Energy Efficient Emulsification using Hydrophobically Modified Alkali Swellable Amphipathic Polymers

Two Proprietary Rheology Modifiers from 3V Inc.

Presented to the Midwest Chapter of the Society of Cosmetic Chemists
January 13, 2015
The Greening of Emulsions

by Joseph Albanese

Let’s Start with a Joke

Vegetarian: “You’re not a vegetarian because I think eating meat is unhealthy for me. It’s because raising cattle is bad for the planet, right?”

Cow: “Yeah, but adding to the ozone layer and the burning of fossil fuel in the raising of cattle is even worse than green plants producing oxygen through photosynthesis. What are you doing to help the environment?”

Ron: “Personally, I’m eating the cover of this can, but I’m only one can.”

Now Let’s Get Serious!

As a cosmetic chemist developing new emulsions, is there anything that you can do to help save the environment? Might I suggest that in your daily work you keep in mind the Twelve Principles of Green Chemistry? See Figure 1. For this brief article, let’s limit the discussion by focusing on Principle No. 6, which calls for the use of “Design for Energy Efficiency - Minimize the energy requirements of chemical processes and conduct synthetic methods at ambient temperature and pressure if possible.”

An early pioneer in this area is Dr. F. Joseph Lin, who published his initial work on Low Energy Emulsification (LEE) in 1974. Long before the EPA came out with their Twelve Principles (see Figure 2), Dr. Lin’s research taught that stable emulsions could be prepared successfully even if all of the external phase is not at elevated temperature. In the case of an oil-in-water (O/W) emulsion, the LEE procedure calls for only a portion of the external water phase (9 phases) to be heated before combining it with the hot internal oil phase. The emulsion concentrate is then diluted to the desired concentration with the remaining ambient temperature water (a phase) to cool down the emulsion. The rate of cooling has a profound effect on particle size of the internal phase and overall stability of the final emulsion.

In a more recent publication, a delightful and educational treatise, Dr. Lin explains, in a story-telling fashion, that by carefully controlling processing variables (pH) and component variables (e.g., also known as ingredients), LEE optimizes the desired properties (e.g., your emulsion). In short, LEE requires less energy input to create stable emulsions than it saves money, reduces processing time, increases plant capacity, and reduces the carbon footprint of your plant without having to retool or invest in new equipment. Dr. Lin also agrees with the “less is more” philosophy. Namely, too much of a good thing can be detrimental to achieving your goals.

Later, we will advance the pioneering research of Dr. Lin to show you how you can include specific types of polymers into your formula that will enable you to create emulsions quickly, with little to no surfactant emulsifiers and requiring less energy input, but first, let’s take a step back, and

NYSCC NOVEMBER CHAPTER MEETING
November 5th · The Terrace at Cilagio’s, Paramus, NJ

https://nyscc.org/
A Primer on Emulsions
Why emulsions?

• Delivery of active ingredients.
• Dilution of actives down to safe yet effective levels.
• Cost effective.
• Elegant aesthetics.
• Easy application.
Definition

An emulsion is a dispersion of two or more immiscible liquids.

• O/W (oil-in-water) - oil is the internal or dispersed phase.

• W/O (water-in-oil) – oil is the external or continuous phase.

• Multiple phase emulsions.
Is it an emulsion or, something else?

**Effect of Particle Size**

- Dispersion  
  *Largest – least stable*

- Suspension

- Emulsion

- Solution  
  *Smallest – most stable*
Types of emulsions

- Macroemulsions
  - Dispersed phase 0.2-50 µ
  - Kinetically stable but ultimately unstable due to the Second Law of Thermodynamics.
  - Opaque
  - Relatively high energy input required

- Microemulsions
  - Dispersed phase 0.01-0.2 µ
  - Thermodynamically stable
  - Transparent since droplet size <25% of wavelength of visible light
  - Very low O/W interfacial tension due to very high surfactant levels
  - Requires lower energy input
# Typical O/W Macro Emulsion

## INGREDIENTS

### WATER PHASE
- **Water**: 60-90%  
- **Humectant**: 2-7%  
- **Preservative**: 0.05-0.5%  
- **Surfactant**: 0.25-2.0%  
- **Thickener**: 0.1-0.75%  
- **Emollient**: 0.5-2.0%

### OIL PHASE
- **Esters**: 1.0-7.5%  
- **Cosmetic Oils**: 2.0-10.0%  
- **Surfactant**: 1.0-5.0%  
- **OTC Actives**: By law

### OTHER
- **Preservative**: 0.1-1.0%  
- **Perfume**: 0.1-1.0%

### Functionality
- **Diluent**  
- **Cushion, prevent drying out**  
- **Product protection**  
- **Emulsifier for stability**  
- **Improved stability**  
- **Elegant skin feel**  
- **Elegant skin feel**  
- **Emulsifier for stability**  
- **Sunscreens, etc.**  
- **Product Protection**  
- **Consumer Preference**
## Factors Effecting Settling Velocity & Emulsion Stability

<table>
<thead>
<tr>
<th>Particle</th>
<th>Suspending Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>• count</td>
<td>• density</td>
</tr>
<tr>
<td>• size</td>
<td>• charge</td>
</tr>
<tr>
<td>• shape</td>
<td>• <strong>Rheology</strong></td>
</tr>
<tr>
<td>• density</td>
<td>• polymer properties</td>
</tr>
<tr>
<td>• charge</td>
<td></td>
</tr>
</tbody>
</table>
Rheology Modifiers

- **Pseudoplastic**
  - Synthetic Polymers: Acrylic Acid Polymers, Carbomers, Hydrophobically Modifier Polymers
  - Gums: Guar, Hydroxypropyl Guar, Xanthan, Carrageenan
  - Clays: Hectorites, Bentonites, Mg/Al Silicates
  - Cellulosics: HEC, HPC
  - Silicas: Hydrated Silicas, Fumed Silicas

- **Newtonian**
  - Polyethylene Glycols

- **Thixotropic**
  - Gums: Karaya, Carrageenan
  - Organoclays: Quaternium-18 Hectorites & Bentonites, Stearalkonium Hectorites & Bentonites, Distearidimonium Hectorites
  - Polyethylenes
  - Silicas: Hydrated Silicas, Fumed Silicas
  - Trihydroxystearin
  - Al/Mg Hydroxystearate
Choosing the right rheology modifier is essential for achieving marketing success

THE HALO EFFECT

Edward Thorndike
Viscosity vs. Typical Shear Rates Experienced by Products

Shear Rate (s\(^{-1}\))

Thixotropic

Pseudoplastic

Newtonian

Viscosity

Storage → Shipping → Dispensing → Application → Homogenization
Why use rheology modifiers?

Stable Emulsions & Suspensions

Gravity

Yield Value

Viscosity

Adopted from “The Rheology of Natural and Synthetic Hydrophilic Polymer Solutions as related to Suspending Ability” By RJ Meyer and L. Cohen (BF Goodrich Chem. Co.) Presented in Nov. 1958, NYC. Published in Journal of Cosmetic Chemists
Stokes Law
predictor of emulsion stability

\[ V = \frac{2r^2g(D_1-D_2)}{9\mu} \]

Where:
- \( V \) = the particle’s settling velocity (m/s)
- \( r \) = the radius of the particle
- \( g \) = the gravitational acceleration (m/s\(^2\))
- \( D_1 \) = the density of the particles (kg/m\(^3\))
- \( D_2 \) = the density of the fluid (kg/m\(^3\))
- \( \mu \) = the viscosity of the fluid (Pa s)

In words – A higher viscosity (denominator) reduces the settling velocity. Therefore, the emulsion or suspension will be more stable.
Yield Value

Insufficient force to induce flow

Enough force to overcome yield value of the toothpaste

<table>
<thead>
<tr>
<th></th>
<th>Yield Point (Pa)</th>
<th>Viscosity (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Honey</td>
<td>0</td>
<td>11.0</td>
</tr>
<tr>
<td>Ketchup</td>
<td>14</td>
<td>0.1</td>
</tr>
<tr>
<td>Mayonnaise</td>
<td>85</td>
<td>0.6</td>
</tr>
</tbody>
</table>
The Evolution of Emulsions

Water + Oil

Increasing emulsion stability & energy savings
WATER & OIL DON’T MIX

Significant energy input is required to create a homogeneous dispersion of two immiscible liquids.

NEWS FLASH!

Once mixing stops syneresis, coalescences, agglomeration, creaming happens very quickly.
The Evolution of Emulsions

Surfactants

Water + Oil

Increasing emulsion stability & energy savings
Definition

• An emulsifier is a surface active agent (surfactant) which *reduces the interfacial tension* between the dispersed phase and the continuous phase.

• Emulsifiers may be also be hydrophilic colloids, finely divided solids (e.g. Pickering Emulsions), amphipathic polymers.
The HLB System

*Surfactant Selection*

- Griffin 1947 Hydrophilic-Lipophilic Balance
- HLB of surfactant = mole % of hydrophilic group / 5
- Maximum HLB = 20
- Required HLB of cosmetic oils
- Spans, Tweens, Poloxymers
Bancroft’s Rule

• Where the emulsifier is the most soluble becomes the external phase by lowering the interfacial tension on that side of the film
• Hydrogen bonding between non-ionic emulsifiers confers their rigidity and stability to interfacial films why ethoxylated materials are great emulsifiers
Emulsion Preparation

• Energy input required to reduce droplet size of internal/dispersed phase and create homogeneous mixture
  – Heat - increased temperature reduces viscosity and decreases interfacial tension so favors emulsification over coalescence
  – Mechanical agitation
  – Homogenization – high shear
  – Ultrasonic vibration

• Amount of work depends upon length of time energy is applied presence of emulsifiers
April 22, 2015
45th Anniversary of Earth Day
What can YOU do to help save the planet?
Twelve Principles of Green Chemistry

1. Prevention - It’s better to prevent waste than to treat or clean up waste afterwards.
2. Atom Economy - Design synthetic methods to maximize the incorporation of all materials used in the process into the final product.
3. Less Hazardous Chemical Syntheses - Design synthetic methods to use and generate substances that minimize toxicity to human health and the environment.
4. Designing Safer Chemicals - Design chemical products to affect their desired function while minimizing their toxicity.
5. Safer Solvents and Auxiliaries - Minimize the use of auxiliary substances wherever possible make them innocuous when used.
6. Design for Energy Efficiency - Minimize the energy requirements of chemical processes and conduct synthetic methods at ambient temperature and pressure if possible.
7. Use of Renewable Feedstocks - Use renewable raw material or feedstock rather whenever practicable.
8. Reduce Derivatives - Minimize or avoid unnecessary derivatization if possible, which requires additional reagents and generate waste.
9. Catalysis - Catalytic reagents are superior to stoichiometric reagents.
10. Design for Degradation - Design chemical products so they break down into innocuous products that do not persist in the environment.
11. Real-time Analysis for Pollution Prevention - Develop analytical methodologies needed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Inherently Safer Chemistry for Accident Prevention - Choose substances and the form of a substance used in a chemical process to minimize the potential for chemical accidents, including releases, explosions, and fires.

SOURCE: [http://www.epa.gov/sciencematters/june2011/principles.htm](http://www.epa.gov/sciencematters/june2011/principles.htm)
Design for Energy Efficiency

6. Minimize the energy requirements of chemical processes and conduct synthetic methods at ambient temperature and pressure if possible.

SOURCE: http://www.epa.gov/sciencematters/june2011/principles.htm
Dr. T.J. Lin

Important Emulsion Variables to Control

• Components (ingredients) = \( cV \)
  – Critical component of any emulsion are rheology modifiers

• Process parameters and Equipment = \( pV \)

• Optimized emulsion property = \( Zp \)

“More is not always better. Sometimes, less is more.”
- Dr. TJ Lin
LOW-ENERGY EMULSIFICATION (LEE)

A. Conventional Hot Process

1. Internal Phase
2. H
3. External Phase
4. H + H

B. LEE

1. Internal Phase
2. H
3. α Phase
4. β Phase
5. H
6. h + βH

Lin, Dr. TJ, Manufacturing Cosmetic Emulsions: Pragmatic Troubleshooting and Energy Conservation, Allured Business Media, p. 124, 2010
The Evolution of Emulsions

Increasing emulsion stability & energy savings

Low Energy Emulsification (LEE)

Surfactants

Water + Oil

Increasing emulsion stability & energy savings
Evolution of Emulsions

Effect of Process & Component Variables

*Comparison of Batch Times (minutes)*

- **Traditional Making Procedure with Surfactant Emulsifiers**
- **Low Energy Emulsification**

- **Hot/Hot**
- **LEE**

- **Preparation**
- **Mix/Homogenize**
- **Mix/Heat**
- **Mix/Cool**
**Low Energy Emulsification**

- Reduces the amount of energy required to make a stable emulsion
- No need to change formula or buy new equipment
- Reduces processing time and increase plant capacity
- Saves money and reduces carbon footprint
The Evolution of Emulsions

Increasing emulsion stability & energy savings

Surfactants

Water + Oil

Non-Associative Polymers
e.g. Carbomer

LEE

Increasing emulsion stability & energy savings
Synthetic Polymeric Thickeners
(Homopolymers, Copolymers, Crosspolymers)

• Non-associative
  – Carbomer
  – Acrylates Copolymer
  – Polyquaternium-37

“Carbomer is the ‘ultimate crutch’ to fix an unstable emulsion.”
  – George Deckner
Action Mechanism

Carbomer

Traditional emulsion
- Oil
- Water
- Emulsifier
- Carbomerer

1. Increasing the viscosity of the continuous phase
The Evolution of Emulsions

Hydrophobically Modified Alkali-Swellable Polymers (HASPs)

- Non-Associative Polymers
  - e.g. Carbomer

Surfactants

Water + Oil

Increasing emulsion stability & energy savings
Synthetic Polymeric Thickeners
(Homopolymers, Copolymers, Crosspolymers)

- **Non-associative**
  - Carbomer
  - Acrylates Copolymer
  - Polyquaternium-37

- **Associative**
  - Acrylates/Vinyl Isodecanoate Crosspolymer
Associative Thickeners
Acrylates/Vinyl Isodecanoate Crosspolymer

Hydrophilic backbone
Thickening properties

Lipophilic Moiety
Emulsifying properties
Resistance to electrolyte
Sensorial improvement
Higher Yield Value
Mode of Action

Traditional emulsion
- Oil
- Water

Polymeric emulsion
- Oil
- Water
- Acrylates/Vinyl Isodecanoate Crosspolymer

1. Increasing the viscosity of the continuous phase
2. Steric and electrostatic repulsion among drops.
Higher BYV. Controlled release of oil phase actives.
Simple Making Procedure

3 steps cold process → easy handling & cost efficient

- **Network building phase** - dispersion and swelling of the polymer particles in either the water or oil phase

- **Emulsification phase** – addition of oil phase and emulsification with continued agitation.  
  *CAUTION: Avoid excessive shear to prevent polymer breakdown and loss of viscosity.*

- **Neutralization** - with a suitable agent
Evolution of Emulsions

Effect of Process & Component Variables
Comparison of Batch Times (minutes)

- Traditional Making Procedure with Surfactant Emulsifiers
  - Hot/Hot
  - Low Energy Emulsification
  - Acrylates/Vinyl Isodecanoate Crosspolymer
  - HASP (p)

Advantages: time saving, energy conservation and increased production capacity
Acrylates / Vinyl Isodecanoate Crosspolymer

HLB Range Tested 7.5 - 13
Associative Thickener

Acrylates/Vinyl Isodecanoate Crosspolymer

0.25% Polymer - 10% Oil - pH 6

Mineral Oil (HLB 10)  
Up to 50%

Caprylic/Capric Triglyceride (HLB 11)  
Up to 30%

C_{12-15} Alkyl Benzoate (HLB 13)  
Up to 30%

Cyclopentasiloxane (HLB 7.5)  
Up to 30%
EFFECT OF OIL CONCENTRATION

0.25% Acrylates/Vinyl Isodecanoate Crosspolymer
(adjusted to pH 6 with NaOH)

- Mineral Oil %
- C12-15 Alkyl Benzolate %
- Caprylic/Capric Triglycerides %
- Cyclopentasiloxane %
EFFECT OF ADDED EMULSIFIERS

15% C12-15 Alkyl Benzoate

0.25% **Acrylates/Vinyl Isodecanoate Crosspolymer** + 1% Emulsifier

<table>
<thead>
<tr>
<th>LIPOPHILIC EMULSIFIERS</th>
<th>NON-IONIC O/W EMULSIFIERS</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>mPa's</td>
</tr>
<tr>
<td>Cetearyl Alcohol</td>
<td>7200</td>
</tr>
<tr>
<td>Glyceryl Stearate</td>
<td>12000</td>
</tr>
<tr>
<td>Methyl Glucose SS</td>
<td>15000</td>
</tr>
<tr>
<td>Sorbitan Laurate</td>
<td>9800</td>
</tr>
<tr>
<td>Sorbitan Palmitate</td>
<td>14500</td>
</tr>
<tr>
<td>Sorbitan Stearate</td>
<td>31500</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>K Cetyl Phosphate</td>
<td>4700</td>
</tr>
<tr>
<td>Na Cetearyl Sulfate</td>
<td>4750</td>
</tr>
</tbody>
</table>
EFFECT OF TRADITIONAL EMULSIFIERS

Reduced oil droplet size and increased whiteness.

**Lipophilic emulsifiers**: high viscosity but a jelly-like consistency.

**Hydrophilic emulsifiers**: lower viscosity but excellent appearance.

**Acrylates Vinyl Isodecanoate Crosspolymer** only

+ 1% Polysorbate-60
Synthetic Polymeric Thickeners (Homopolymers, Copolymers, Crosspolymers)

• **Non-associative**
  – Carbomer
  – Acrylates Copolymer
  – Polyquaternium-37

• **Associative**
  – Acrylates/Vinyl Isodecanoate Crosspolymer
  – Acrylates/Palmeth-25 Acrylate Copolymer
Hydrophobic alkylation enhances performance in many systems.

HASE = Hydrophobically Modified Alkali Swellable Emulsion

HASE After Neutralization with Base

Drawing courtesy of Raymond Rigoletto
Acrylates/Palmeth-25 Acrylate Copolymer

### Simple Emulsion Base

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>A Wgt %</th>
<th>B Wgt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetearyl Glucoside &amp; Cetearyl Alcohol</td>
<td>2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ceteary Alcohol</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Ethylhexyl Stearate</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Dicaprylyl Ether</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Caprylic/Capric Triglyceride</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Potassium Cetyl Phosphate</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Preserved Water</td>
<td>QS to 100 %</td>
<td>QS to 100%</td>
</tr>
</tbody>
</table>

Emulsion A
(Non-ionic)

Emulsion B
(Anionic)

Brookfield, RV 20 rpm, 25°C

Viscosity vs. Polymer %
O/W Emulsions at pH 6.5 with NaOH
Acrylates Palmeth-25 Acrylates Copolymer

HLB Range Tested 5-6 and 7.5-13
Acrylates Palmeth-25 Acrylates Copolymer

**Oils of different HLB requirements**

### 10% Polymer + 30% Oil

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI Water</td>
<td>56</td>
<td>56</td>
</tr>
<tr>
<td>Polymer (30%)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>C12-15 Alkyl Benzoate (HLB 13)</td>
<td>30</td>
<td>---</td>
</tr>
<tr>
<td>Cyclomethicone (HLB 7.5)</td>
<td>---</td>
<td>30</td>
</tr>
<tr>
<td>NaOH (10%)</td>
<td>QS</td>
<td>QS</td>
</tr>
<tr>
<td>pH</td>
<td>6.1</td>
<td>6.3</td>
</tr>
<tr>
<td>Viscosity (cps) @ 25°C</td>
<td>72,000</td>
<td>75,000</td>
</tr>
<tr>
<td>Viscosity (cps) @ 45°C</td>
<td>39,000</td>
<td>41,000</td>
</tr>
</tbody>
</table>

**Cold Process**

Procedure – Add polymer to water. Then add oil and homogenize for 5 minutes using Silverson L4RT-A at 4,000rpm. Neutralize with base to pH 6.25. 500 gram batch size.

QS to pH 6.25 +/- 0.25
Brookfield RVT T-E spindle @ 10rpm

10% Polymer + 30% C12-15 Alkyl Benzoate

10% Polymer + 30% Cyclomethicone
## Acrylates /Palmeth-25 Acrylates Copolymer
### Effect of Increasing Oil Phase

10% **Polymer** & Mineral Oil increased from 20% to 40%

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Wgt %</th>
<th>Wgt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI Water</td>
<td>66</td>
<td>46</td>
</tr>
<tr>
<td>Polymer (30%)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>M.O.</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>NaOH (5%)</td>
<td>QS</td>
<td>QS</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
<td>6.7</td>
</tr>
<tr>
<td>Viscosity (cps) @ 25C</td>
<td>34,500</td>
<td>106,000</td>
</tr>
<tr>
<td>Viscosity (cps) @ 45C</td>
<td>21,500</td>
<td>57,000</td>
</tr>
</tbody>
</table>

QS to pH 6.25 +/- 0.25  
Brookfield RVT T-E spindle @ 10rpm

### Cold Process

Procedure – Add polymer to water. Add M.O. homogenizing for 5 minutes using Silverson L4RT-A at 4,000rpm. Then neutralize to about pH 6.5 with sweep agitation. 500 g batch size.

Procedure – Dilute Batch B 50:50 with DI Water after the emulsion is formed.  
5,000 cps @ 25C  
1,000 cps @ 45C

### Photomicrographs 500X

- 10% Polymer + 20% M.O.
- 10% Polymer + 40% M.O.
- 5% Polymer + 10% M.O. (Batch B diluted 50:50)
Acrylates /Palmeth-25 Acrylates Copolymer

**Effect of Polymer Concentration**

Decrease polymer concentration from 5.0% down to 1.25% keeping M.O. constant at 20%

### Ingredients

<table>
<thead>
<tr>
<th>J</th>
<th>K</th>
<th>L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wgt %</td>
<td>Wgt %</td>
<td>Wgt %</td>
</tr>
<tr>
<td>DI Water</td>
<td>74.5</td>
<td>78.0</td>
</tr>
<tr>
<td>Polymer (30%)</td>
<td>5.0</td>
<td>2.5</td>
</tr>
<tr>
<td>M.O.</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>NaOH (5%)</td>
<td>QS</td>
<td>QS</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>100.0</td>
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</table>

**Cold Process**

Procedure – Add polymer to water. Add M.O. homogenizing for 5 minutes using Silverson L4RT-A at 4,000rpm. Then neutralize to about pH 6.5 with sweep agitation. 500 g batch size.

**Photomicrographs 500X**

NOTE: A viscosity drop of 20% for every 10C above 25C is a general accepted norm.
# Acrylates Palmeth-25 Acrylates Copolymer

## Emulsification of Low HLB Oils

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Wgt %</th>
<th>Wgt %</th>
<th>Wgt %</th>
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</thead>
<tbody>
<tr>
<td>DI Water</td>
<td>67.0</td>
<td>67.0</td>
<td>67.0</td>
</tr>
<tr>
<td><strong>Polymer (30%)</strong> *</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>M.O. (HLB 10)</td>
<td>20.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Almond Oil (HLB 6)</td>
<td>-</td>
<td>20.0</td>
<td>-</td>
</tr>
<tr>
<td>Dimethicone (HLB 5))</td>
<td>-</td>
<td>-</td>
<td>20.0</td>
</tr>
<tr>
<td>NaOH (5%)</td>
<td>QS</td>
<td>QS</td>
<td>QS</td>
</tr>
<tr>
<td>pH</td>
<td>6.2</td>
<td>6.3</td>
<td>6.5</td>
</tr>
<tr>
<td>Viscosity (cps) *** @ 25C</td>
<td>74,500</td>
<td>92,500</td>
<td>53,000</td>
</tr>
</tbody>
</table>

**Cold Process**

**Procedure** – Add polymer to water. Add M.O. homogenizing for 5 minutes using Silverson L4RT-A at 4,000rpm. Then neutralize to about pH 6.5 with sweep agitation. 500 g batch size.

QS to pH 6.25 +/- 0.25  
Brookfield RVT T-E spindle @ 10rpm

**Photomicrographs 500X**

- Mineral Oil HLB 10
- Almond Oil HLB 6
- Dimethicone HLB 5
The Evolution of Emulsions

HASP Polymeric Emulsifiers

\{ Acrylates/Vinyl Isodecanoate Crosspolymer (powder) \\
Acrylates/Palmeth-25 Acrylate Copolymer (liquid) \\
\}

Non-Associative Polymers \\
e.g. Carbomer

Surfactants

Water + Oil

LEE

Increasing emulsion stability & energy savings
The Greening of Emulsions

HASP Polymeric Emulsifiers
- Acrylates/Vinyl Isodeccanoate Crosspolymer (powder)
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Non-Associative Polymers
- e.g. Carbomer

Surfactants
- LEE

Water + Oil

Increasing emulsion stability & energy savings
Evolution of Emulsions

Advantages of Cold Process Emulsification: time saving, energy conservation and increased production capacity

<table>
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<tr>
<th>Process Type</th>
<th>Preparation</th>
<th>Mix/Homogenize</th>
<th>Mix/Heat</th>
<th>Mix/Cool</th>
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<td>Acrylates/Vinyl Isodecanoate Crosspolymer</td>
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<td>HASP (p)</td>
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<td>Acrylates/Palmeth-25 Acrylate Copolymer</td>
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<td>HASP (liq)</td>
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One Pot Process Possible

- **Acrylates/Vinyl Isodecanoate Acrylates Crosspolymer** (powder)
  - Direct Addition
    - Add Polymer to Water Phase in main mix tank
    - Add Oil Phase to the main mix tank with rapid agitation / homogenization
    - Add suitable to neutralize to pH 5-7
  - Indirect Method
    - Add Polymer to Oil Phase in side kettle. Do not heat above 60°C
    - Add Oil Phase to Water Phase containing sufficient neutralizing base to pH 5-7
      with rapid agitation in main mix tank
    - Do not over homogenize

- **Acrylates/Palmeth-25 Acrylates Copolymer** (liquid)
  - Add Polymer to Water Phase in main mix vessel
  - Add Oil Phase with homogenization
  - Neutralize with suitable base to pH 6-7
Acrylates Vinyl Isodecanoate Crosspolymer

• Properties
  – Amphipathic polymer (powder form) for emulsification & thickening
  – High suspending properties & improved electrolyte tolerance
  – Enhanced water-resistance for sunscreen actives

• Applications
  – O/W emulsions
  – Clear styling gels
  – Surfactant systems
  – Clear hydroalcoholic hand sanitizers

• Easy to use
  – May be dispersed either into water following the normal procedure for Carbomer or into the Oil Phase of emulsions.
  – Functional over a broad pH range. Neutralization can be carried out with alkali (NaOH, KOH or NH₄OH) or with hydrophilic organic amines (such as TEA, AMP, TrisAmino).
Acrylates/Palmeth-25 Acrylate Copolymer

• Properties
  – Hydrophobically modified associative thickener and emulsifier
  – Liquid 30% polymer solids water-thin white emulsion

• Applications
  – O/W emulsions
  – Clear sulfate-free surfactant systems
  – Styling products
  – High pH products depilatories and relaxers

• Easy-to-use
  – Adds instantly to water
Review

Tips to Improve Emulsion Stability

• Prevent particle interaction
• Increase viscosity & yield value of continuous phase.
• Add polymer(s).
• Increase concentration of dispersed phase.
• Low levels of electrolytes.
• Reduce particle/droplet size of dispersed phase.
• Increase mechanical and/or heat energy.
• Emulsifier selection and concentration.
• Avoid aeration.
SUMMARY

Hydrophobically modified amphiphatic polymers are one way to making even lower energy emulsions. Cold process emulsification provides greater savings, increased manufacturing capacity and . . .

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working with the Carbon Trust

148g CO₂

Trust Botanics

British Standard from Carbon Trust

40kg CO₂e

PAS 2050
3V cares about the environment

http://www.3vgreeneagle.com/en
References

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3. Deckner, George and O’Lenick, Tony, Lamellar Gel Network Lab Workshop, C&T Summit Philadelphia, June 2014