The Techniques of Emulsification
Dec. 09, 2015
Steven Chan, PhD – Applications Manager
Agenda

• Introduction
  • Fundamentals of surfactants
  • Emulsification

• The HLB System – Formulation Aid

• The Emulsification Processes
  • Direct emulsion
  • Phase inversion technique

• Summary
What Is An Emulsion?

- Oil and Water Do Not Mix
- Hydrophobic and/or High Molecular Weight Materials that are Not Soluble/Miscible in Water
- Simplest Definition - a Kinetically Stable Mix of Two Immiscible Liquids
  - A continuous or external phase
  - A dispersed phase or internal phase
Emulsion Types

Oil-in-Water (O/W)
- Continuous Phase - Water, Dispersed Phase - Oil Droplets
- Conducts electricity
- Dilutes in water

Water-in-Oil (W/O)
- Continuous Phase - Oil, Dispersed Phase - Water Droplets
- Does not conduct electricity
- Does not dilute in water
Croda has >75 Years Experience in Emulsification in Different Industries

- Lotions
- Detergent
- Metal Working Fluids
- Tertiary Oil Recovery
Emulsions In Coatings & Polymers

• Conversion from Solvent Borne to Water Borne Systems
• VOC Elimination: Oil in Water Emulsion
  • Resin emulsification - alkyd, epoxy, and polyester resins
  • Emulsion Polymerization
• VOC Reduction: Water in Oil Emulsion
  • Partial solvent replacement with water for VOC reduction
• Additives for Water Borne Systems
  • Wax Emulsion
  • Silicone Emulsion

Choice of Emulsifier/Surfactant Process of Emulsification
What Are Surfactants?

- Contraction for “Surface Active Agent”
- Molecular Structure
  - Water loving hydrophilic part
  - Oil loving lipophilic part
- Accumulate and Orient at the interfaces and reduce surface/interfacial tension at low concentrations

Hydrophilic Head  Lipophilic Tail

Reduce Surface Tension

Adsorption at O/W Interface
The Role Of The Surfactant in Emulsion

- Interfacial Tension Reduction
  - Facilitates droplet formation and particle size

- Emulsion Stabilization
  - Protection against coalescence of droplets
  - Control of stability and shelf life
  - Compatibility with other formulation ingredients
Where do you currently find use for surfactants?

- Wetting
- Emulsion polymerization
- Resin Emulsifications
- Emulsifying others (If not listed, please write in the Q&A box.)
Classes of Surfactants

• **Anionic:**
  - Sulfate, Sulfonate
  - Phosphate - Crodafos™
  - Sulfosuccinate - Multiwet™

• **Cationic:**
  - Quaternary Ammonium Compounds - Crodaquat™
  - Imidazoline - Crodazoline™

• **Nonionic (Contains EO):**
  - Alkylphenol Ethoxylate
  - Ethoxylated Natural Fatty Alcohol – Brij™
  - Ethoxylated Synthetic Fatty Alcohol – Synperonic™
  - Ethoxylated Sorbitan Ester – Tween™
  - Sorbitan Ester – Span™
  - Ethoxylated Fatty Acid - Myri™
  - Formulated - Multiwet™

• **Zwitterionic (Amphoteric):**
  - $\text{CH}_3(\text{CH}_2)_{11}\text{NMe}_2^+(\text{CH}_2)_3\text{SO}_3^-$
Conventional vs Polymeric Surfactants

Conventional, Low MW Hydrophobe

- Insoluble Moiety
- Soluble Moiety

Polymeric, High MW or Multiple Hydrophobes

- AB Block
  - Maxemul™
- ABA Block, Synperonic PE, T
- Comb or Grafted
The HLB System
- How to Choose Emulsifier
History of the HLB System

The letters HLB stand for:

- **H**ydrophile (water loving)
- **L**ipophile (oil loving)
- **B**alance (ratio)

It was developed for use with conventional **NONIONIC** surfactants. A number (0–20) indicates emulsification behavior.

The HLB system was invented 60 years ago by **William C. Griffin** of the Atlas Powder Company, now Croda Inc.
HLB System Definition

• Nonionic Surfactants Have an HLB Value
  • The higher the number, the more hydrophilic (water soluble)
  • The lower the number, the more lipophilic (oil soluble)

• Oils Have Specific HLB Requirements

Matching the oil HLB requirement with a surfactant’s HLB value yields optimum performance.
Calculating HLB of Surfactants (Griffin)

\[
\text{HLB} = \frac{\text{Wt} \text{ % of EO}}{5}
\]

- Oleth-20 is a 20 Mole Ethoxylate of Oleyl Alcohol
- The 20 Moles of EO are the Hydrophilic Portion
  - Molecular weight = 20 \times 44 = 880
- The One Mole of Oleyl Alcohol is the Lipophilic Portion
  - Molecular weight = 270
- Molecular Weight of Oleth-20 = 880 + 270 = 1150
- \(\frac{880}{1150} = 76.5\%\)
- \(\text{HLB} = \frac{76.5}{5} = 15.3\)
## Hydrophile-Lipophile Balance

<table>
<thead>
<tr>
<th>Approximate HLB Values</th>
<th>Water Solubility</th>
<th>HLB</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>No dispersibility in water</td>
<td>1-3</td>
<td>Oil coupling</td>
</tr>
<tr>
<td>3-6</td>
<td>Poor dispersion in water</td>
<td>4-6</td>
<td>W/O emulsifier</td>
</tr>
<tr>
<td>6-8</td>
<td>Milky dispersion after agitation</td>
<td>7-9</td>
<td>Wetting agent</td>
</tr>
<tr>
<td>8-10</td>
<td>Stable milky dispersion</td>
<td>8-18</td>
<td>O/W emulsifier</td>
</tr>
<tr>
<td>10-13</td>
<td>Translucent to clear dispersion</td>
<td>13-15</td>
<td>Detergent</td>
</tr>
<tr>
<td>13-20</td>
<td>Clear solution</td>
<td>15-18</td>
<td>Solubilizer</td>
</tr>
</tbody>
</table>
## Typical HLB Requirements for Oils

<table>
<thead>
<tr>
<th>Class</th>
<th>Required HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetable Oil Family</td>
<td>6</td>
</tr>
<tr>
<td>Silicone Oils</td>
<td>8-12</td>
</tr>
<tr>
<td>Petroleum Oils</td>
<td>10</td>
</tr>
<tr>
<td>Typical Ester Emollients</td>
<td>12</td>
</tr>
<tr>
<td>Fatty Acids &amp; Alcohols</td>
<td>14-15</td>
</tr>
</tbody>
</table>
Audience Poll 2

What type of resin system are you most interested in improving?

- Epoxy
- Polyurethane
- Latex
- Alkyd
- Other (If not listed, please write in the Q&A box.)
HLB Values of Blended Components

The **HLB Value** of a Surfactant Blend is the Weighted Average of the HLBs of the Blended Surfactants

( 50 / 50 blend of HLB 4 with HLB 16 = HLB 10 )

The **HLB Requirement** of an Oil Blend is the Weighted Average of the HLB Requirements of the Blend Components

( 50 / 50 blend of Req. 10 oil with Req. 14 oil = Req. 12 )
HLB Practice

• Knowing the Required HLB of Oils - Match the HLB by Selecting the Right Surfactant or Combinations
  • Necessary condition but not sufficient condition
  • Wrong HLB – will never make stable emulsion
  • Right HLB – does not guarantee stable emulsion

• Blend of At Least Two Emulsifiers for Optimum Stability
  • Mixtures of different HLB surfactants give better surface coverage (packing) at the interface

Single emulsifier

Mix of high and low HLB
The Three-Step System

I. Determine the HLB Requirement of Oil

II. Determine the Most Effective Surfactant Chemistry
   I. Select the surfactant with similar hydrophobe as the oil

III. Determine Surfactant Concentration Required to Achieve Desired Stability / Rheology

Required HLB’s are accurate to
+ / - 0.5 HLB units
Required HLB Test

- In a Series of 2 oz. Jars, Add:
  - 20 grams oil to each jar
  - 2 grams emulsifier systems with HLB = 2, 4, 6, 8, 12, 14, 16

- Shake Well

- Add 28 g Water to Each Jar. Shake Well

- Required HLB Corresponds to the Blend that Separates Least
Step 1 - Determine the Required HLB

Use applicable water hardness, pH and temp.
Step 1 - Determine the Required HLB

![Step 1 - Determine the Required HLB](image)
Steps 2 and 3

Select Chemistry → Determine Concentration

All surfactants: HLB = 12

% Surfactant is based on Amount of Oil
HLB System Flexibility

• Any Number of Components can be Added to the Oil Before the HLB Requirement is Determined
  • Corrosion inhibitors
  • Biocide / preservative package
  • Amine
APE Replacement

**HLB can be a Guide to Surfactant Substitution**

<table>
<thead>
<tr>
<th></th>
<th>HLB</th>
<th></th>
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<tbody>
<tr>
<td>NP-4</td>
<td>8.9</td>
<td>NP-5</td>
<td>10.5</td>
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<tr>
<td>NP-6</td>
<td>10.9</td>
<td>NP-7</td>
<td>11.7</td>
</tr>
<tr>
<td>NP-8</td>
<td>12.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NP-9</td>
<td>12.8</td>
<td>NP-10</td>
<td>13.3</td>
</tr>
<tr>
<td>NP-12</td>
<td>13.9</td>
<td>NP-13</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td></td>
<td>Tween™ 61</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Synperonic™ 13/6</td>
</tr>
<tr>
<td></td>
<td>11.4</td>
<td></td>
<td>Brij™ C10</td>
</tr>
</tbody>
</table>

**Croda Coatings & Polymers – Innovation you can build on™**
How To Use HLB System

• The HLB System Predicts How Oils and Surfactants Will Likely Interact

• Surfactants Have **HLB Values**
  • The higher the number, the more hydrophilic
  • The lower the number, the more lipophilic

• Oils Have **HLB Requirements**

• Matching the Surfactant **HLB Value** with the **HLB Requirement** will Yield **Optimum Performance**
Audience Poll 3

Which of these is the most significant attribute from a surfactant?

- Low foam
- Low or zero VOC
- Bio-based
- FDA compliant
- Other (If not listed, please write in the Q&A box.)
The Process

- Emulsion is Thermodynamically Unstable
  - Path dependent

- Direct Emulsification usually for Large Continuous Phase System
  - Dispersed phase added to continuous phase (usually containing emulsifier) directly under agitation
  - May require special equipment like rotor stator or homogenizer

- Phase Inversion Technique
  - No special equipment required
  - Need the right impeller design for adequate mixing
  - Preferred for producing O/W emulsions
  - Can handle viscous oil
Phase Inversion Technique

- Emulsifier(s) Preferably Dissolved in the Oil (Resin) Phase at Elevated Temperature
- Water is Added to the Oil Phase While Mixing
- Initial Formation of a W/O Emulsion, Viscosity Increases with Water Addition
- At Inversion Point (Highest Viscosity) - Spontaneous Inversion From a W/O to an O/W Emulsion upon Further Addition of Water
Impellers for Low Speed Process

Surfactant reduction with optimum mixing efficiency

Intermig

Paravisc
Blade Type For High Speed Process

- Cowles blade, used for grinding pigments
- Hockmeyer blade (square toothed), used for emulsification
Benefits of Phase Inversion Technique

• Capable of Making Emulsion Containing High Fraction of Dispersed Phase
• Easy Control of Temperature for Optimal Viscosity for Mixing Especially High Viscosity Oil
• Phase Inverts at Low Interfacial Tension to Produce Consistent Small Particle Size and narrow distribution
• Emulsification Possible at Low Speed
• No Special Equipment Required
  • Minimal Investment Cost
  • Low Energy Consumption
Limitation of Conventional Surfactant

- Poor Affinity to the Oil/Water Interface; Dynamic Equilibrium with Micelles in the Continuous Phase
- Risk of Preferential Adsorption in Pigmented Systems
  - High surfactant levels
  - Desorption upon dilution
- Migration to Film Surface During Drying
  - Plasticization of film, poor blocking resistance, dirt pickup
  - Water sensitivity, poor water resistance
- Polymeric Surfactants Do Not Have These Negative Effects
Specifically Designed Polymeric Surfactants

- Copolymerizable Non-Migratory Surfactants (Emulsion Polymerization)
  - Maxemul™ 5010 / 5011 (non-ionic)
  - Reactive Maxemul™ 6106 / 6112 (anionic)
- Alkyd Emulsion
  - Maxemul™ 7301 (non-ionic) and 7302 (anionic)
  - Reactive Maxemul™ 8201 (non-ionic)
- VOC Reduction in SB Alkyd
  - LoVOCOat™ Form 100 (for w/o) – direct emulsification
- Epoxy Emulsion
  - Maxemul™ 9107
Summary

- >75 Years of Experience in Emulsification
- Offers Wide Product Ranges
- Bio Based EO in 2017
- Environmentally Friendly Products
- Specific Designed Products
- Unique Solutions for Resin Emulsifications
- Both Products and Formulation Knowledge
Additional Information

To order free samples, click here.

To contact us, email Torrey.Adams@croda.com

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Thank You