Saponification Values

• What they are
• Why they are what they are
• How to measure them for yourself
Acknowledgements

• Stephen English
• Kevin Thompson
• Brad Benedetti
• Alex Garcia
• William Slack
SAP’s: What They Are

• 144 g NaOH per 1000 g of palm oil
• 144 g NaOH per kg of palm oil
• 144 mg NaOH per g of palm oil
• 144 parts NaOH per thousand parts of palm oil (144 ppt)
• 14.4 parts NaOH per hundred parts of palm oil (14.4%)
• 0.144 g NaOH per g of palm oil
SAP’s: In Other Units

- 144 oz NaOH per 1000 oz of palm oil
- 144 lb NaOH per 1000 lb of palm oil
- 144 ton NaOH per 1000 ton of palm oil
- 0.144 oz NaOH per oz of palm oil
- 0.144 lb NaOH per lb of palm oil
- 0.144 ton NaOH per ton of palm oil
SAP’s In Practice

? oz NaOH = 120 oz Palm Oil \left( \frac{144 \text{ oz NaOH}}{1000 \text{ oz Palm Oil}} \right) = 17.3 \text{ oz NaOH}

? oz NaOH = 30 oz Coconut Oil \left( \frac{191 \text{ oz NaOH}}{1000 \text{ oz Coconut Oil}} \right) = 5.7 \text{ oz NaOH}

• You need (17.3 + 5.7) or 23.0 oz of NaOH
• At 5% discount you need 21.9 oz of NaOH
The Fundamental Equation
SAP’s: What They Are

Water
Hexadecane
Alkanes

- Ethane: \( \text{C}_2\text{H}_6 \)
- Propane: \( \text{C}_3\text{H}_8 \)
- Butane: \( \text{C}_4\text{H}_{10} \)
- Pentane: \( \text{C}_5\text{H}_{12} \)
- Hexane: \( \text{C}_6\text{H}_{14} \)
- Heptane: \( \text{C}_7\text{H}_{16} \)
- Octane: \( \text{C}_8\text{H}_{18} \)
- Nonane: \( \text{C}_9\text{H}_{20} \)
- Decane: \( \text{C}_{10}\text{H}_{22} \)
- Undecane: \( \text{C}_{11}\text{H}_{24} \)
- Dodecane: \( \text{C}_{12}\text{H}_{26} \)
- Tridecane: \( \text{C}_{13}\text{H}_{28} \)
- Tetradecane: \( \text{C}_{14}\text{H}_{30} \)
- Pentadecane: \( \text{C}_{15}\text{H}_{32} \)
- Hexadecane: \( \text{C}_{16}\text{H}_{34} \)
Acids
Alcohols
Esters
Stearic Acid
Fatty Acids

- Lauric acid
  - \[\text{C}_{12}\text{H}_{24}\text{O}_{2}\]
- Dodecanoic acid, \(C_{12}H_{23}COOH\)
- Myristic acid
  - \[\text{C}_{14}H_{27}COOH\]
- Tetradecanoic acid, \(C_{14}H_{27}COOH\)
- Palmitic acid
  - \[\text{C}_{16}H_{35}COOH\]
- Hexadecanoic acid, \(C_{16}H_{32}COOH\)
- Stearic acid
  - \[\text{C}_{18}H_{36}COOH\]
- Octadecanoic acid, \(C_{18}H_{36}COOH\)
- Oleic acid
  - \[\text{C}_{18}H_{34}COOH\]
- Linoleic acid
  - \[\text{C}_{18}H_{34}COOH\]
- Linolenic acid
  - \[\text{C}_{18}H_{34}COOH\]
Glycerol
The Fundamental Reaction

3 NaOH + 1 Fat = 3 Soaps + 1 Glycerol
SAP’s: Why They Are What They Are

• How many eggs to make a 3-egg omelet?
• How many dozens of eggs to make a dozen 3-egg omelets?
• How many gross of eggs to make a gross of 3-egg omelets?
• How many moles of eggs to make a mole of 3-egg omelets?
Lyes and More Lyes

- How many NaOH to react with one fat?
- How many dozens of NaOH to react with a dozen fat?
- How many gross of NaOH to react with a gross of fat?
- How many moles of NaOH to react with a mole of fat?
Atomic Weights

- 1 gram of hydrogen = 1 mole
- 12 gram of carbon = 1 mole
- 16 gram of oxygen = 1 mole
- 23 gram of sodium = 1 mole
- 39 gram of potassium = 1 mole
Formula Weights

- 40 grams of NaOH = 1 mole \((23 + 16 + 1)\)
- 56 grams of KOH = 1 mole \((39 + 16 + 1)\)
- 638 grams of \(C_{39}H_{74}O_6\) (glyceryl trilaurate) = 1 mole
- 806 grams of \(C_{51}H_{98}O_6\) (glyceryl tripalmitate) = 1 mole
- 890 grams of \(C_{57}H_{110}O_6\) (glyceryl tristearate) = 1 mole
Stoichiometry

\[ ? \text{ g NaOH} = 1000 \text{ g fat} \left( \frac{1 \text{ mol fat}}{890 \text{ g fat}} \right) \left( \frac{3 \text{ mol NaOH}}{1 \text{ mol fat}} \right) \left( \frac{40 \text{ g NaOH}}{1 \text{ mol NaOH}} \right) \]

= 135 g NaOH

\[ ? \text{ g KOH} = 1000 \text{ g fat} \left( \frac{1 \text{ mol fat}}{890 \text{ g fat}} \right) \left( \frac{3 \text{ mol KOH}}{1 \text{ mol fat}} \right) \left( \frac{56 \text{ g KOH}}{1 \text{ mol KOH}} \right) \]

= 189 g KOH
## SAP’s

<table>
<thead>
<tr>
<th>Fat</th>
<th>g NaOH/kg fat</th>
<th>g KOH/kg fat</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycercyl trilaurate</td>
<td>188</td>
<td>263</td>
</tr>
<tr>
<td>coconut oil</td>
<td>191</td>
<td>268</td>
</tr>
<tr>
<td>glycercyl tripalmitate</td>
<td>149</td>
<td>208</td>
</tr>
<tr>
<td>palm oil</td>
<td>142</td>
<td>199</td>
</tr>
<tr>
<td>glycercyl tristearate</td>
<td>135</td>
<td>189</td>
</tr>
<tr>
<td>tallow</td>
<td>140</td>
<td>196</td>
</tr>
</tbody>
</table>
Why Measure SAP Values?

- The SAP of an oil will vary from supplier to supplier
  - Different ratios of fatty acids
  - Different quantities of unsaponifiables
  - Seasonal variation
Why Measure SAP Values?

- The purity of NaOH and KOH will vary from supplier to supplier
  - Different moisture content
  - Sodium and potassium carbonate
  - Hygroscopic nature

- Quality Assurance
- Oils with unknown or uncertain SAP’s
SAP’s by Brute Force

- Suppose Palm Oil has an SAP between 140 and 146: make 9 batches of soap
  - 139, 140, 141, 142, 143, 144, 145, 146, 147 g NaOH / kg oil
- Test each cured soap for excess alkali
- About half of these soaps will be too alkaline for use
Making Little Soaps for Analysis

- Precise weighing of small quantities
- Battery acid and phenolphthalein
- KOH and alcohol instead of NaOH and water
- 20 g of oil or fat
- Oven curing of sample soaps
The Jennings JScale JS-50x can weigh up to 50 g to within 0.01 g. The auto-off feature can be disabled. It uses AAA batteries. It costs about $50.
Weighing Synthetically
Measuring SAP Values

Weighing Analytically
Battery Acid
Standardizing the Battery Acid

- Half-fill a one-quart glass jar with distilled water
- Analytically weigh 10.XX g of NaOH or KOH into the jar
- Add 3 drops of 1% phenolphthalein indicator
- Analytically weigh battery acid into jar until endpoint
- Record the weight of acid required to neutralize 10.XX g of base
Start of Titration
The Endpoint
Standardized Battery Acid

- In this case it took 33.52 g of acid to titrate 9.96 g of NaOH
- In this case it took 22.74 g of acid to titrate 10.07 g of KOH
Measuring SAP Values

6% Alcoholic KOH
Making Liquid Soap

- Synthetically weigh 100.00 g of alcoholic KOH into a one-quart glass jar
- Analytically weigh 20.XX g of melted oil into the jar
- Screw lid onto jar--lid should have small hole in it
- Shake the solution until thoroughly mixed
- Cure in oven for one hour at 160°F
Soap Curing in the Oven
Measuring SAP Values

Titrating the Blank

- Synthetically weigh 100.00 g of alcoholic KOH into a one-quart glass jar
- Add distilled water until jar is half full
- Add 3 drops of 1% phenolphthalein indicator
- Analytically weigh battery acid into jar until endpoint
- In this case it took 16.68 g of acid to titrate 100.00 g of KOH solution
Titrating the Soap

- Remove cured liquid soap from oven
- Add distilled water until jar is half full
- Add 3 drops of 1% phenolphthalein indicator
- Analytically weigh battery acid into jar until endpoint
- In this case it took 7.02 g of acid to titrate soap
The Important Measurements

- 33.52 g acid = 9.96 g NaOH
- 22.74 g acid = 10.07 g KOH
- 20.00 g of palm oil to make soap
- 16.68 g acid = blank
- 7.02 g acid = soap
The SAP Calculation

\[ ? \text{ g NaOH} = 1000 \text{ g Fat} \left( \frac{16.68 - 7.02 \text{ g Acid}}{20.00 \text{ g Fat}} \right) \left( \frac{9.96 \text{ g NaOH}}{33.52 \text{ g Acid}} \right) \]
\[ = 144 \text{ g NaOH} \]

\[ ? \text{ g KOH} = 1000 \text{ g Fat} \left( \frac{16.68 - 7.02 \text{ g Acid}}{20.00 \text{ g Fat}} \right) \left( \frac{10.07 \text{ g KOH}}{22.74 \text{ g Acid}} \right) \]
\[ = 214 \text{ g KOH} \]
### Palm Oil SAP’s

<table>
<thead>
<tr>
<th>Fat</th>
<th>g NaOH/kg fat</th>
<th>g KOH/kg fat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hurst (1907)</td>
<td>144</td>
<td>202</td>
</tr>
<tr>
<td>Gadd (1913)</td>
<td>144</td>
<td>202</td>
</tr>
<tr>
<td>Thomssen and Kemp (1937)</td>
<td>140-146</td>
<td>196-205</td>
</tr>
<tr>
<td>Levitt (1951)</td>
<td>143-146</td>
<td>200-205</td>
</tr>
<tr>
<td>Cavitch (1997)</td>
<td>142</td>
<td>199</td>
</tr>
<tr>
<td>McDaniel (2000)</td>
<td>142</td>
<td>199</td>
</tr>
<tr>
<td>Dunn and English (2006)</td>
<td>144</td>
<td>214</td>
</tr>
</tbody>
</table>
Is It Worth the Trouble

- About 2 hours, start to finish
- Save time by testing several oils at once
  - Several soaps can oven-cure simultaneously
  - The same blank can be used for several soaps
- Good SAP needed when lye discount is small
Lye Discount

- Why do we discount lye?
2% Lye Excess

![Graph showing pH changes with Acid Weight (grams)]
1% Lye Discount

![Graph showing pH vs. Acid Weight (grams) for 1% Lye Discount]
2% Lye Discount

![Graph showing pH changes with acid weight]
5% Lye Discount

Graph showing the relationship between pH and Acid Weight (grams).
10% Lye Discount

Graph showing the relationship between pH and acid weight (grams). The pH decreases as the acid weight increases.
DOS Update

- 8 additives were tested at 3 different concentrations
- Treated olive oil soaps were aged at 50°C for 1800 hours
- Shelf life was determined by measuring color of soaps over time
- When color density reached twice its initial value, soap was deemed to have expired
- Ineffective additives: Vitamin E, BHA, Sodium Citrate, Carnosic Acid
Effective Additives

- 0.03% EDTA
- 0.07% BHT
- 0.12% Rosemarinic Acid

- When buying ROE, maximize Rosemarinic Acid content if possible
- EDTA was very effective even at very small concentrations
Metal Contamination

- EDTA seems to work by sequestering metals
- Calcium and Iron reduce shelf life
- Copper has no effect on shelf life
- Use distilled water if your tap water is high in Calcium or Iron
- Calcium and Iron may be present in oils or lyes
EDTA Safety


- Cosmetic Ingredient Review Expert Panel
- Oral toxicity in test animals was minimal
- Dermal toxicity and irritation was minimal
- Conclusion: EDTA is safe for use in cosmetics
Why Talk of Cancer?

- Very small amounts of Nitrilotriacetate can be found in EDTA
- Nitrilotriacetate is a potential oral carcinogen in rats at large doses
- Nitrilotriacetate is absorbed in the gut of the rat but not the human
- Nitrilotriacetate is absorbed in the gut of the rat but not the human
- Ask for MSDS when you purchase EDTA, look for nitrilotriacetate
Conclusions

- You can measure SAP with a $50 scale
- Excessive lye discount is not necessary
- You can eliminate DOS
- A chemistry book for soapmakers?
- (cavemanchemistry.com)
Questions
Saponification Values

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HSMG 2006

- (http://cavemanchemistry.com)
- (http://oldwillknott.com) Jennings JScale JS-50x
- (http://cynmar.com) Transfer pipettes, phenolphthalein
- (http://boyercorporation.com) NaOH, KOH
- Auto Parts Store: battery acid
- Walmart, etc.: Denatured alcohol
Equations

- 33.52 g acid = 9.96 g NaOH
- 20.00 g of palm oil to make soap
- 16.68 g acid = blank (100.00 g of 6% alcohol)
- 7.02 g acid = soap

\[
? \text{ g NaOH} = 1000 \text{ g Fat} \left( \frac{16.68 - 7.02 \text{ g Acid}}{20.00 \text{ g Fat}} \right) \left( \frac{9.96 \text{ g NaOH}}{33.52 \text{ g Acid}} \right) = 144 \text{ g NaOH}
\]
Preventing DOS

- Use 0.03% EDTA (0.3 g / kg oil) add to lye
- Or 0.07% BHT (0.7 g / kg oil) add to lye
- Or 0.12% Rosemarinic Acid (1.2 g ROE / kg oil) add to oil

- When buying ROE, maximize Rosemarinic Acid content if possible
- Ask for MSDS when you purchase EDTA, avoid nitrilotriacetate impurity
- Avoid Calcium and Iron in water used for soapmaking
EDTA Safety


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• Conclusion: EDTA is safe for use in cosmetics