Simplifying Formulation in Hard Surface Cleaners

January 26, 2017

Presented by: Eric “Rick” Theiner

EVONIK
POWER TO CREATE

Presentation Outline

I. Ask the Background Questions

- What are you cleaning?
- Why are you cleaning?

II. Answer the Questions

- Select the necessary materials
- Establish necessary levels

III. Look for Opportunities

- Synergies/incompatibilities
- Multi-functional materials

IV. Finalize the Formula

- Ensure initial stability
- Ensure performance
- Ensure shelf stability

EVONIK
POWER TO CREATE

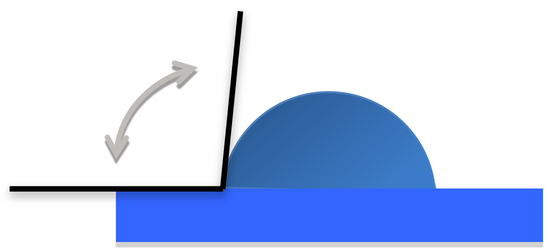
Background Questions

Understand the conditions, the surface, and the soil of the target application!

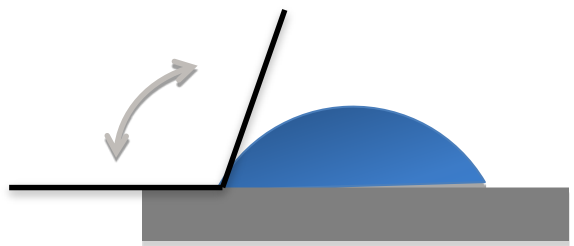
EVONIK
POWER TO CREATE

What are You Cleaning?
Examples of Substrates

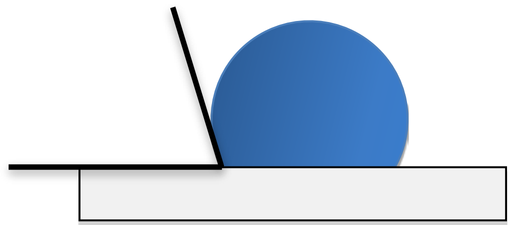
- **Glass**
  - – Medium energy surface
  - – Non-porous and generally uniform



- **Metal**
  - – High energy surface
  - – Electron surface density (likes positive charges)
  - – Can be reactive!



- **Plastic**
  - – Med to very low energy surface
  - – May be porous and/or have micro-scratches



Why Are You Cleaning?
Examples of Soils

- **Organic Soils**
  - Lipids/fats, proteins, and carbohydrates
  - Noncharged; tend to like low energy surfaces
- **Scale**
  - Mineral complex from water salts
  - May tightly hold to metal surfaces; has limited affinity for glass or plastic
- **Complex Soil**
  - Mineral complex suspended in organic soil
  - “Soap scum” is a perfect example
- **Biofilm**
  - Planktonic bacteria aggregating under a polysaccharide cover
  - Bacteria uses biopolymers to “glue” themselves to a surface
  - More of a concern for industrial applications, particularly F&B

What Response Do You Want?

- **Surfactant Action**
  - Wetting
  - Emulsification
- **Alkali**
  - Lipid soil removal
  - Dispersion of soils
  - Lower surfactant CMC
  - Damage to surface?
- **Chelants/Sequestrants**
  - Soften water
  - Remove mineral soils
  - Some protein soil removal
- **Solvents**
  - Penetration
  - Dispersion
  - Emulsification
- **Performance Additives**
  - Enzymes
  - Oxidizers
  - Surface modifiers
- **Aesthetic Additives**
  - Perfume/fragrance
  - Dye/colorant

Typical Formulation Components

Type	Purpose	Considerations	Examples
Alkaline Builders	-Provide alkalinity -Soften water -Disperse soils -Lower CMC of surfactants	-These will lower the cloudpoint -pH>9 will break down ester linkages	NaOH/KOH EDTA, etc. Silicates Carbonates
Builders	-Soften water -Suspend soils	-Generally require alkaline pH to soften water -May require a specific pH range for solubility -Generally lowers cloudpoint	Polymers Phosphates
Solvents	-Disperse and loosen soils -May stabilize formula -(Lower CMC of surfactants)	-Higher concentrations necessary for performance (>2%) -Hydrophobic solvents must be emulsified	EB, DB, etc. Hydrophobic solvents
Surfactants	-Wet surfaces -Lift soils -Suspend/emulsify soils	-Consider target substrate and soil -Consider specific performance benefit -Note how they interact with other formula components	Surfactants
Coupling Agents	-Stabilize formula -May be co-surfactant	-May introduce foaming -Some have limited utility beyond coupling -Choice can be formula dependant	Amphoterics SXS (Solvents)
Additives – Performance	-Enzymes -Oxidizers -Anti-redeposition agents	-Enzymes must be stabilized -Enzymes and Oxidizers require particular pH -Anti-redep agents tend to lower cloud point	Polymers Bleaches Enzymes Optical Brighteners
Additives - Appearance	-Fragrance -Dye	-Dyes generally have no impact on performance -Fragrances always require emulsification	

Physico-Chemical Reactions

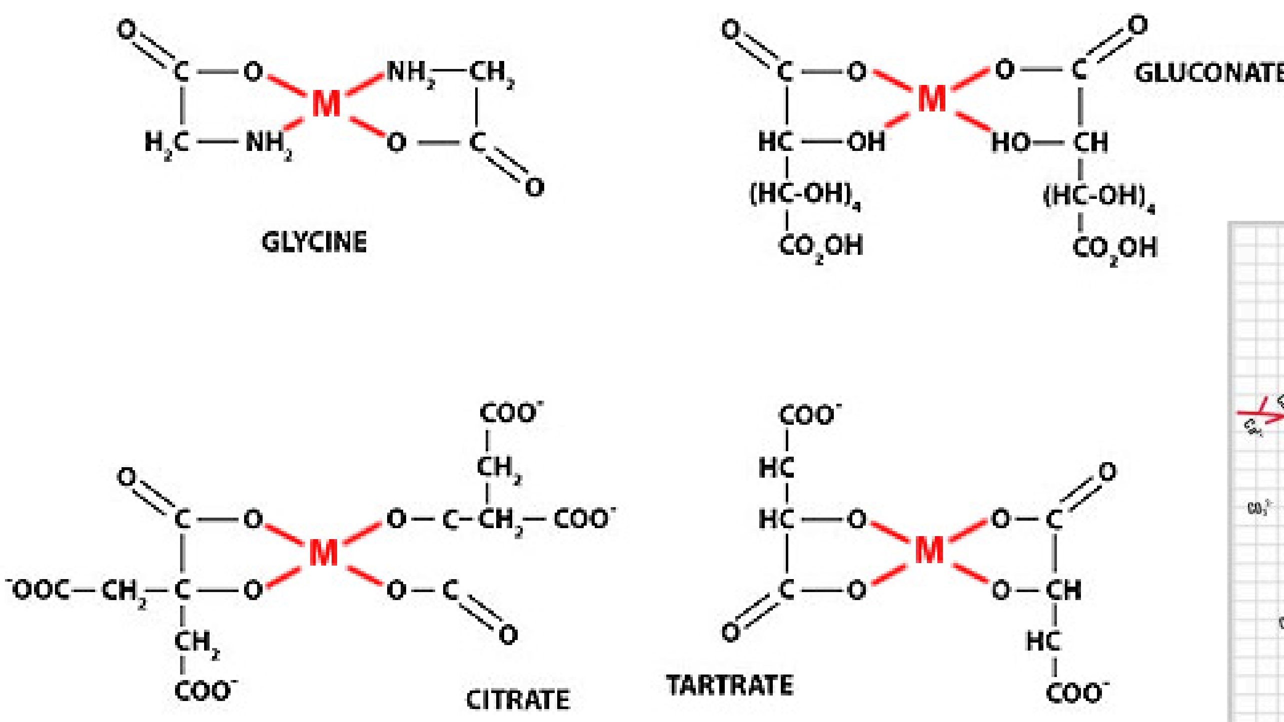
- **Wetting**
  - Responsible for water getting between soils and substrates.
  - Often called the “peel-up” effect.
- **Deflocculation**
  - Performed action of alkali, silicates and agitation.
  - Bulky solids are broken into smaller pieces and easily removed.
- **Suspension**
  - Detergents, alkalies, and silicates hold particles in suspension to prevent redeposition and easier removal.
- **Dissolution**
  - Water soluble soils such as sugars and starches are removed by water; some compounds aid in this process.
- **Emulsification**
  - Fats and oils are broken into small globules which are suspended in the washing solution.
- **Neutralization**
  - Much of soil is acidic and alkaline compounds removes it by altering its properties

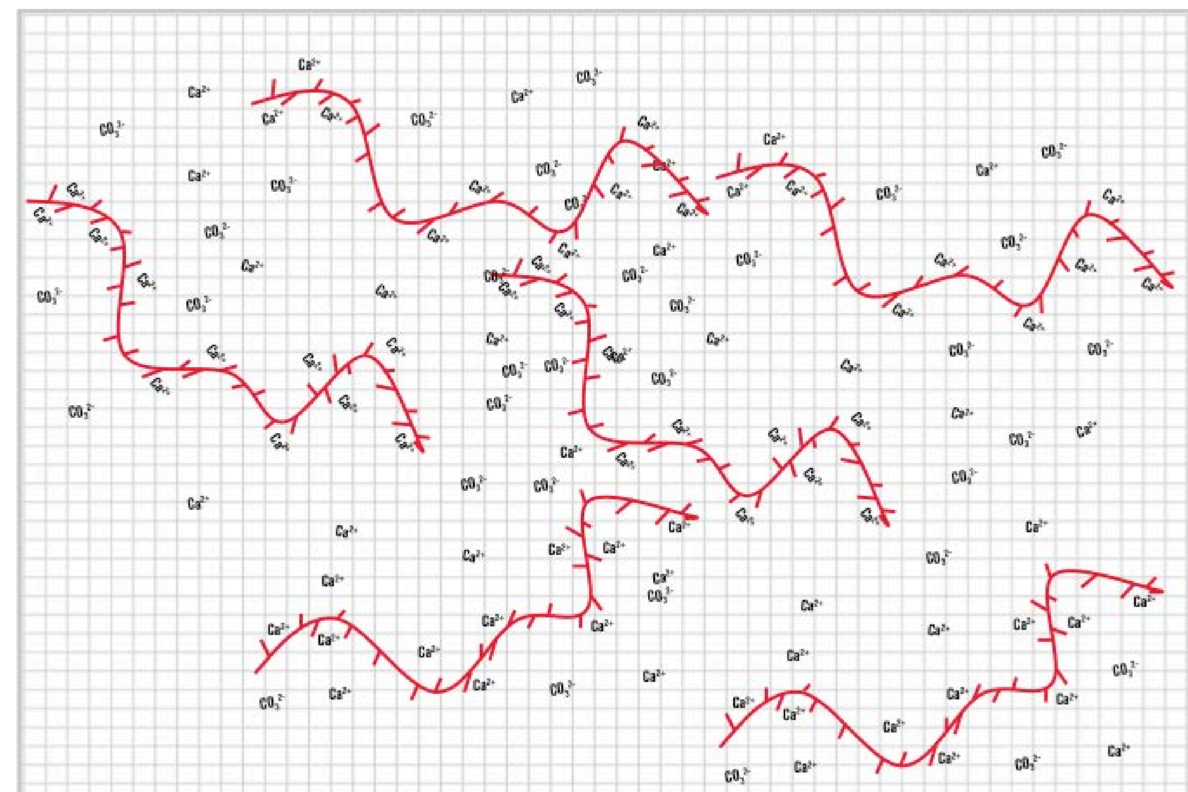
EVONIK POWER TO CREATE

Common Alkaline Builders

- **Strong Bases**
  - Primarily NaOH and KOH
- **Silicates**
  - Combination of alkaline (Na_2O or K_2O) and silicate (SiO_2) radicals
  - Provide alkalinity while also aiding in surface activity and soil suspension
- **Sodium Carbonate/Soda Ash**
  - Will raise the pH, but not a good source of active alkalinity
- **Phosphates (or not)**
- **Chelants**
  - Nitrogenous chelants provide alkalinity because of how they are neutralized
  - Enough to raise the pH above 10, but need a buffer to support them

Chelating Agents





This effect requires deprotonation!!
(pay attention to pK_a and pH)

EVONIK
POWER TO CREATE

Polymers
Many polymers… many reasons

- **Variances**
  - Types (Polyacrylic, copolymers of acrylic/maleic, nonionic)
  - Hydrophobicity
  - Molecular weight
- **Uses**
  - Thickening
  - Thixotropic impact/"cling"
  - Protein dispersion
- **Considerations**
  - Viscosity effects may be unintentional
  - Solubility often linked to pH

EVONIK POWER TO CREATE

RTU or Dilutable?
Impact of materials is concentration dependent!

- **Surfactants**
  - Bare minimum is the CMC, in reality 10x CMC is necessary in a light duty cleaner
  - Don’t forget that CMC changes with other factors
- **Alkalinity**
  - pH is necessary for chelating agents to work properly
  - Soils, especially food soils, will consume alkalinity
- **Chelation Capacity**
  - Must chelate water hardness from dilution
  - Are mineral soils going to be cleaned?

Optimizing for Cost and Performance

Getting the most bang for your buck!

Are We Using Materials Efficiently and Correctly?
If you use something the wrong way, why bother at all?

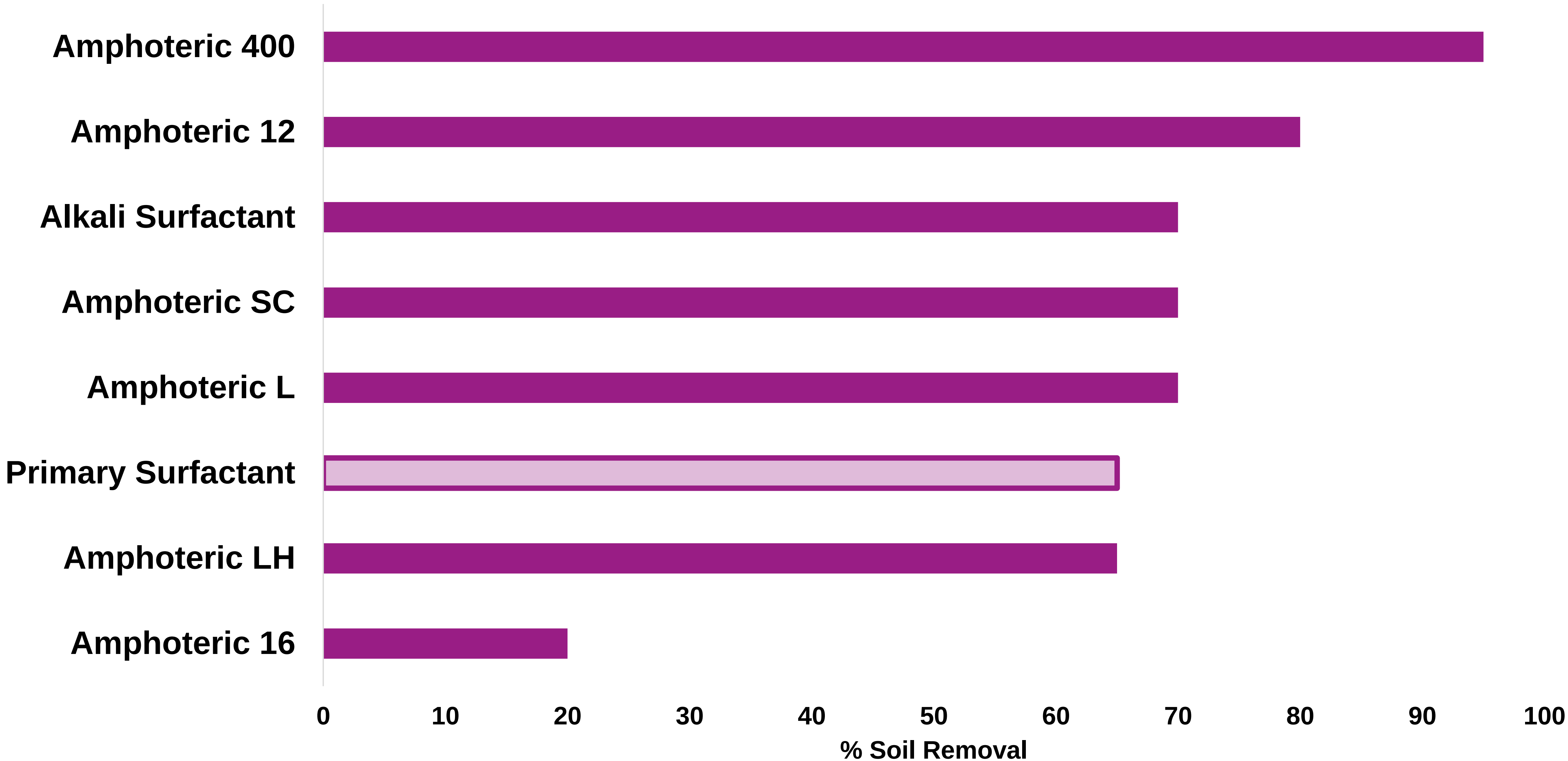
- **Surfactants**
  - Bare minimum is the CMC, in reality 10x CMC is necessary in a light duty cleaner
  - Don’t forget that CMC changes with other factors
- **Alkalinity**
  - pH is necessary for chelating agents to work properly
  - Soils, especially food soils, will consume alkalinity
- **Chelation Capacity**
  - Must chelate water hardness from dilution
  - Are mineral soils going to be cleaned?
- **Coupling Agents**
  - Using too much can inhibit surfactant effectiveness at lower temperatures
  - Are you using enough to maintain shelf stability?
- **Performance Additives**
  - Enzymes: Are they stable?
  - Bleach: Is there enough activity/concentration at use to matter?
- **Polymers**
  - Do they need to be neutralized to function?
  - Are you using too much (and leaving surface residue)?

Where Can We Combine Functions?
A lot of materials can serve double-duty!

- **Coupling Agents:** Co-surfactants, primary surfactants, foam modifiers
- **Alkaline Builders:** Caustic is cheap, but silicates are effective!
- **Chelating Agents:** Another alkaline material
- **Solvents:** Rheology modifier
- **Surfactants:** Rheology modifier
- **Solvents:** Fragrance!

Coupling Agents: Alkaline Systems

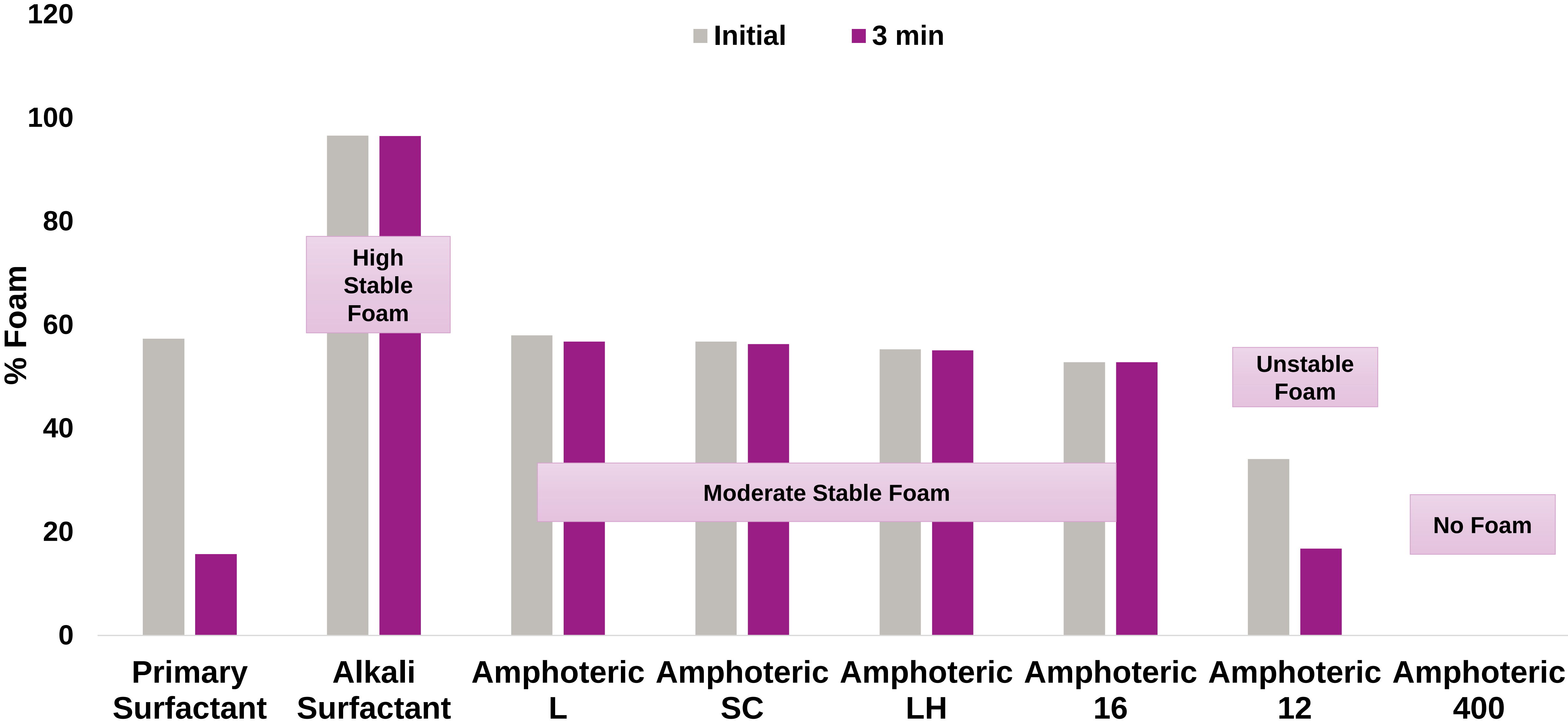
Immersion Degreasing Test of Transportation Soil on Stainless Steel Slides, pH14



Formula = 94.5% Water, 2% KOH (45%), 0.5% Kasil 6, 1% Baypure CX100, 1%Tomadol 1-73B, 3% Amphoteric
Note: Primary Surfactant is with 4% Tomadol 1-73B and no replacing 3% Amphoteric

High Throughput Air Sparge Test

High Foaming Cationic Surfactant



EVONIK
POWER TO CREATE

Protocols in Formulation

How do we pull it all together?

Order of Addition

Order of addition (generally):

1. Anything dry (start with the least soluble)
2. Liquid builders (go from inorganic to organic) (although sparingly soluble polymers wait)
3. Hydrophilic solvents
4. Coupling agents
5. Surfactants (put sparingly soluble polymers in after surfactants)
6. Hydrophobic solvents
7. Performance additives
8. Fragrance and Dye

And always ensure the solution is homogenous (and, hopefully, clear) prior to the next step

But what if there are problems?

EVONIK
POWER TO CREATE

Problems in Addition

And potential solutions (no pun intended!)

1. **Anything dry (start with the least soluble) – Doesn't dissolve**
   - Are you beyond the limit of solubility at that temp?
   - Have you lowered the pH of a silicate solution to below 10.5?
   - Will adjusting pH improve solubility? Will partial neutralization?
   - Are you adding more water bearing materials? Those can go here.
2. **Liquid builders (go from inorganic to organic) – Solution turns cloudy or materials precipitate**
   - Are polymers neutralized? If not, put them in after step 4.
   - Have you overloaded the system with sodium?
   - Have you brought a silicate solution pH to below 10.5?
   - Is this really because of the second step?
3. **Hydrophilic solvents – Solution turns cloudy**
   - Solvent not compatible with this level of builder; move in order of addition

EVONIK
POWER TO CREATE

Problems in Addition con’t
And potential solutions (no pun intended!)

4. **Coupling agents – Solution turns cloudy**
   - What is the counterion of the coupling agent? Sodium excess?
   - Is the coupling agent compatible with that level of builder or alkalinity? Ensure it’s the right coupling agent for this job.
   - Could the cloudiness be due to foam? Turn off the mixer and watch.
5. **Surfactants (put sparingly soluble polymers in after surfactants) – Solution turns cloudy**
   - Surfactant compatible with existing level of builder? Add coupling agent or lower builders.
   - Surfactant soluble at existing pH level? Check surfactant in that pH solution; check TDS.
   - Surfactant too hydrophobic for existing system? Add higher HLB surfactant or coupling agent.
6. **Hydrophobic Solvents – Solution turns cloudy**
   - Surfactant not solubilizing solvent. Add more surfactant, add more hydrophilic solvent, or convert to a two-part formula.

Two Phase Formulas
For when no one wants to play nice

Part I	Part II
1. Water	1. Hydrophobic Material
2. Anything dry	2. Surfactant
3. Liquid builders	3. (Maybe) Coupling agents
4. (Maybe) Coupling Agents or (Maybe) Performance additives	4. (Maybe) Performance additives

Combine

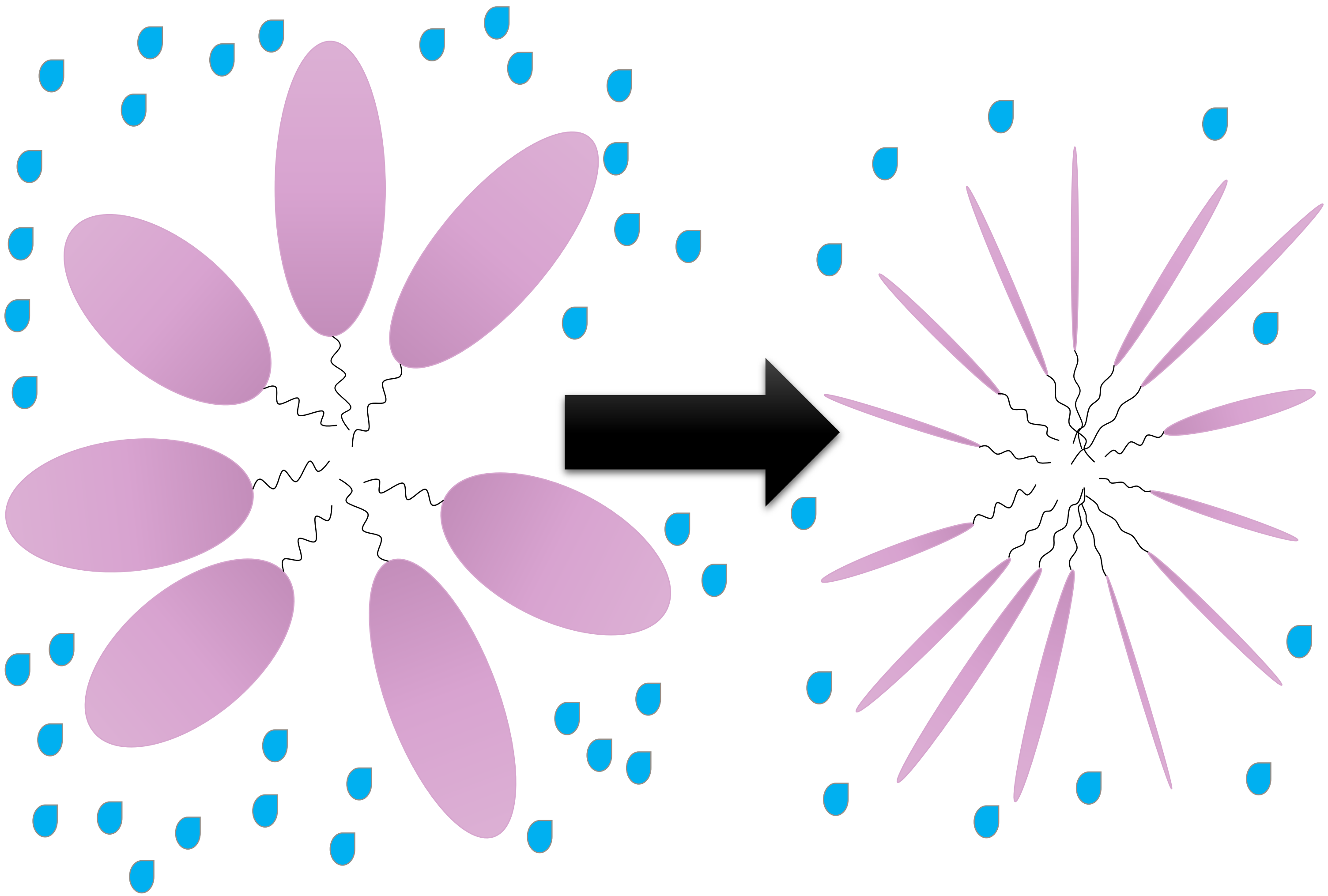
1. Slowly add Part I to Part II while stirring
2. Continue even if the system turns a little cloudy; the emulsion may reform
3. If the solution clouds, it is likely pointless to continue trying to fix the system from this point…go back to start

The Two Biggest Reasons for Problems…

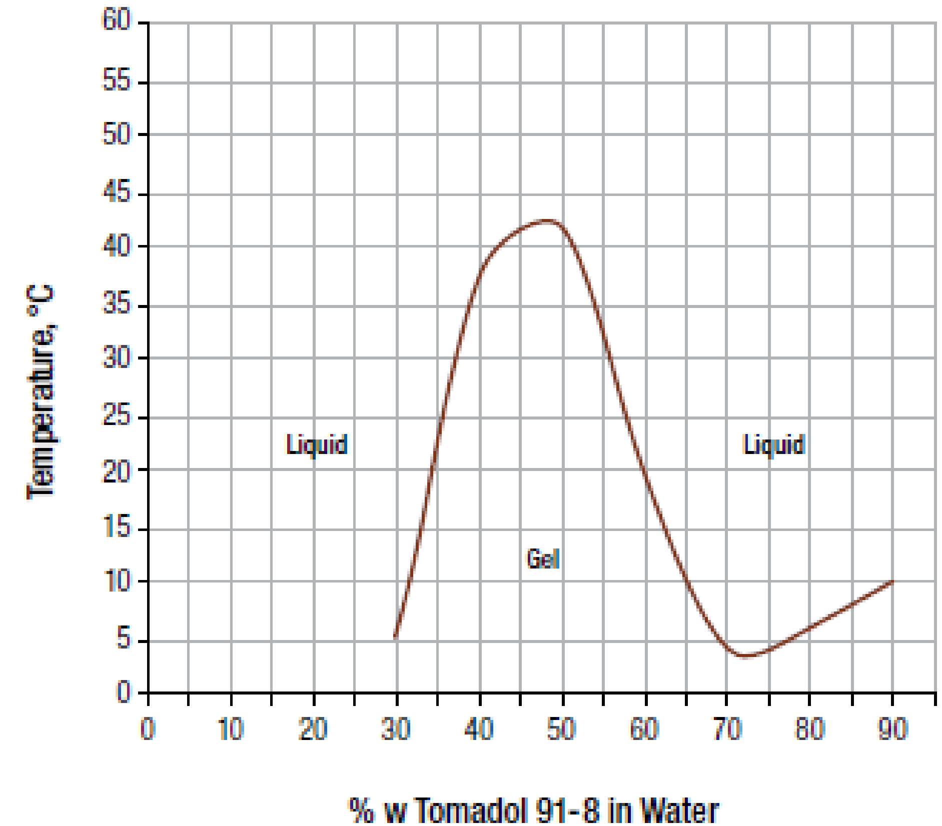
1. **Water Scarcity**
   - These materials are attaching themselves to the water molecules in order to dissolve. If there's not enough water to go around, then there will be no dissolution!

2. **Insolubility**
   - Some materials will not interact with water molecules to begin with. These hydrophobic materials must be made compatible with the aqueous environment.

Water Scarcity Impact
(Nonionic surfactants as an example)



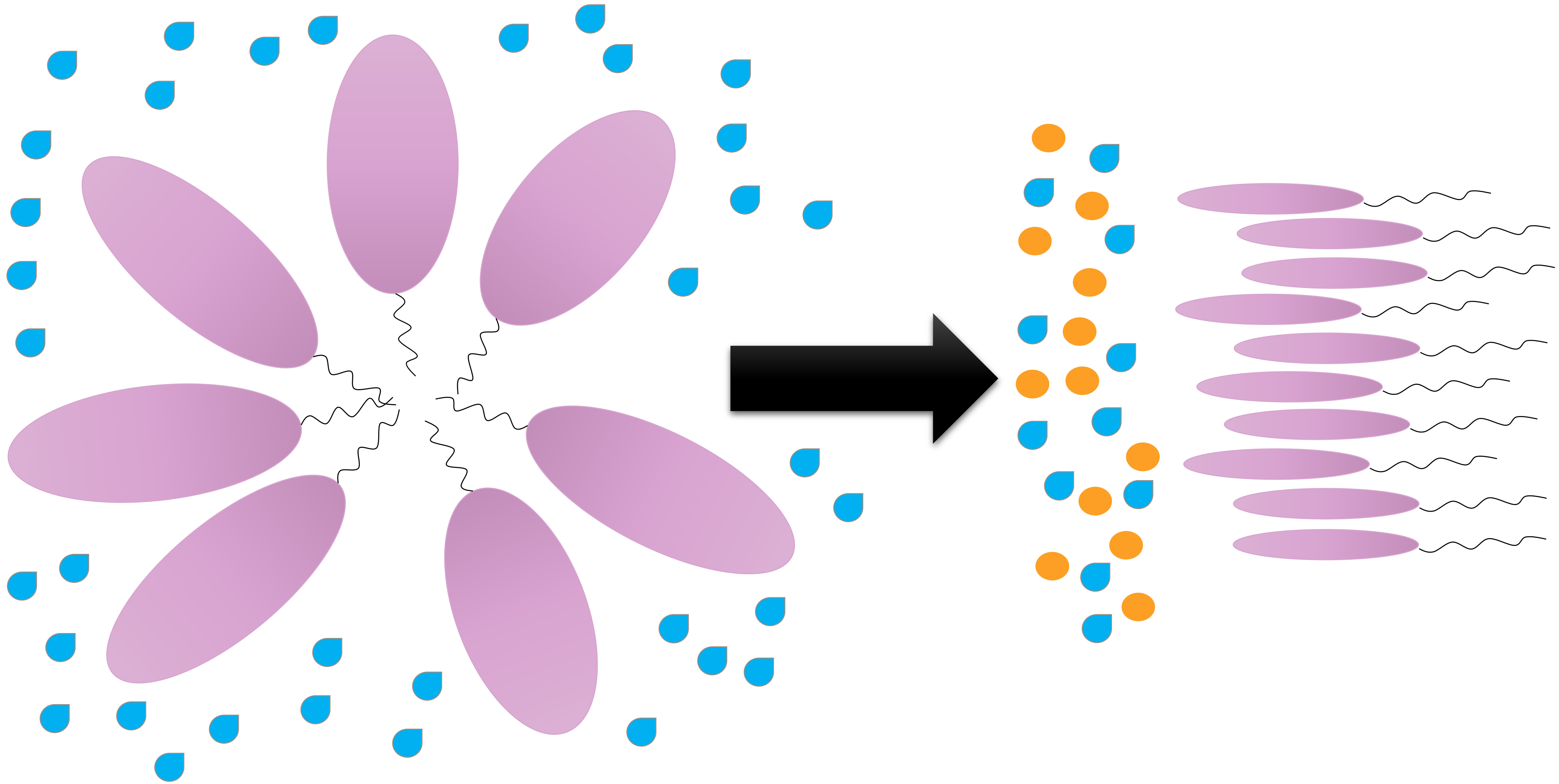
Gel Curve for Tomadol 91-8 Surfactant



As water molecules disappear, chains fight for remaining molecules and create a gel phase in the solution

EVONIK POWER TO CREATE

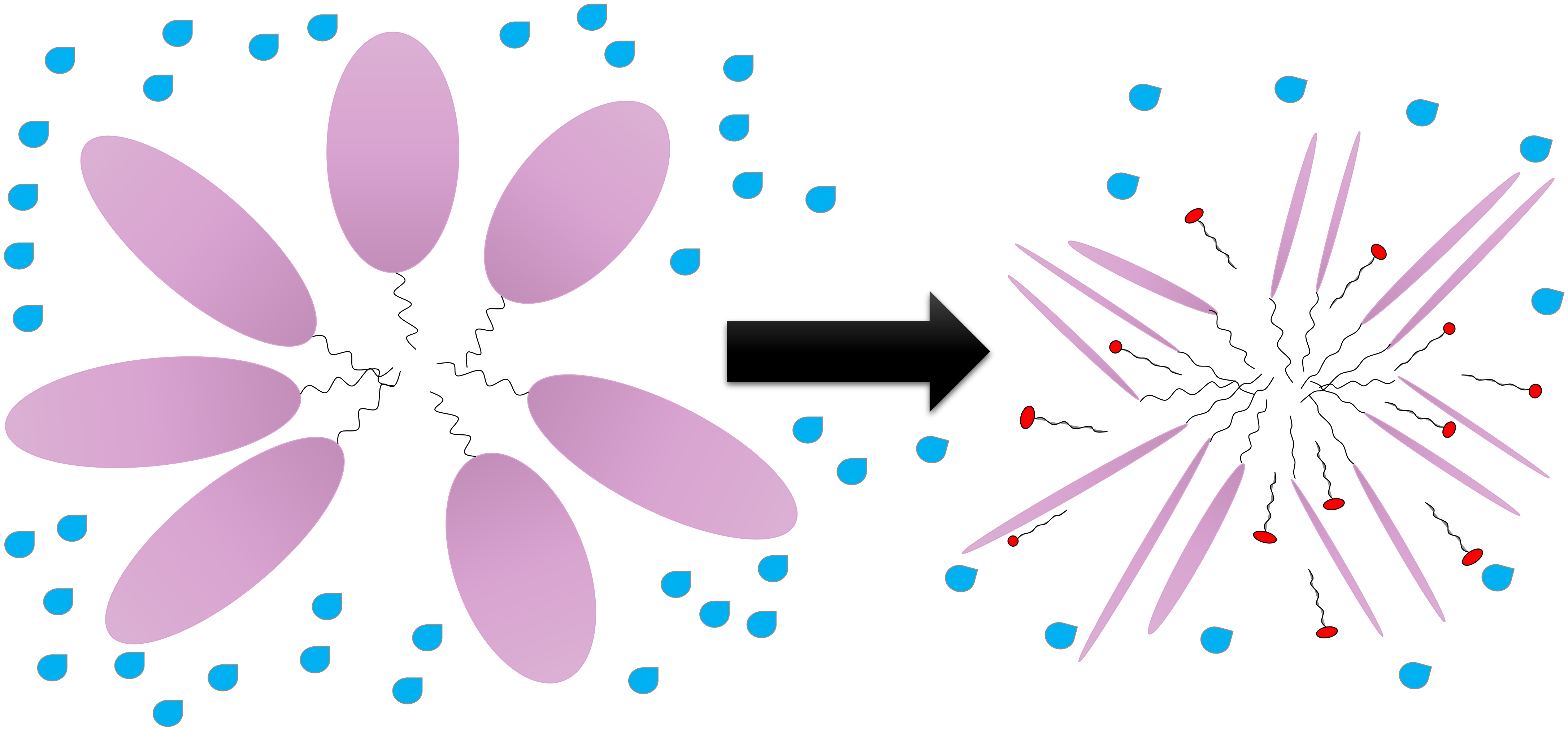
Water Scarcity Impact
(Nonionic surfactants with alkaline salts as an example)



Alternatively, when high alkalinity levels are present in the solution, the water molecules associate more closely with them, rather than surfactant hydrophiles

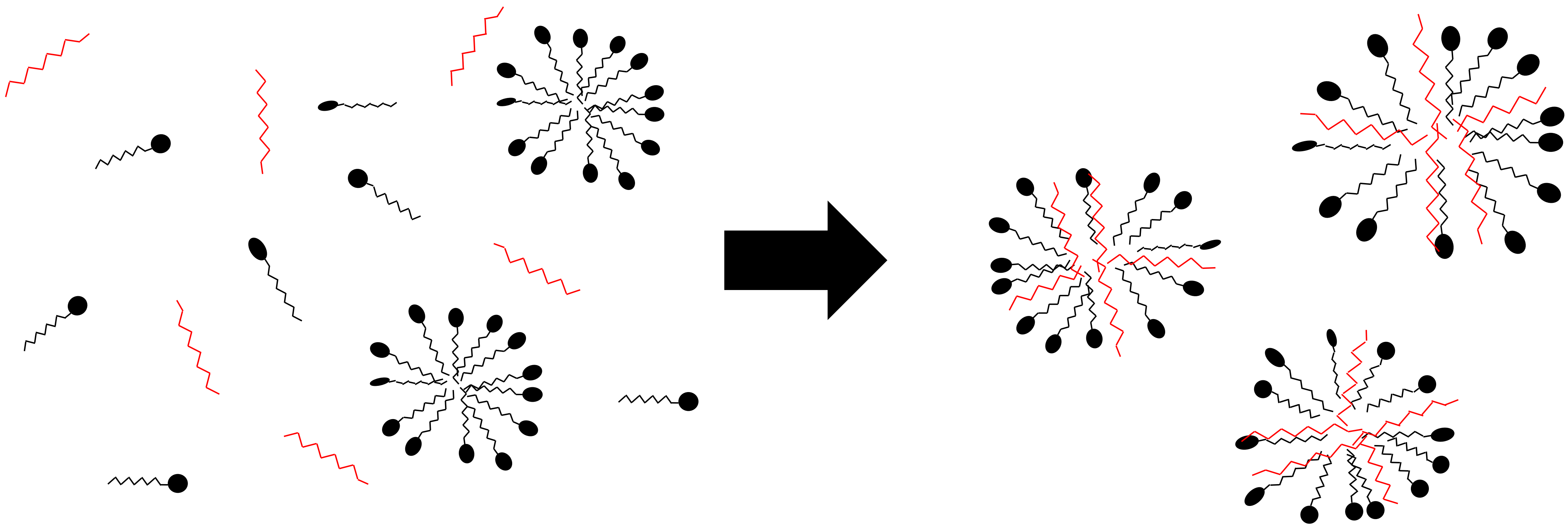
EVONIK
POWER TO CREATE

Water Scarcity Impact
(Nonionic surfactants with alkaline salts as an example)



A Coupling Agent is designed to actively break up the surfactant association that leads to the crystallization and resulting insolubility of surfactants

Insolubility
(This is actually a bit more straight forward…)



Insoluble hydrocarbons are taken up during micelle assembly to be incorporated with the surfactant hydrophobe

Remember "like dissolves like?"

-Consider hydrophobe size/source

-Consider Packing Factor and Net Average Curvature

-But remember that those are not absolutes in performance

EVONIK POWER TO CREATE

Examination of the Final Formula

Does it work?

EVONIK
POWER TO CREATE

The Standard Stability Tests…

- Freeze/Thaw 3x
- 4^{o} C (1 – 6 month)
- 50 or 60^{o} C (1 – 4 weeks)

Do You Have Suitable Chelation Capacity?

If you have a concentrated formula intended to be diluted, then it is vital that you ensure that the formula can handle dilution from hard water.

If you have a formula that is intended to penetrate and remove mineral scale, then this test will allow you to compare your performance against existing benchmarks.

- Make a stock solution of Na_2CO_3
- Add the sample detergent in the proper amount
- Titrate with a standard CaCl solution
- A hazy endpoint indicates that you have over-run your chelation capacity
- You can now back calculate the equivalent hardness that the formula could handle
- ***NOTE:*** *This test becomes more accurate the slower you run it*

EVONIK POWER TO CREATE

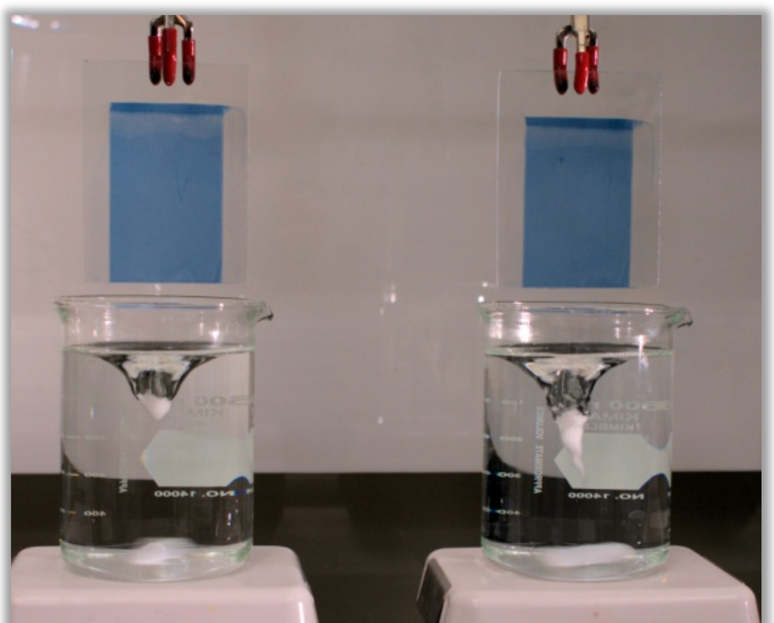
Examining Cleaning Performance

Two semi-quick, semi-standardized methods

- **Immersion Degreasing**
  - Touchless method that relies on the solution and corresponding agitation
  - Multiple substrates may be employed
  - Multiple soils maybe be employed
  - Visual evaluation is often sufficient to produce repeatable results

- **Gardner Scrub***
  - Requires a Gardner Abrasion apparatus
  - Works best when the soil is cured onto the Surface and difficult to remove
  - Concentration and number of strokes must be determined prior to testing

** (ASTM 4488-A5 Modified)*



General Hard Surface Cleaner

Your First Task:

- Look at the formula below
- Why would we use these materials?
- What kind of foam and emulsification properties should it have (unfair question; we'll discuss)?

Component	Wt%
Water	87.5
Sodium Metasilicate	5.0
Baypure CX100	2.5
Amphoteric 12	0.5
Nonionic Surfactant	4.0

Hand Dishwashing Detergent

Your Second Task:

- Look at the formula below
- What kind of problems might we run into with this formula?
- What's with the salt?

Component	Wt%
Water	77.5
Sodium Hydroxide	3.0
Sodium Laurel Ether Sulfate (70%)	15.0
Sodium Hexametaphosphate	1.5
Amphoteric L	2.0
Salt	3.0

Automatic Dishwashing Detergent

Your Third Task:

– What kind of soils would you expect to encounter for a formula of this type?

– What kind of considerations would you need to have?

– Does this formula address those considerations?

Component	Wt%
Water	77.5
Baypure CX100	5.0
Potassium Hydroxide (45%)	23.0
Tomamine Amphoteric 400	1.5
Tomamine AO-455	1.0
Calcium Hydroxide	5.0
Acusol 445N	0.5

For More Information, Please Visit:

specialty-additives.evonik.com

Join us **March 29, 2017** for our next webinar:

Using Solvent Replacement as an Opportunity

Contact Us:
U.S. 800-345-3148
PICUS@evonik.com

EVONIK
POWER TO CREATE

EVONIK

POWER TO CREATE