (NTU) | 27.5 | 35.6 |

SurfaThix™ N polymer maintains clarity & exhibits compatibility with polyaquaternium-7 and polyaquaternium-10
SurfaThix™ N polymer: New “Suspending” ASI Polymer

Less dry Friction = Smoother hair

At equivalent Silicone level, benchmark will impair silicone deposition = higher dry friction.

Shampoo 12:2, 0.2% Cat NHBF13, 1% or 2% DC1788, perfume, preservative, 0.15% mica.
Consumer Evaluations Indicate Superior Performance in Silicone Shampoo

Better performance observed in wet and dry hair

SurfaThix™ N polymer in silicone shampoo formulation offers improved ease of dry comb, smooth feel (wet), detangling (wet) and viscosity.
Clear Performance and Elegance in Shampoos

Formulate with better aesthetics and efficiency

SurfaThix™ N polymer offers:

• Improved dry comb in silicone containing shampoo
• Smooth feel on wet hair
• Enhanced detangling
• Improved viscosity in finished formulations
• Benchmark clarity
• Efficient use of pearlizers for visual effects
The Formulator’s Advantage [SKIN & HAIR]

Single Technology & Performance without trade-offs

- Formulate a range of clear cleansing systems easily, and across both Skin & Hair formulation chassis, with highly compatible acrylates technology
- Thicken more efficiently with or without sulfates & compatible across broad range of surfactants / salts
- Single step pH adjustment, no back acidification & ease of use
- Obtain clarity and aesthetics without negatively impacting silicone or oil deposition
- Achieve special visual effects through suspension such as beads, shimmer and pearlescence with greater efficiency in formulations
SurfaThix™ N Polymer: INCI: Acrylates Copolymer for Skin & Hair Formulations

- Suspending Stability
- Aesthetic-Visual
- Cleansing Performance
- Oil & Si Deposition
- ACP Benchmark

Acknowledgements

Co-Authors: E. DiAntonio, V. Johnson, H. Fares & L. Foltis
Material Science: T. Gillece, K. Vasserman, S. Ozkan, & R. McMullen
Formulations: N. Issa, C. Clarion, E. Zea, D. Kennedy & C. Musto
Global Skin Marketing: S. Thiewes
Hair Applications: E. Everaert & A. Pickett
Molecular Science: D. Petty & D. Jack
Scale up & Processing: M. Martinez & P. Rao
Consumer Science: C. Uzel, S. Cooper & G. Puccetti
Rheology / Analytical: L. Feeley & G. Cheng
NMR: A. Augatis, C. Leiba & B. Clark
Microbiology: D. Dennis
THANK YOU

Questions?

in-cosmetics
Hamburg, Germany 1-3 April 2014
visit us on stand 4F30
Imagine. Collaborate. Succeed
Disclaimer

The information contained in this presentation and the various products described are intended for use only by persons having technical skill and at their own discretion and risk after they have performed necessary technical investigations, tests and evaluations of the products and their uses. This material is for informational purposes only and describes the scientific support for the use of the products described herein as an ingredient in cosmetic products intended to enhance appearance and other cosmetic benefits or to enhance performance of an end product. Certain end uses of these products may be regulated pursuant to rules governing medical devices or other regulations governing drug uses. It is the purchaser’s responsibility to determine the applicability of such regulations to its products. While the information herein is believed to be reliable, we do not guarantee its accuracy and a purchaser must make its own determination of a product’s suitability for purchaser’s use, for the protection of the environment, and for the health and safety of its employees and the purchasers of its products.

Neither Ashland nor its affiliates shall be responsible for the use of this information, or of any product, method, formulation, or apparatus described in this brochure. Nothing herein waives any of Ashland’s or its affiliates’ conditions of sale, and no statement, information and data is to be taken as a guarantee, an express warranty, or an implied warranty of merchantability or fitness for a particular purpose, or representation, express or implied, for which Ashland and its affiliates assume legal responsibility. We also make no warranty against infringement of any patents by reason of purchaser’s use of any information, product, method or apparatus described in this presentation.

The testing information (the “Testing Information”) has been gratuitously provided by Ashland. The Testing Information is based on many factors beyond Ashland’s control, including but not limited to, the conditions prevailing when the testing was conducted, and in some cases, is based on data generated with development samples of the Active Ingredient. Although it is intended to be accurate, ASHLAND DISCLAIMS ANY AND ALL LIABILITY, EITHER EXPRESS OR IMPLIED. The Testing Information is confidential or proprietary to Ashland, and may not, except as provided below, be disclosed to any third party. You may not make commercial use of the Testing Information, or make claims with respect to your products based the Testing Information, without the written agreement with Ashland covering such use.

© Registered trademark, Ashland or its subsidiaries, registered in various countries
™ Trademark, Ashland or its subsidiaries, registered in various countries
* Trademark owned by a third party
© 2014, Ashland
ASHLAND

With good chemistry great things happen.