

Overcoming Challenges of Replacing APEs Within Cleaning Formulations with Tomadol[®] 902

Presented by:

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November 10, 2016



Why the Move from APEs?

Regulation is being driven by concerns over the effects of NPE exposure on the environment and on people

“...it was proved in *in-vitro* tests that nonylphenol has strong binding affinity to estrogen receptor and

strong estrogenic effects on fish.”

Draft Rpt on Test Results of Endocrine Disrupting Effects of Nonylphenol on Fish, OECD

“NPEs degrade relatively easily in the environment to form short-chained NPEs and (especially under anaerobic conditions) NP, which **are toxic to aquatic organisms.**”

Background Doc. On NP/NPEs. Ospar Commission

“... this report concludes that current environmental levels of alkylphenolic compounds are probably high enough to be affecting the hormonal control systems of some organisms. It is also possible that **human health could be being affected.**”

An Env. Ass. of Alkylphenol Ethoxylates and Alkylphenols. Friends of the Earth, Jan 95

“APEs have been shown to mimic estrogen and are **strongly suspected of causing endocrine disruption.** Both the nonylphenol and octylphenol forms have been found to cause breast cancer cells to multiply in the lab... All of this makes APEs a good thing to avoid.”

EWG's Healthy Child initiative website guidance

What Has Been the Response?

Many regions are restricting the use of nonylphenol ethoxylates (NPEs) through regulation

- Europe:** Regulated under REACH Annex XVII which limits use to very low use-levels in cleaning
- Canada:** Notification requirements for facilities using NPEs
- California:** Included NPEs in the Candidate List
- USA:** US EPA has issued new SNUR covering notification in use of NPEs for new uses and placed some NPs as reportable TRI chemicals

46. (a) Nonylphenol $C_9H_{19}(OH)C_{12}H_{25}$
(b) Nonylphenol ethoxylate $(C_2H_4O)_n C_{15}H_{29}O$

concentrations higher than 0,1 % by mass.

Shall not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0,1 % by mass for the following purposes:

- (1) industrial and institutional cleaning except:
 - controlled closed dry cleaning systems where the washing liquid is recycled or incinerated

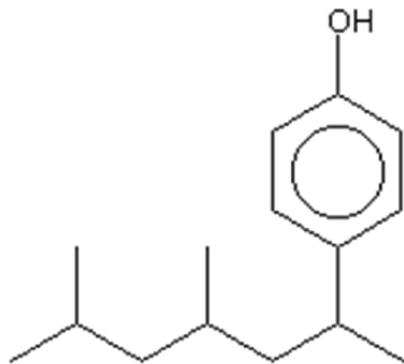
What Does This Mean for Formulators?

- Safeguard from future regulatory concerns
- Avoid risk of future consumer/worker backlash
- Position to meet environmental trends and international customer requirements
- **Improve formulation properties and performance by reformulating with (mostly) linear alcohol ethoxylates**

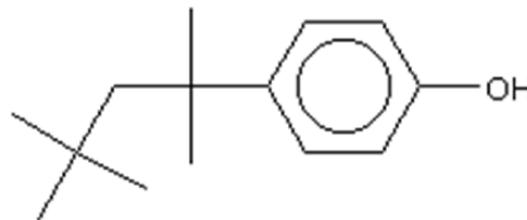
What are Your Options?

- Don't reformulate
 - Let's just wait and see what happens...
- Reformulate
 - Work from the ground up to develop a new formula that meets the current requirements yet does not contain APE
 - Select a single material that will come "close enough" in meeting requirements and may simply replace APE
 - Take the opportunity to use a high performance product that will improve your formula while lowering the cost

How are **Alkylphenol Ethoxylates** Different from **Linear Alcohol Ethoxylates**?



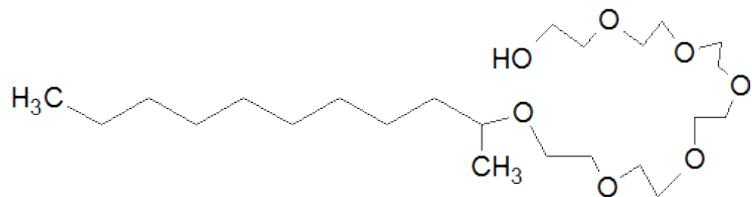
Nonylphenol



Octylphenol

Tomadol® Advantage:

15-20% Branching at α -position



Linear

Branched

Biodegradation

Liquidity

Solubility

Selecting an Ideal Candidate from HLB

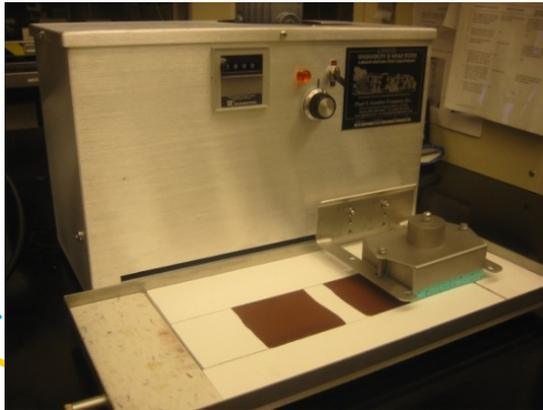
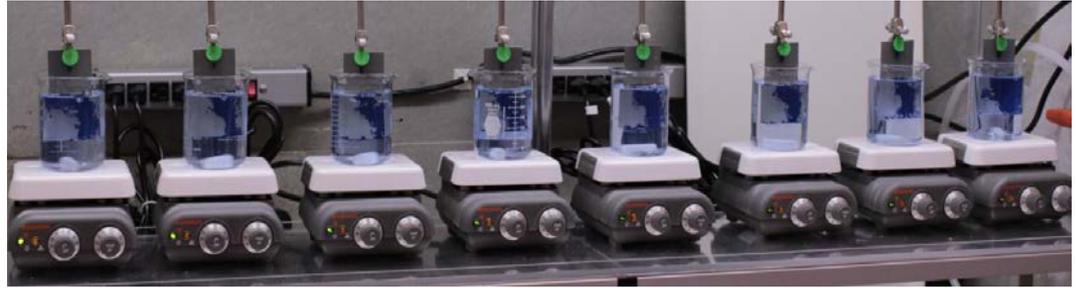
Property	NP-9	Tomadol 91-6	Tomadol 1-7	Tomadol 25-7
Structure	Nonylphenol, 9EO	C ₉ -C ₁₁ , 6EO	C ₁₁ , 7EO	C ₁₂ -C ₁₅ , 7EO
HLB	12.9	12.4	12.9	12.3
Cloudpoint (°C)	54	52	58	50
Critical Micelle Conc. (wt%)	0.006	0.025	0.010	0.001
EST at CMC (dyne/cm)	32	29	28	30

Performance Testing

Hard Surface

Immersion Degreasing

- Various soil compositions
- Various substrates
- Cleaning solution agitated at a constant rate
- Soil removal determined by image analysis



Gardner Scrub (ASTM 4488-A5, Modified)

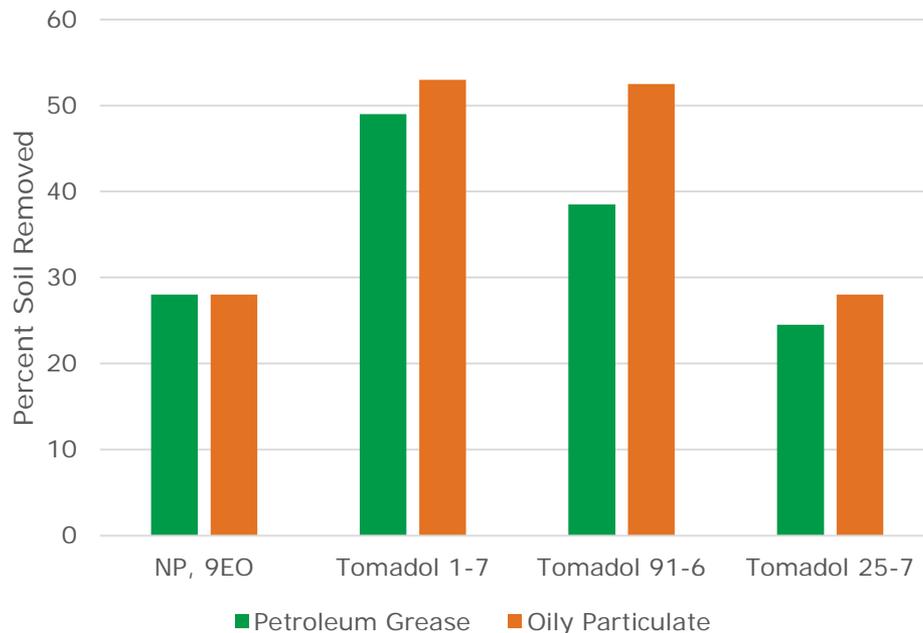
- Oily particulate soil or greasy food soil
- Various substrates
- Standard ASTM 4488-A5 procedure to clean
- Soil removal determined by reflectance or image analysis

Selecting an Ideal Candidate from HLB

Immersion Degreasing, Noted Soil on Stainless Steel

Component	Wt%
DI Water	96.0
Sodium Metasilicate (5H ₂ O)	1.0
Potassium Hydroxide (45%)	1.0
EDTA Solution (39%)	1.0
Surfactant Noted	1.0

Hard Surface Cleaning Performance



Selecting an Ideal Candidate from HLB

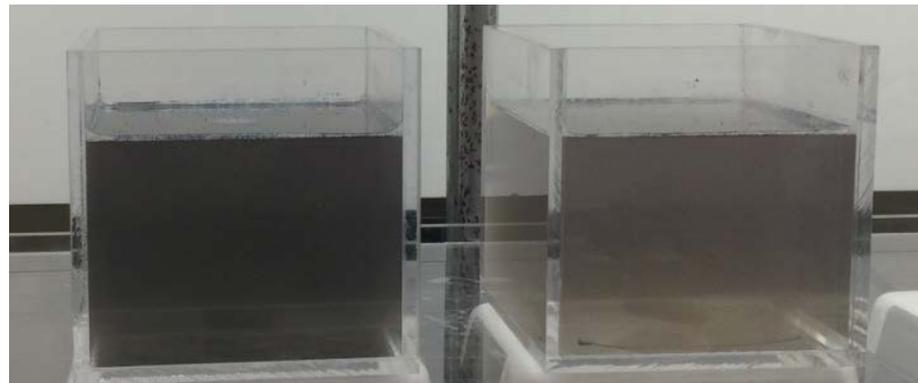
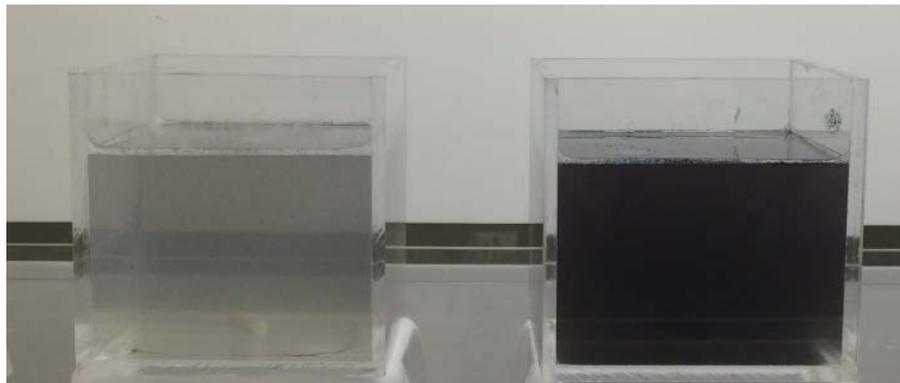
Emulsion Performance for Oily Particulate Soil

Nonylphenol, 9EO

Tomadol 91-6

Tomadol 1-7

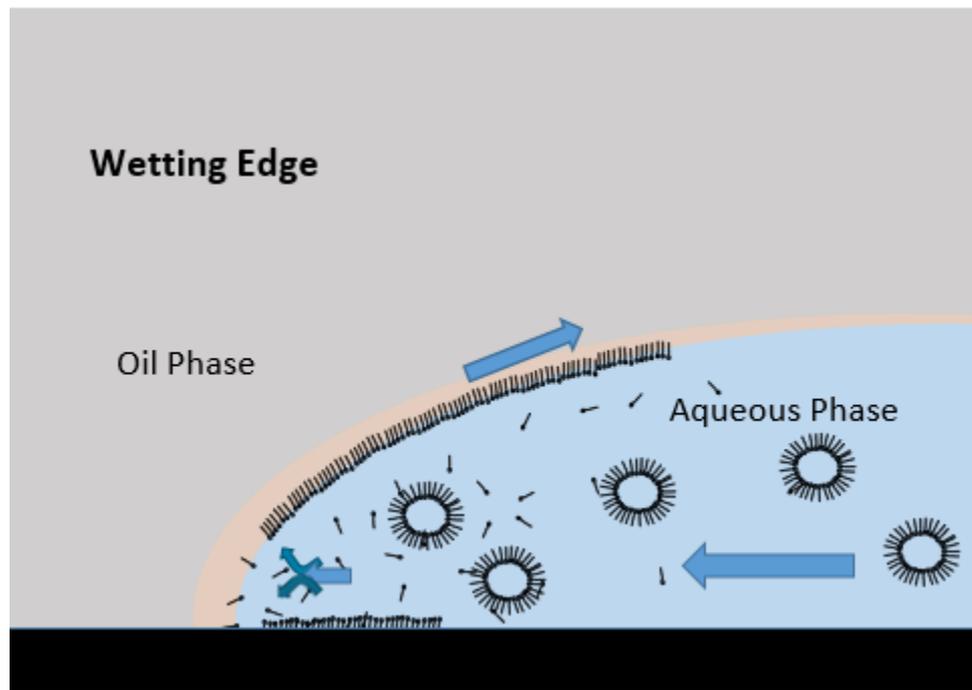
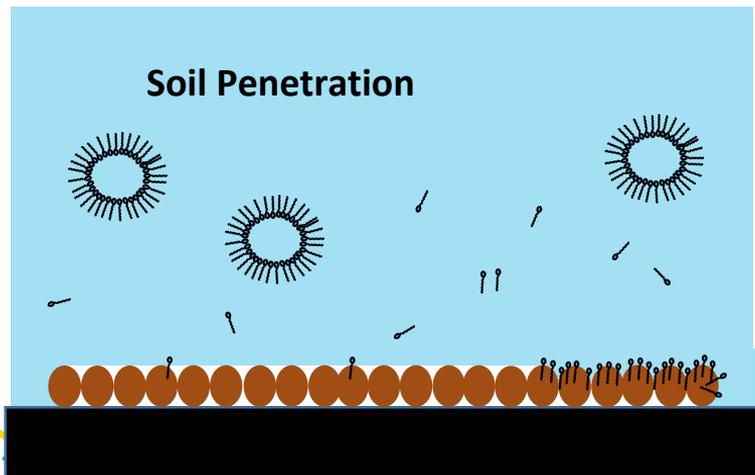
Tomadol 25-7



Hard Surface Cleaning Mechanisms

Functions of:

- Surface Tension Reduction
- Migration to Interface
- Critical Micelle Concentration
- Micelle Relaxation Time

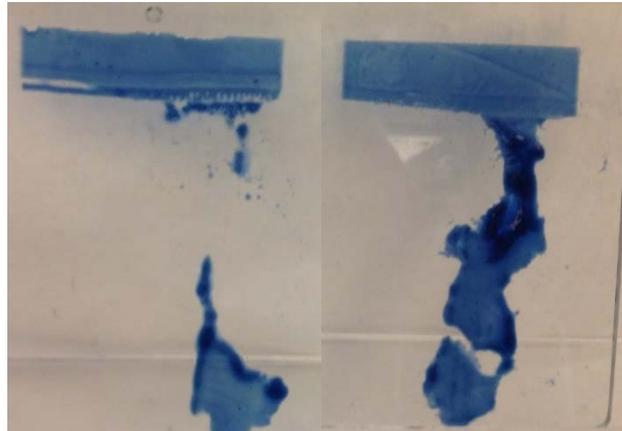


Looking More Closely at Tomadol 25-7

Immersion Degreasing; Petroleum Grease on Glass

Tomadol 25-7

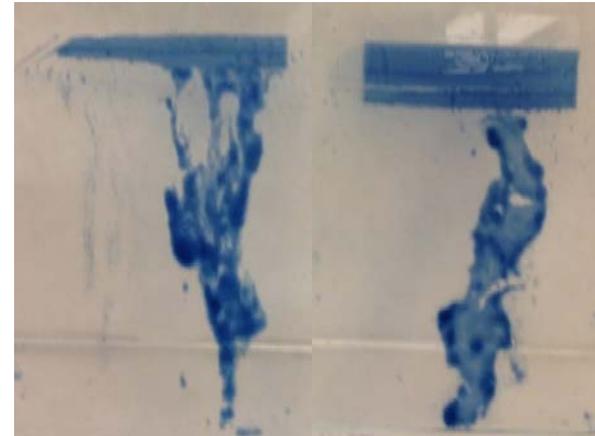
NP-9EO



1.0% Surfactant
2.5% Sodium Citrate
0.5% Sodium Carbonate
1.0% Tomamine Amphoteric 12

Tomadol 25-7

NP-9EO



1.0% Surfactant
2.0% KOH (45%)
1.0% Sodium Metasilicate
1.0% Tomamine Amphoteric 12

Performance Testing

Laundry

Tergotometer

- Various soil compositions
- Various cloth substrates
- Cleaning solution agitated at a constant rate and temperature
- Soil removal determined either by approach of reflectance to "ideal" or change in reflectance



Swatch Fabrics

- Cotton
- Cotton/Poly Blend
- Polyester
- Nylon

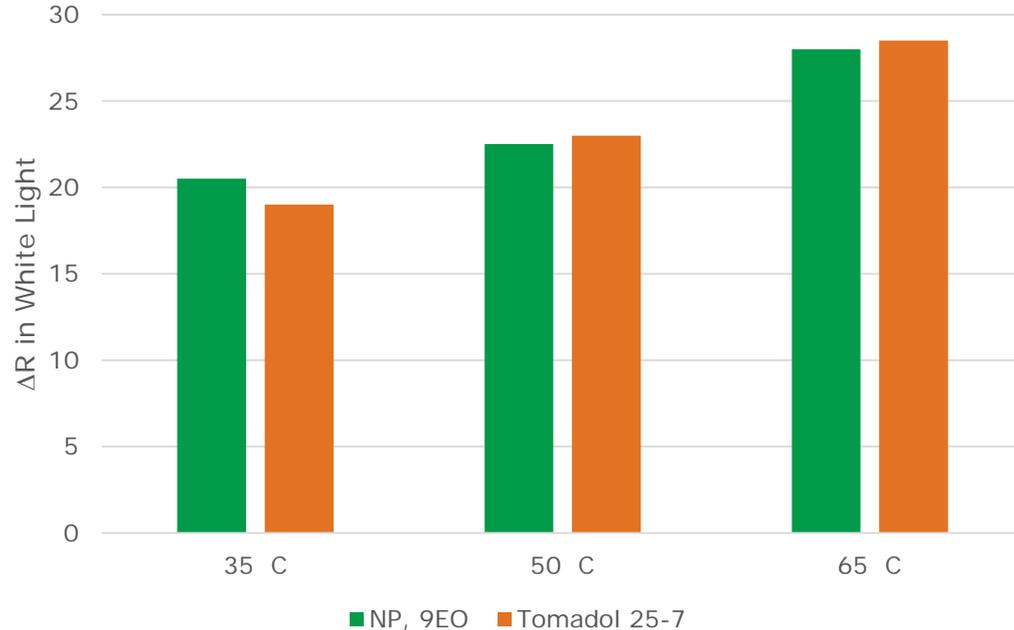
Swatch Soils

- Dust Sebum
- Used Motor Oil
- Ground in Clay
- Lanolin
- Blood/Milk/Ink
- Grass Stain
- Carbon Black/Olive Oil
- Lipstick

Selecting an Ideal Candidate from HLB

Conditions	
Surfactant	800ppm
Alkalinity (as Na ₂ O)	600ppm
Sodium Polyphosphate	300ppm
Water Hardness (as Ca ²⁺)	150ppm
Tergotometer	60rpm
Equal parts dust sebum and used motor oil on cotton	

Laundry Performance at Various Temperatures



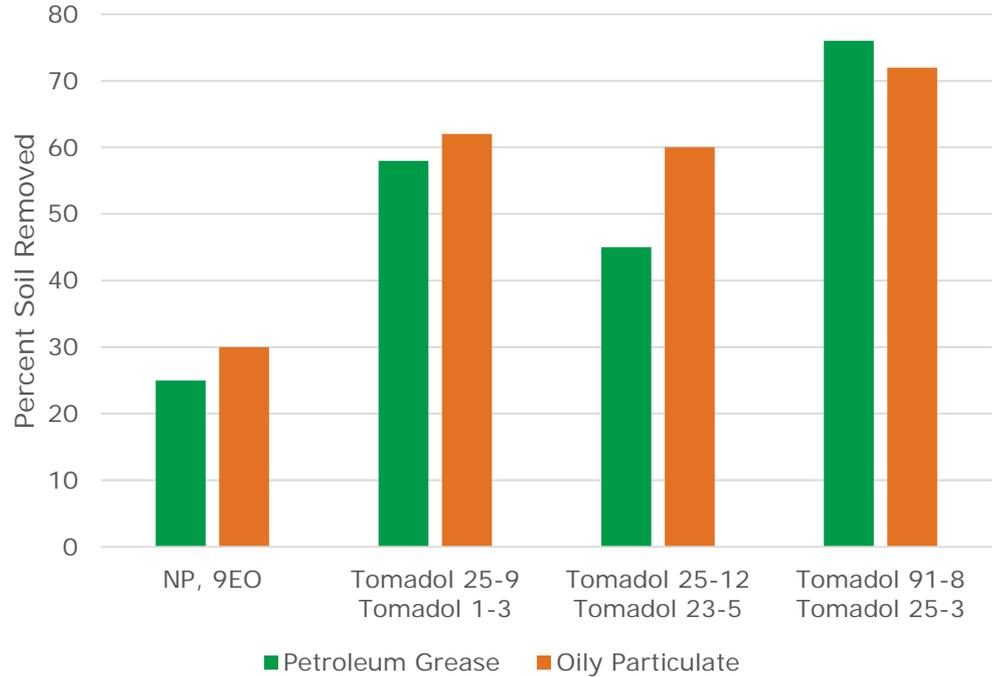
Candidates from Blending HLB

Property	NP-9	Tomadol 25-9 Tomadol 1-3 (90/10)	Tomadol 91-8 Tomadol 25-3 (85/15)	Tomadol 25-12 Tomadol 23-5 (65/35)
HLB	12.9	12.7	12.9	13.1
Cloudpoint (°C)	54	63	66	69
Critical Micelle Conc. (wt%)	0.006	0.002	0.022	0.001
EST at CMC (dyne/cm)	32	31	30	28

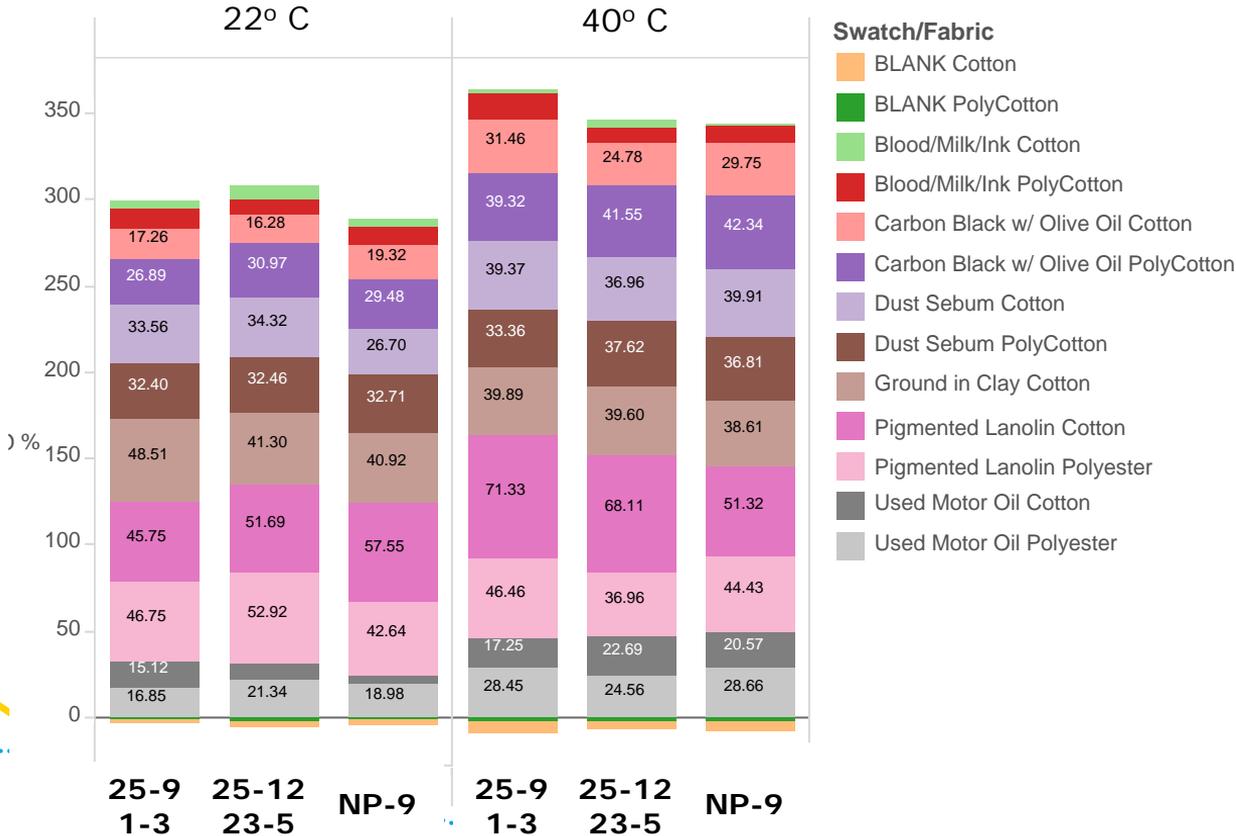
Selecting an Ideal Candidate from HLB

Component	Wt%
DI Water	96.0
Sodium Metasilicate (5H ₂ O)	1.0
Potassium Hydroxide (45%)	1.0
EDTA Solution (39%)	1.0
Surfactant Noted	1.0

Hard Surface Cleaning Performance



Selecting an Ideal Candidate from HLB

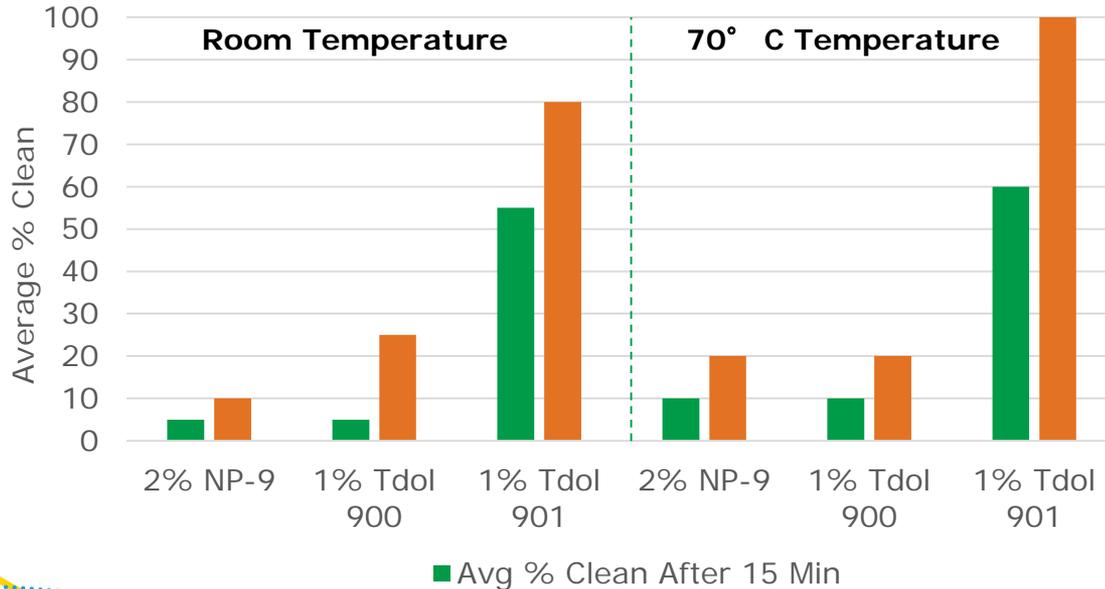


Conditions	
Surfactant	600ppm
Alkalinity (as Na ₂ O)	200ppm
Sodium Citrate	300ppm
Water Hardness (as Ca ²⁺)	150ppm
Tergotometer	60rpm

Tomadol 901 vs NPE Surfactants

Tomadol 901 can outperform Tomadol 900 and NP-9

Immersion degreasing test results of stainless steel slides soiled with transportation soil at room temperature and 70° C, Tomadol 901, 900, and NP-9



Tomadol 901 Surfactant is able to provide superior cleaning in some formulations where Tomadol 900 is unable to be effective

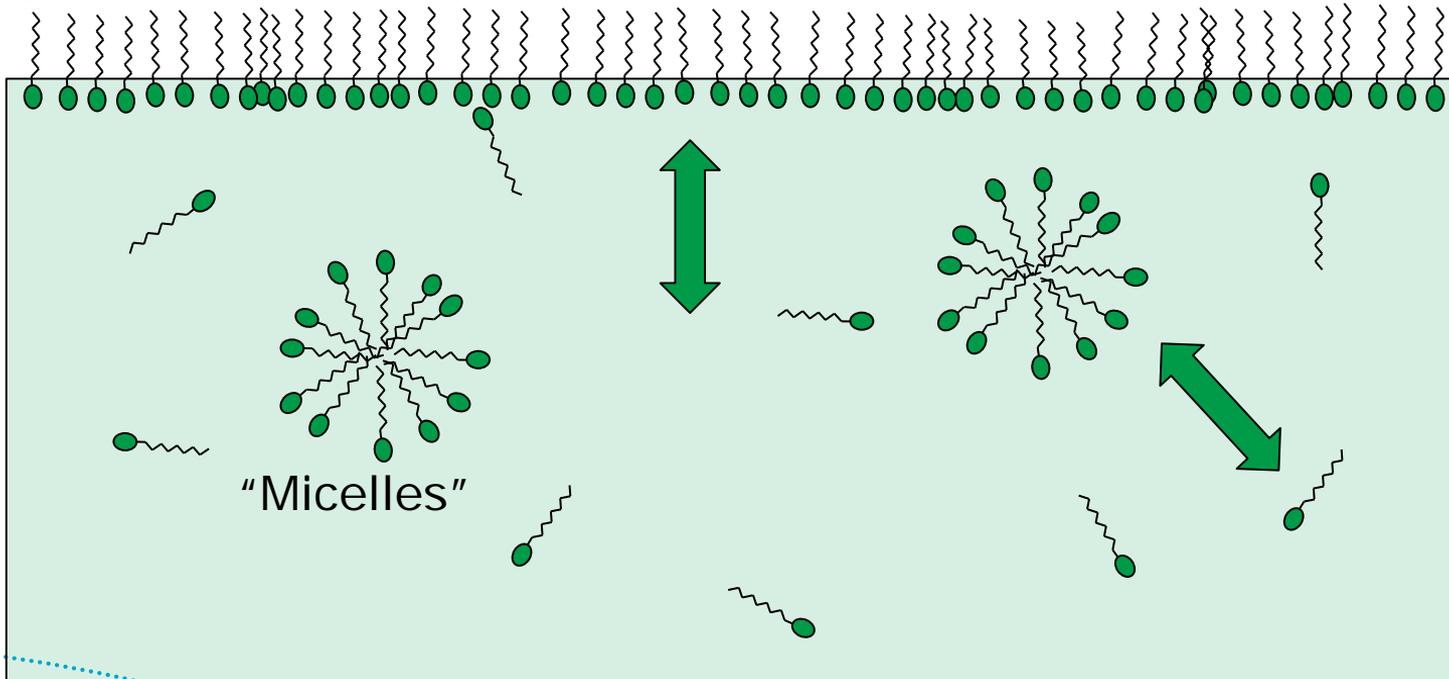
Formulation

Components	Wt%
Water	q.s.
Sodium Metasilicate, Penta	1.0
Potassium Hydroxide	0.5
EDTA (39%)	1.0
Surfactant (as stated)	X

Surfactant Behavior

Traditional View

"Surface Excess"



Tomadol® 902 Surfactant

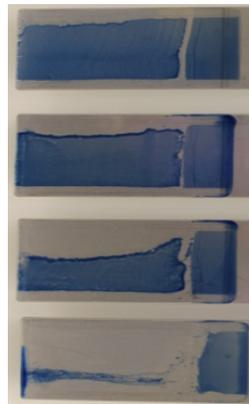
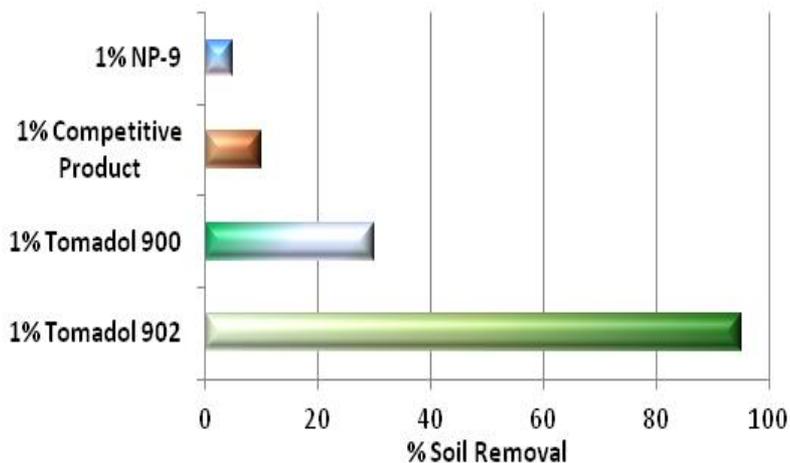
The Next Generation in High Performance Nonionics

- Improved speed of cleaning
- Superior degreasing performance
- Reduced cost-in-use
- Favorable environmental profile

Tomadol[®] 902 Surfactant

Improved speed of cleaning

Lithium Grease and Motor Oil on Stainless Steel



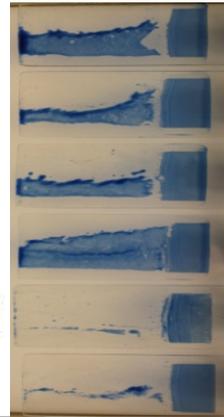
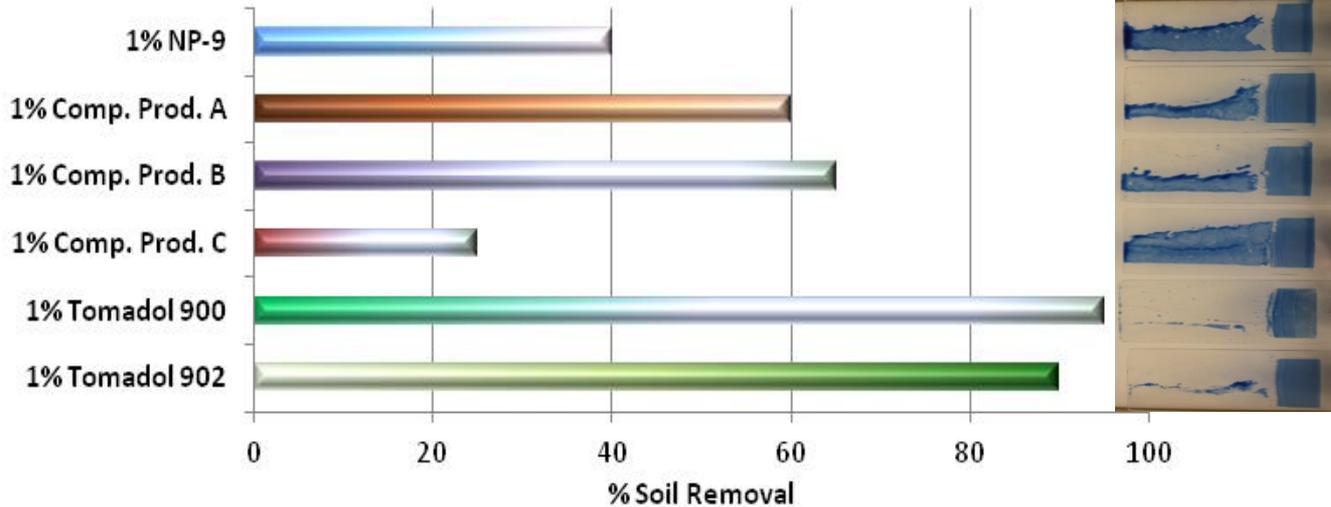
Tomadol 902 Surfactant
Increases the speed of soil removal on stainless steel, achieving faster cleaning after six minutes of immersion

Test Formulations: 1% as supplied of either: NP-9, Competitive Product, Tomadol 900, or Tomadol 902, 1% Sodium Metasilicate, 1% KOH (45% aqueous).
Procedure: Stirred under constant conditions at room temperature for 6 minutes

Tomadol[®] 902 Surfactant

Superior cleaning performance

Lithium Grease/Motor Oil on Glass



Tomadol 902 Surfactant
Improves overall cleaning outcomes relative to competitive benchmarks on glass.

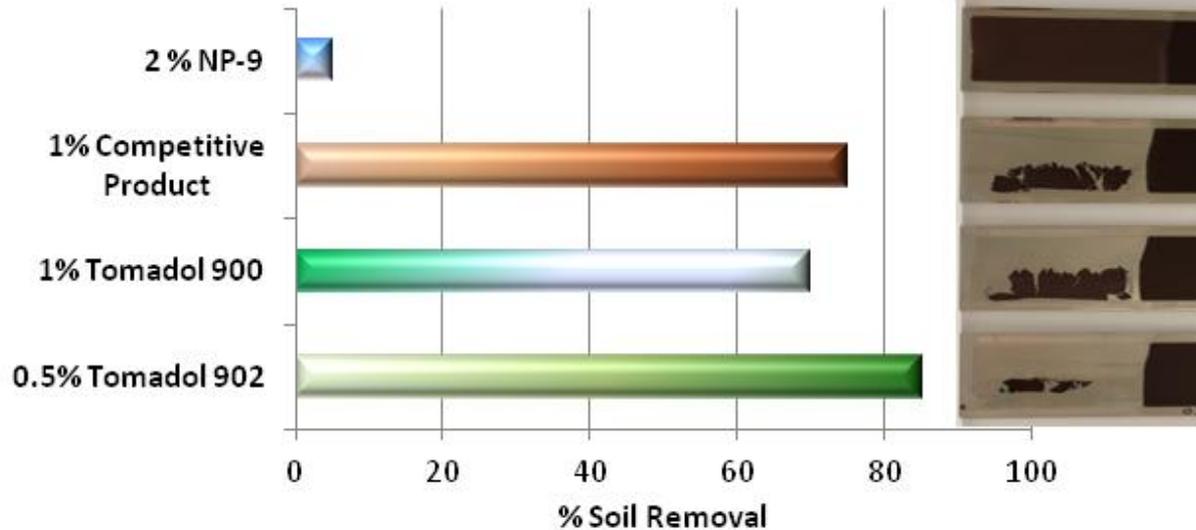
In repeated testing, Tomadol 902 performs better than Tomadol 900 on a glass substrate

Test Formulations: 1% as supplied of either: NP-9; Competitive Product A, B, or C; Tomadol 900; or Tomadol 902, 1% Sodium Metasilicate, 1% KOH (45% aqueous).
Procedure: Glass slides, soiled with tenacious Li grease/motor oil. Stirred under constant conditions at room temperature for 6 minutes

Tomadol[®] 902 Surfactant

Reduce Cost-In-Use

Transportation Soil on Stainless Steel Plates



Tomadol 902 Surfactant at half the level removes the same or even more soil than other NPE replacement surfactants

Test Formulations: Surfactant [2% NP-9, or 1% Competitive Product, or 1% Tomadol 900, or 0.5% Tomadol 902], 1% Sodium Metasilicate, 1% KOH (45% aqueous), DI water.

Procedure: Stainless Steel plates heavily soiled with Transportation Soil. Stirred under constant conditions at room temperature for 6 minutes

Tomadol® 902 Surfactant

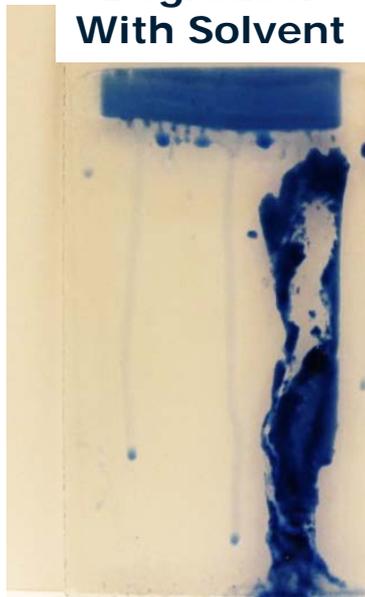
Superior Cleaning with Nearly zero VOC and No Solvents

Degreaser WITH Solvent Formulation

(1.6% VOC)

- 2.5% Sodium Citrate
- 0.5% Sodium Carbonate
- 0.65% Competitive product
- 1.6% Ethylene Glycol Monobutyl Ether

Degreaser With Solvent



Degreaser Without Solvent



Degreaser WITHOUT Solvent Formulation

(0.35% VOC)

- 2.5% Sodium Citrate
- 0.5% Sodium Carbonate
- 1.3% Tomadol 902

Procedure: Glass slides soiled with tenacious Li grease/motor oil. Stirred under constant conditions at room temperature

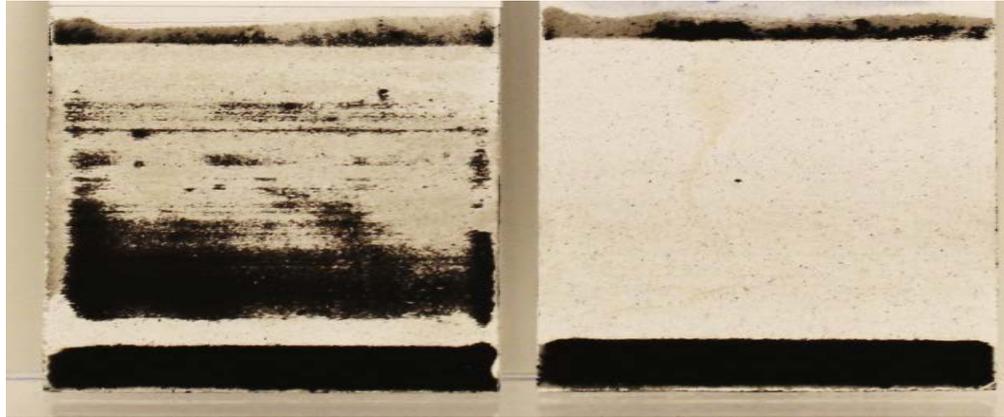
Tomadol[®] 902 Surfactant

Effective for cleaning of vinyl COMPOSITE tiles

Tiles scrubbed with Gardner Scrub Tester for 10 scrub cycles using modified ASTM 4488-95 A5

Competitive Product

Tomadol 902



Tomadol 902 Surfactant

Is effective at cleaning via the ASTM 4488 "Gardner Scrub" method as well!

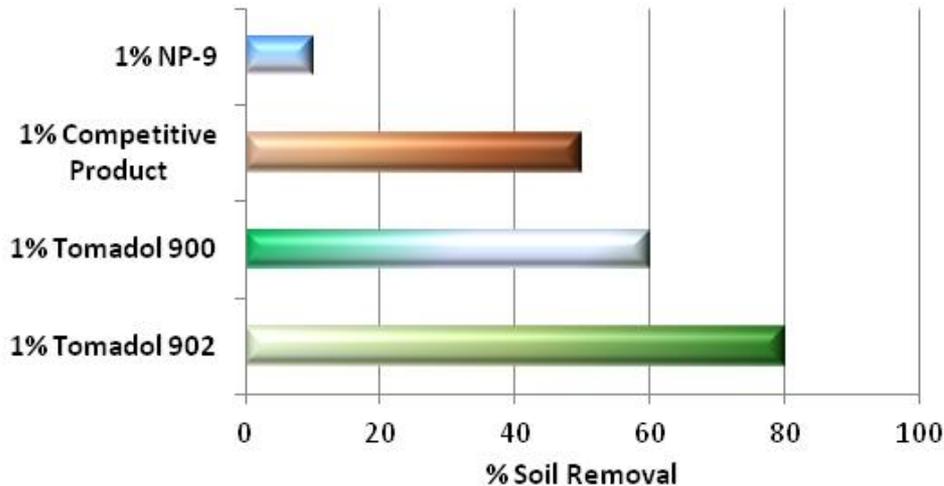
Test Formulations: 1% Tomadol 902 vs. 1% Competitive product (as supplied), 1% Sodium metasilicate, 1% KOH (45%).

Procedure: Vinyl coated tiles with baked on oily particulate soil.

Tomadol® 902 Surfactant

Effective in both low and high temperature cleaning

Lithium Grease/Motor Oil on Stainless Steel at 4°C



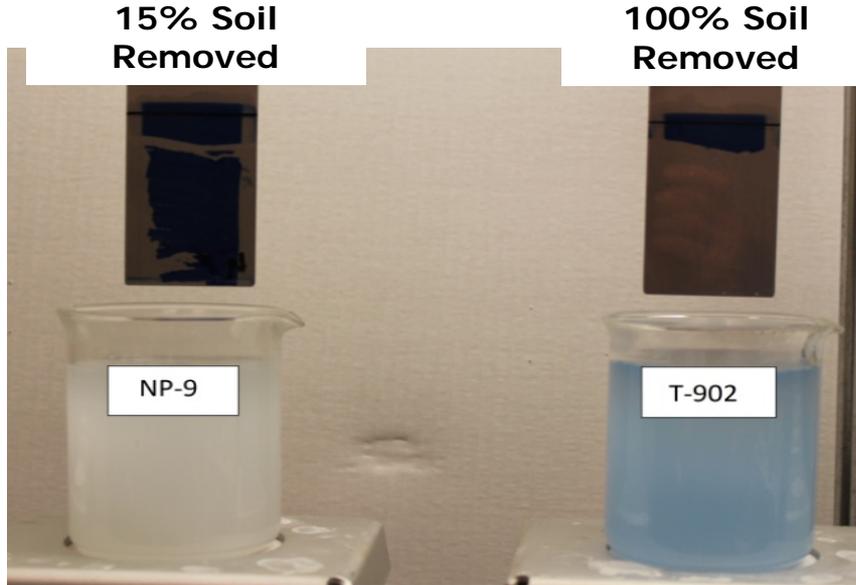
Tomadol 902 Surfactant

Cleaned better at low temperatures, generally achieving **20% better performance** than the nearest benchmark in repeated testing

Test Formulations: 1% as supplied of either: NP-9, Competitive Product, Tomadol 900, or Tomadol 902, 1% Sodium Metasilicate, 1% KOH (45% aqueous).
Procedure: Soiled plates stirred at 4°C for 20 minutes. Stainless steel plates soiled with tenacious Li grease/motor oil.

Tomadol® 902 Surfactant

Effective in both low and high temperature cleaning



Tomadol 902 Surfactant

At half the level of the NP-9 showed significantly better cleaning

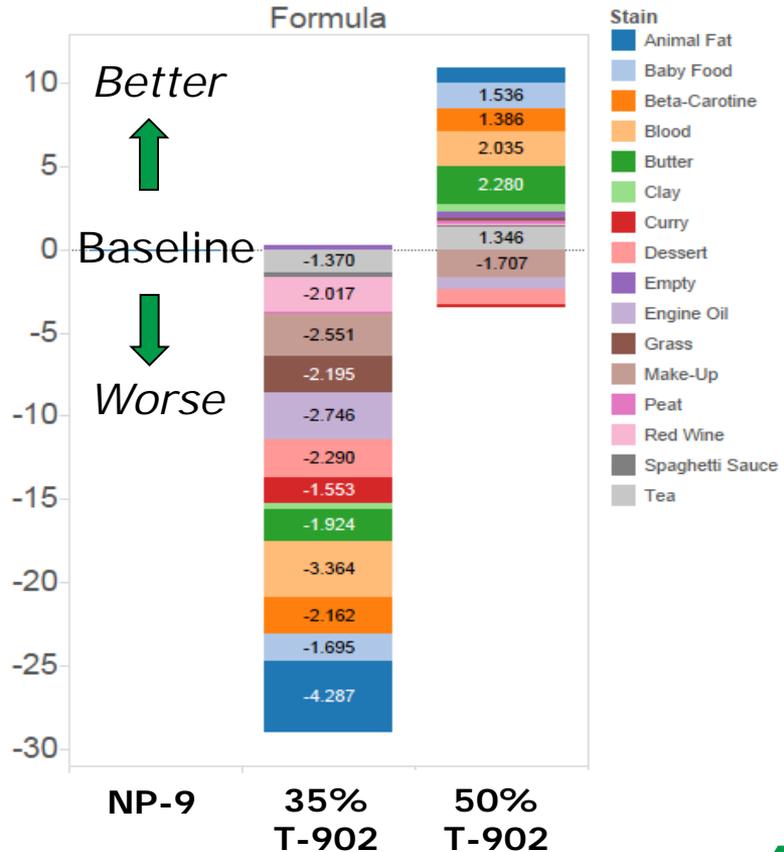
Test Formulations: 1% NP-9 vs 0.5% Tomadol 902 (as supplied), 1% Sodium metasilicate, 1% Versene 100 (39% Na₄EDTA), 1% KOH (45%).

Procedure: Soiled plates lowered into stirred formulations heated at 50°C. Stainless steel plates soiled with tenacious Li grease/motor oil.

Tomadol 902 Replaces APE in Laundry

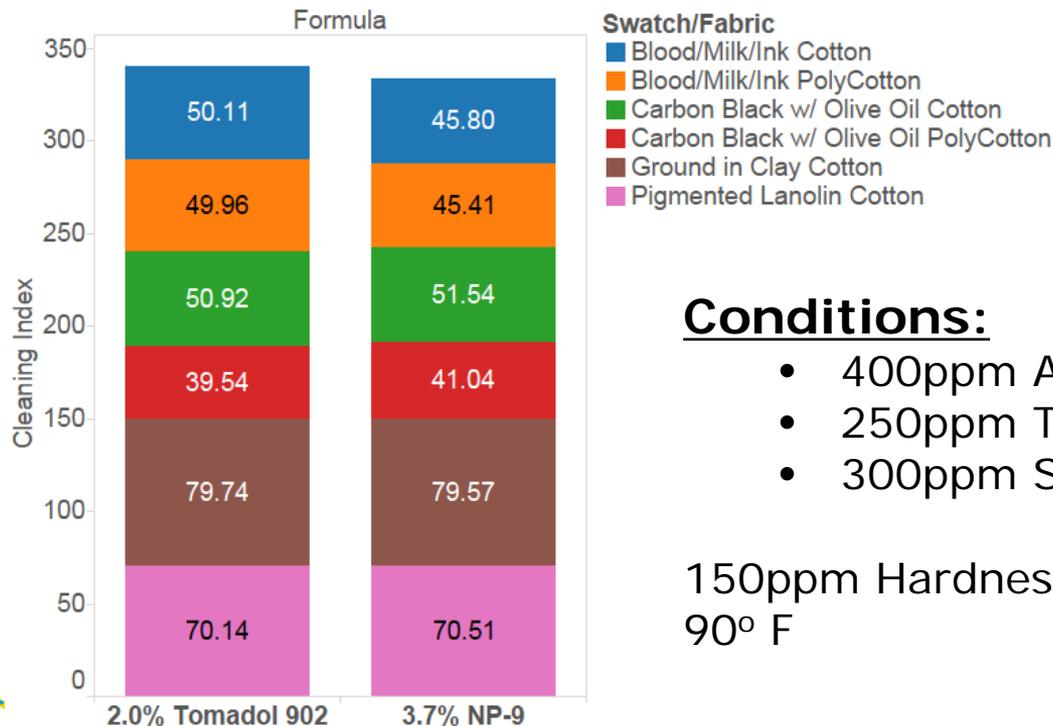
A proprietary formula was provided to our Applications Testing laboratory to determine if **lowering the amount of nonionic surfactant** was possible with **Tomadol 902**.

The results indicated that it is!



Tomadol 902 Replaces APE in Laundry

We compared our own formulas using 2% Na-DDBSA and surfactant as shown...



Conditions:

- 400ppm Alkalinity
- 250ppm Tetrapotassium Pyrophosphate
- 300ppm Surfactant

150ppm Hardness (as CaCO₃)
90° F

Tomadol 902 – the solution to your APE replacement challenges

- Increased regulation is being driven by concerns over the effects of APE exposure on the environment and on people
- Formulators have 2 choices – “wait and see” or work through reformulation challenges
- Tomadol 902 can replace APEs, as well as improve the overall performance of your formulation

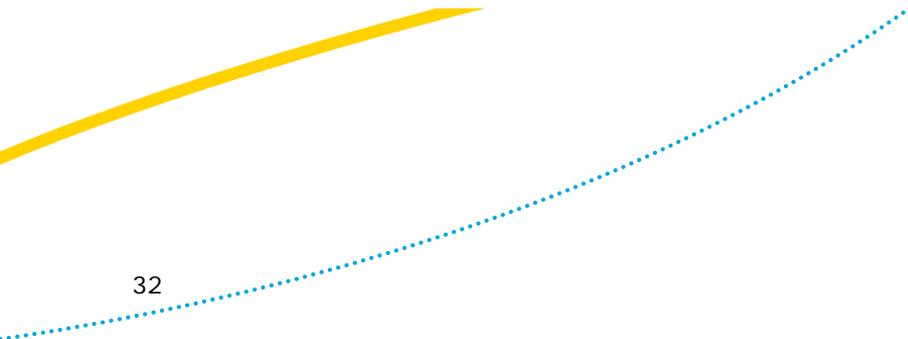


For More Information, Please Visit:

airproducts.com/cleaning

Join us **January 26, 2017** for our next webinar:

Simplifying Formulation in Hard Surface Cleaners



Contact Us

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