Little White Lyes

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Apr 2015

$Revision: 1.2 $

Acknowledgements

- Derek Hodges/Essential Depot
- Mike Lawson/Columbus Foods
- Hampden-Sydney College
  - Matthew Chapman
  - Jefferson Thompson
  - Mitch Owens

Soapmaking Topics

- Part 1: When Lye Goes Bad
- Part 2: Background Chemistry
- Part 3: Is it possible to lower the alkalinity of soap?
- Part 4: Is it desirable to lower the alkalinity of soap?

These slides may be seen at

CavemanChemistry.com/HscgAlkali2015.pdf

When Lye Goes Bad

First let's refine our vocabulary to avoid confusion.

- Caustic Soda: the white solid in the bottle that will either eat your face off or make soap from oil
- Sodium Hydroxide: the principle component of caustic soda
- Lye: a solution of caustic soda in water

Certificate of Analysis

ESSential Depot®
GREENER LIFE ESSENTIALS

2029 US Hwy 27 South
Sebring, FL 33870
866-840-2495

QUALITY CERTIFICATE

Ship Date	Shipment No.
03/06/2015	965807-00
Purchase order Item	
532434 – Orl	
Delivery Item	
BMS0935789	
Order Item	
918458	
Customer number	Net Wt: 42,000.000 LB
405065	
Ship Point: Lake Charles	

Container: 225894

Seal: 24628

Material: 8000289 CAU SODA PELS
50 LB BAG

Batch: LCJ2814

Package Qty: 60 BAG

Characteristic	Unit	Value	Lower Limit	Upper Limit	METHOD
FE AB	Ppm	1		15	ICP
HG AB	Ppm	0.0		0.1	HG BY CVAA
NA2CO3 AB	%wt	0.35		1.60	CD-27-1
NA2O	%wt	77.6	74.4	100.0	CD-27-1
NACL AB	%wt	0.01		2.20	NP-04-04
NAOH	%wt	99.9	96.0	100.0	CD-27-1
NI AB	ppm	1		9	ICP
THR 16M	%wt	99	90	100	NP-05-14
THR 60M	%wt	0		2	NP-05-14

NSF Standard 60 Drinking Water Treatment Chemicals – This product is certified for a maximum use level of 100.

IMPORTANT: All information provided is believed to be accurate and complete. The data provided is representative of the product quality on the date of analysis for the lot number indicated. This certificate of analysis may not include all of the constituents of the product. Persons using this information should make their own determination regarding its suitability for their particular application. This certificate of analysis shall not in any way limit or preclude the operation and effect of the applicable terms and conditions of sale.

Certificate of Analysis

Characteristic	Unit	Value	Lower Limit	Upper Limit	METHOD
FE AB	Ppm	1		15	ICP
HG AB	Ppm	0.0		0.1	HG BY CVAA
NA2CO3 AB	%wt	0.35		1.60	CD-27-1
NA2O	%wt	77.6	74.4	100.0	CD-27-1
NACL AB	%wt	0.01		2.20	NP-04-04
NAOH	%wt	99.9	96.0	100.0	CD-27-1
NI AB	ppm	1		9	ICP
THR 16M	%wt	99	90	100	NP-05-14
THR 60M	%wt	0		2	NP-05-14

Certificate of Analysis

The COA gives you information about the quality of the product as measured by the manufacturer. The most important contaminant, however, is not even listed because it is beyond the control of the manufacturer: water. If you leave caustic soda open to humid air, it picks up water. You can see this by recording the weight of the sample over time. In the extreme case, it will absorb so much that it dissolves in this water. You may have seen spilled caustic soda turn to puddles.

Certificate of Analysis

Caustic soda may be exposed to moisture:

- In the manufacturer’s warehouse
- In the disributor’s warehouse
- In your own workshop

What effect will "bad" caustic soda have on soap?

Simulating Weak Lye

Normally, we make Duckbar's Delight using master batched oil and 50.0% (500 ppt) lye. A bar of soap can then be made using 100.00 g of oil, 28.80 g of lye, and 14.40 g of water. That's equivalent to 14.40 g of NaOH and 28.8 g of H_2O. If, however, our caustic soda has absorbed atmospheric water, 14.40 g of caustic soda will contain less than 14.40 g of NaOH.

Simulating Weak Lye

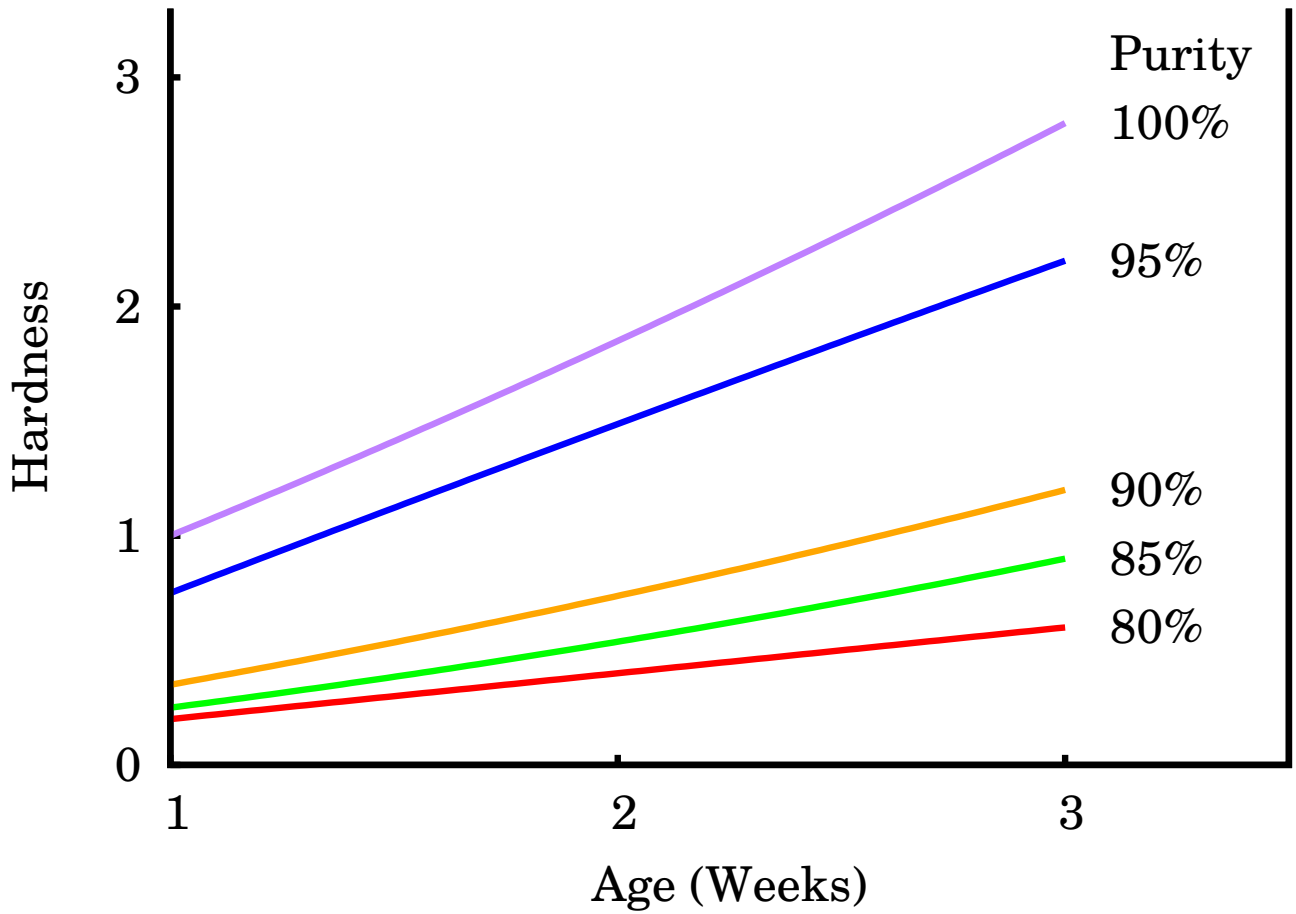
If caustic soda is 95% NaOH and 5% H_2O, then 14.40 g of caustic soda will actually contain only 13.68 g of NaOH and 0.72 g of H_2O. We can simulate this by making bad soap on purpose. We use 100.00 g of oil (as usual), 27.36 g of 50% lye, and 15.84 g of H_2O. This gives us the same amount of NaOH and H_2O as if we had used a caustic soda that was only 95% NaOH.

Simulating Weak Lye

Castic Soda Purity	Oil (g)	Lye (g)	Water (g)	Total (g)
100%	100.00	28.80	14.40	143.20
95%	100.00	27.36	15.84	143.20
90%	100.00	25.92	17.28	143.20
85%	100.00	24.47	18.72	143.20
80%	100.00	23.04	20.16	143.20

The Soil Penetrometer

Soap Hardness



Measuring Caustic Soda Purity

Let's do a titration to determine casutic soda purity. Briefly, we use phenolphthalein indicator to determine how much base it takes to neutralize a given amount of acid. Traditionally, a glass buret is used to measure carefully prepared solutions, but the the advent of cheap, high-quality scales gives us another option. We can weigh solid acids and bases.

MyWeigh Durascale D2 300

300 x .01 capacity and resolution. Only $26.08. Auto off after 60 seconds of inactivity.

Ohaus YA102

100 x .01 capacity and resolution. Only $52.40. Good brand. Auto off after 10-30 seconds of inactivity.

MyWeigh i201

200 x .01 capacity and resolution. $119.48. Rugged. Auto off can be disabled. AC adapter.

Ohaus TAJ202

200 x .01 capacity and resolution. $170.00. Good Brand. Auto off can be disabled. AC adapter.

Measuring Caustic Soda Purity

Procedure summary:

- Analytically weigh some citric acid into water
- Add phenolphthalein indicator
- Analytically weigh some caustic soda until solution turns pink
- Calculate percent NaOH in caustic soda

Analytical Weights

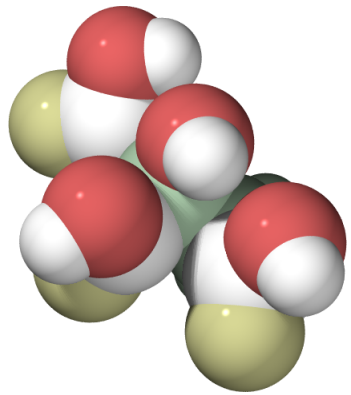
The goal here is not to hit a target weight exactly, but to know exactly how much material was weighed. For example:

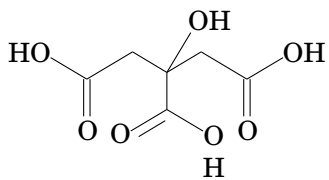
- Place a disposable plastic cup on the balance and press the zero or tare button.
- Add 10-11 grams of citric acid to the cup using a stainless steel spoon and press the tare button.
- Pour citric acid from the disposable cup into a Pyrex measuring cup.
- Return the empty cup to the balance and record the tare weight (this will appear as a negative number). Record all of the digits: 10.XX g (e.g. 10.31 g)

Analytical Weights

Why do we weigh *from* the balance?

Citric Acid





$$H_3Cit + 3\ NaOH = 3\ Na_3Cit + 3\ H_2O$$

Anhydrous Citric Acid

Citric acid comes in two forms: anhydrous citric acid and citric acid monohydrate. Chemically, they are the same, but the water has weight, just as it does for caustic soda. We can check which kind we have:

- Analytically weigh 10.XX grams of citric acid onto aluminum foil. Include the weight of the foil in the tare weight.
- Place it into an oven at 200°F for 1 hour.
- Let the foil cool and reweigh. The weight of the anhydrate will remain unchanged. The weight of the monohydrate will fall to 91% of its original value.

Anhydrous Citric Acid

If you have the monohydrate, you can dry it in the oven. Citric acid for analytical use should be stored in an air-tight container.

Phenolphthalein

Phenolphthalein comes as a dry, white powder or as a solution in alcohol. The concentration is not critical, but a 1% solution in ethanol is convenient. Phenolphthalein is colorless in an acidic solution and pink in an alkaline one. The color change starts at pH 8.2 and ends at 9.8. This makes it a particularly useful indicator for soap work.

Cups and Spoons

We will use a Pyrex 1-Quart measuring cup for the titration. We will need three stainless steel spoons, one to measure citric acid, one to measure caustic soda, and one to stir with. We will also use bathroom-sized disposable plastic cups for weighing.

Measuring Caustic Soda Purity

- Add 500 mL or 2 cups of distilled water to a Pyrex measuring cup.
- Place a disposable cup on the balance and press the tare button.
- Add 10-11 grams of anhydrous citric acid to the cup on the balance using spoon #1 and press the tare button.
- Pour the citric acid into the measuring cup and stir with spoon #2 until completely dissolved.

Measuring Caustic Soda Purity

- Return the empty cup to the balance and record the tare weight. Record all the digits: 10.XX g.
- Add 3 drops of 1% phenolphthatlein solution to the measuring cup. Stir with spoon #2.
- Place a second disposable cup on the balance and press the tare button.
- Add 10-11 grams of caustic soda to the cup on the balance using spoon #3 and press the tare button.

Measuring Caustic Soda Purity

- Use spoon #3 to transfer no more than 6 grams of caustic soda from the cup on the balance to the measuring cup. The solution will turn pink in areas of high pH. Stir with spoon #2 until the caustic soda has completely dissolved. The solution should now be colorless. *Do not press the tare button.*

Measuring Caustic Soda Purity

- Continue transferring caustic soda about 0.05 grams at a time and stir until completely dissolved. The solution will turn pink as the caustic soda dissolves, but will turn colorless again as the citric acid neutralizes it. As you get close to the “endpoint,” the pink color will take longer to disappear. As you get close, you can transfer the caustic soda in smaller increments. *Do not press the tare button.*

Measuring Caustic Soda Purity

- When the pink color remains for more than a minute, you have reached the endpoint. The weight of caustic soda now appears as a negative number on the balance. Record all the digits: Y.YY g.
- %NaOH = 62.46 * 10.XX / Y.YY (use the actual values of XX and Y.YY).

62.46?

$$? \text{ g NaOH} = 100 \ \cancel{g \ caustic \ soda} \left(\frac{10.XX \ \cancel{g \ H_3Cit}}{Y.YY \ \cancel{g \ caustic \ soda}} \right) \left(\frac{1 \ \cancel{mol \ H_3Cit}}{192.12 \ \cancel{g \ H_3Cit}} \right) \left(\frac{3 \ \cancel{mol \ NaOH}}{1 \ \cancel{mol \ H_3Cit}} \right) \left(\frac{40.00 \text{ g NaOH}}{1 \ \cancel{mol \ NaOH}} \right)$$

$$C_{\text{NaOH}} = 62.46 \left(\frac{10.XX}{Y.YY} \right) \% \text{ NaOH}$$

Using the Durascale

- Add 10+ g of anhydrous citric acid to a weighing cup. Press Tare. Dump citric acid into 500 mL of distilled water and return empty cup to the scale. Record weight, 10.XX g.
- Add a few drops of 1% phenolphthalein.
- Fill a weighing cup with caustic soda and record total weight, including the cup, 10.ZZ g.
- Press Tare and transfer about 6 g of caustic soda to solution.
- Continue adding caustic soda until the endpoint is reached.
- Notice that the scale turned itself off while your were not looking.

Using the Durascale

- *Don't freak out.* Turn the scale back on. Remove the weighing cup and record the weight of leftover caustic soda: Y.YY.
- %NaOH = 62.46 * 10.XX / (10.ZZ - Y.YY)

Dealing with Bad Caustic Soda

To boil the water out of citric acid, you need only heat it to 200°F, something easily accomplished in a home oven. To do the same thing for sodium hydroxide, you would have to heat it above 760°F. Not so easy. If water is the only contaminant, consider that you are about to add your caustic soda to water. You can use the percent NaOH to correct for the absorbed water.

Dealing with Bad Caustic Soda

For example, suppose you want to weigh 16 ounces of NaOH and you know that your caustic soda is 95% NaOH. All you have to do is divide 16 by 0.95:

oz caustic soda = 16 oz NaOH / 0.95 = 16.84 oz caustic soda

As long as water is the only contamination, this simple calculation will allow you to use caustic soda that has absorbed moisture.

Carbon Dioxide

Carbon dioxide is the other major contaminant that can spoil your caustic soda. Like water, it is picked up from the atmosphere when you leave your caustic soda open to the air. It reacts with sodium hydroxide to produce sodium carbonate. Remember sodium carbonate from the COA?

We can test for it, but there is no easy way to get rid of it. To check your caustic soda, make a 50% solution in distilled water, stirring occasionally to prevent clumps from forming. Sodium carbonate is not soluble in concentrated sodium hydroxide. If it is present, you will see it floating on the surface. A little bit cannot be avoided. If there is a lot, however, your caustic soda is not fit for making soap.

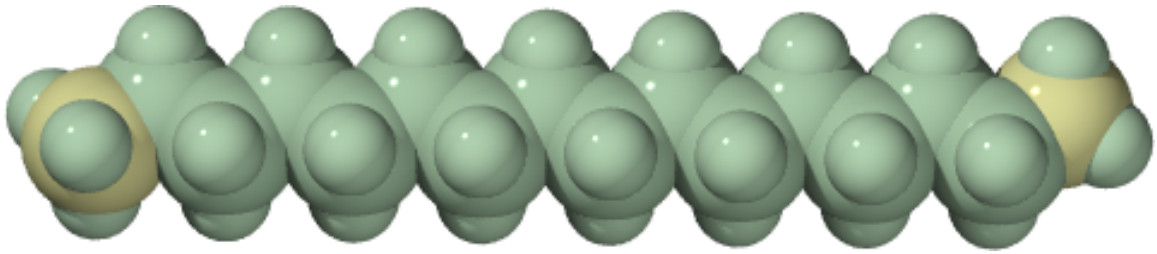
Carbon Dioxide

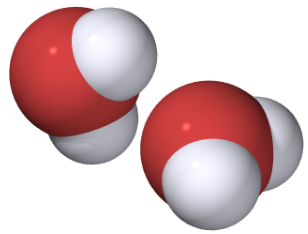
An ounce of prevention is worth a pound of cure. Keep your citric acid and caustic soda in sealed containers, protected from the atmosphere, and both can have very long shelf lives.

Background Chemistry

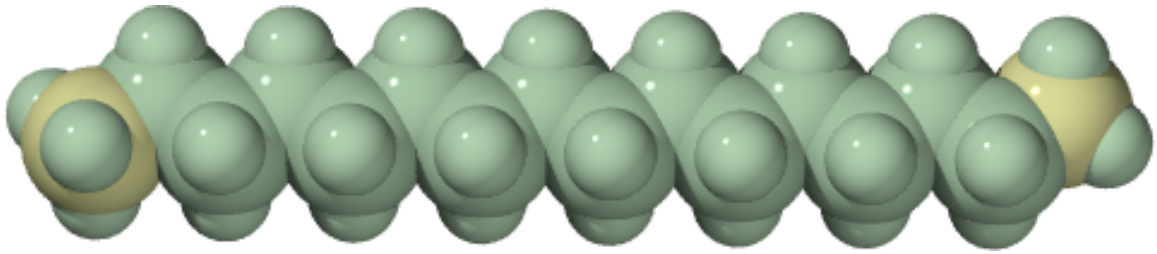
Oil and water don’t mix.

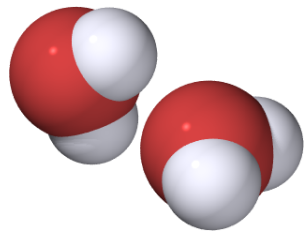
Oil and Water



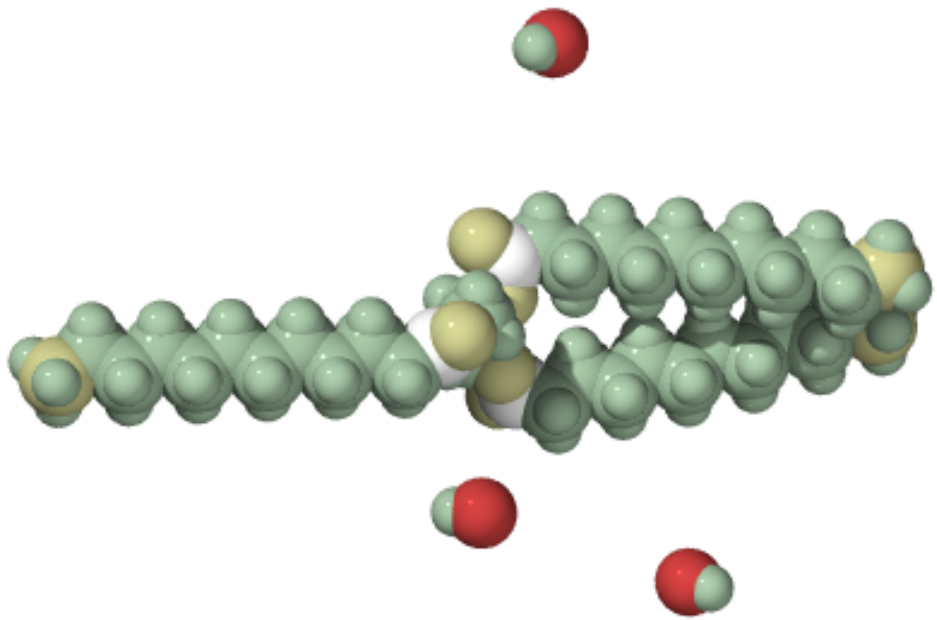


Nerds and Cheerleaders

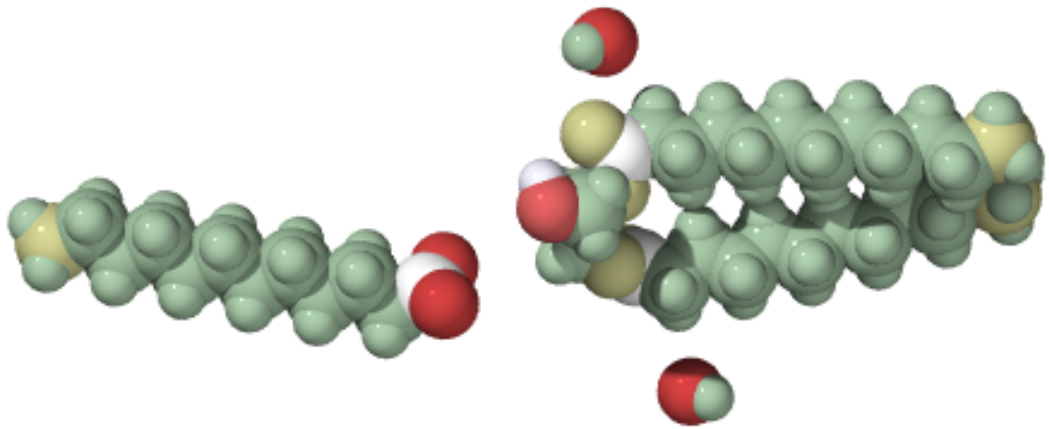




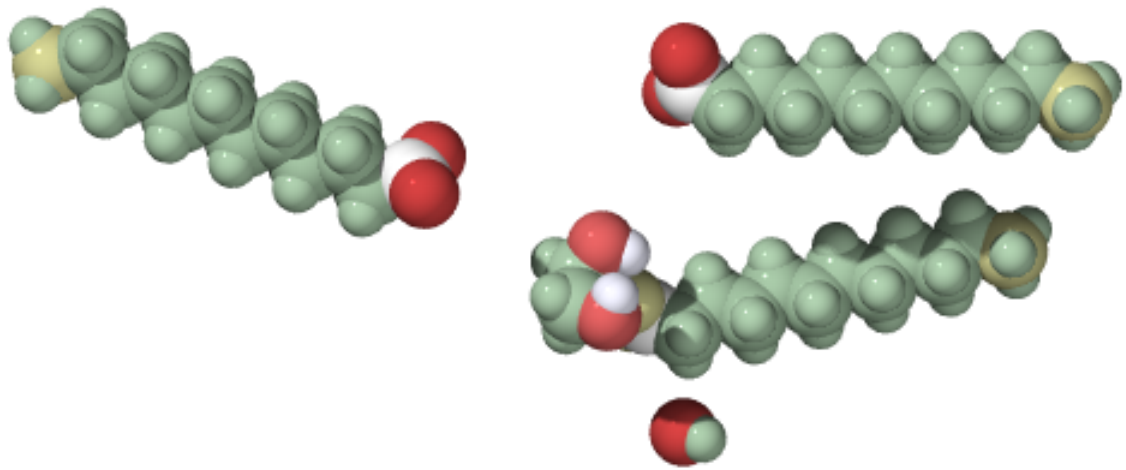
Oil and Lye



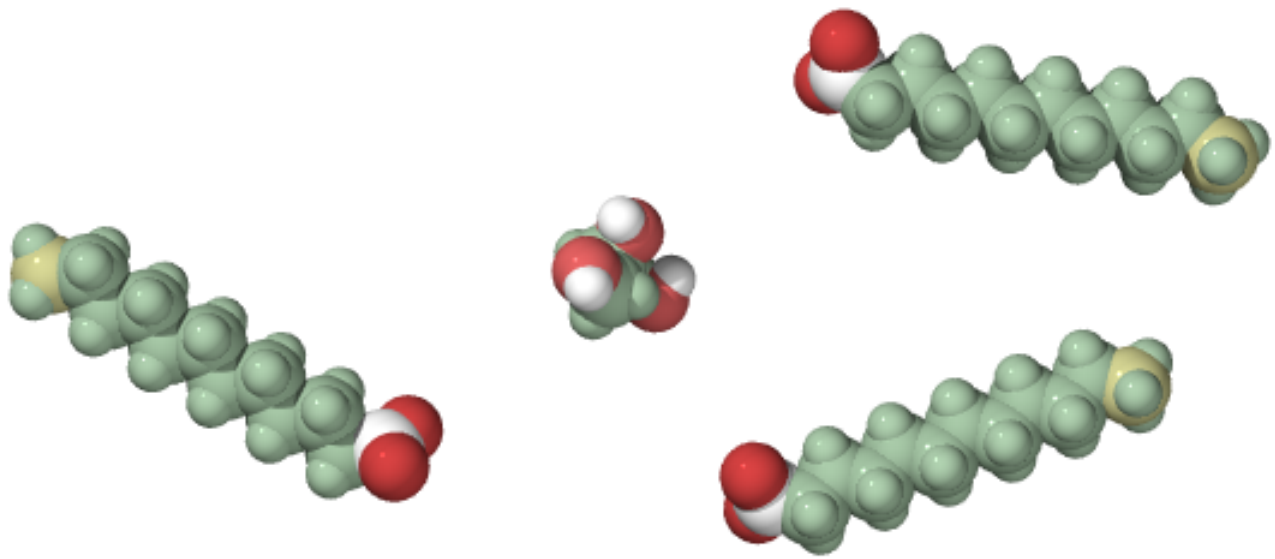
One Soap



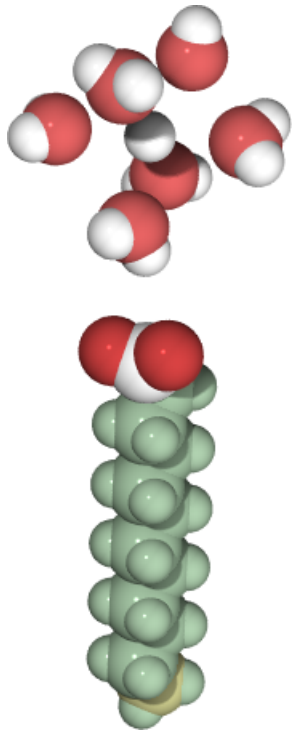
Two Soaps



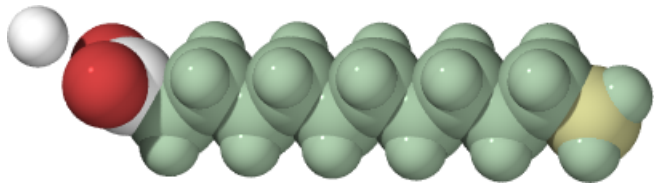
Three Soaps and a Glycerin



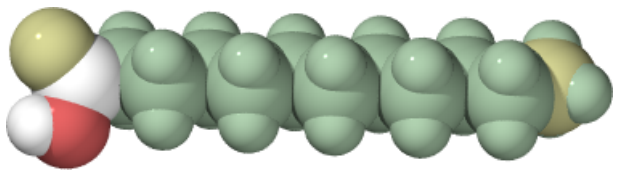
Soap: A Nerdy Cheerleader



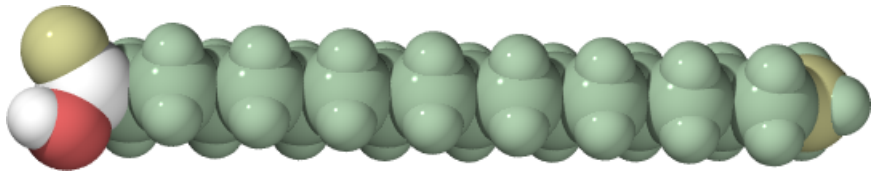
Sodium Laurate

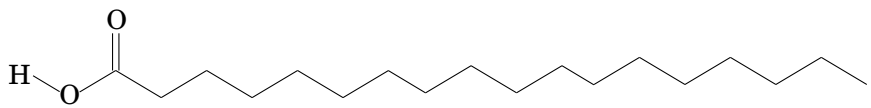


Lauric Acid

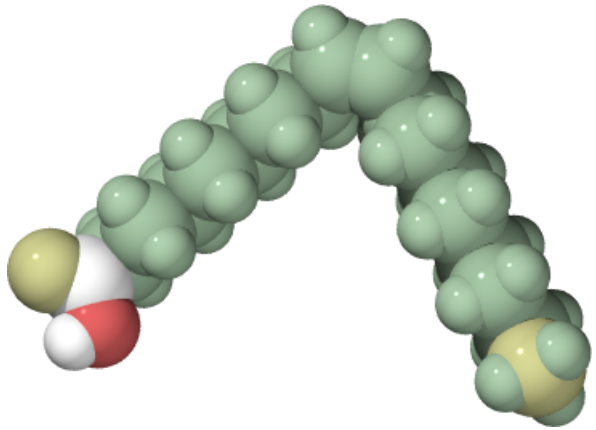


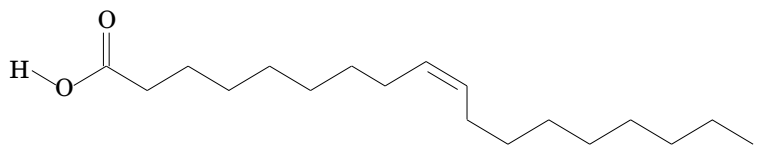
Stearic Acid





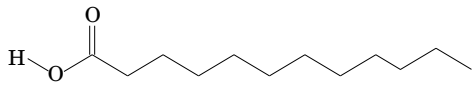
Oleic Acid





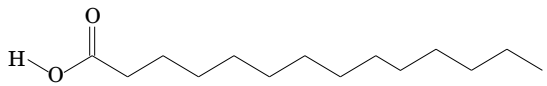
Four Saturated Fatty Acids

lauric acid



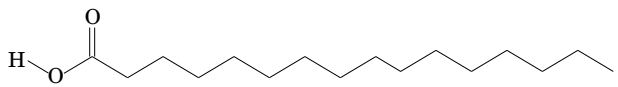
200.32 g/mol dodecanoic acid, $C_{11}H_{23}COOH$

myristic acid



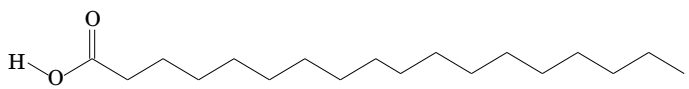
228.42 g/mol tetradecanoic acid, $C_{13}H_{27}COOH$

palmitic acid



256.42 g/mol hexadecanoic acid, $C_{15}H_{31}COOH$

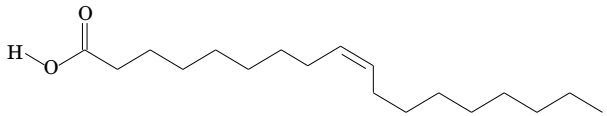
stearic acid



284.48 g/mol octadecanoic acid, $C_{17}H_{35}COOH$

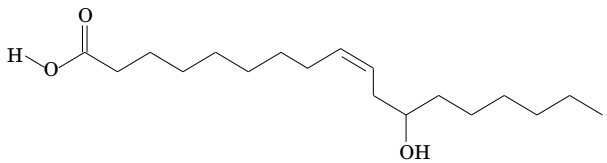
Four Unsaturated Fatty Acids

oleic acid



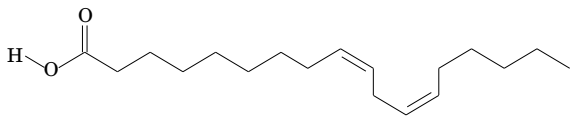
282.46 g/mol 9-octadecenoic acid, $C_{17}H_{33}COOH$

ricinoleic acid



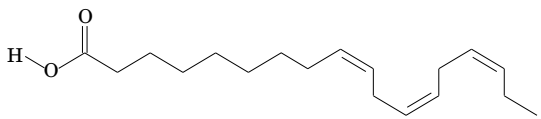
298.45 g/mol 12-hydroxy-9-octadecenoic acid, $C_{17}H_{33}OHCOOH$

linoleic acid



280.46 9,12-octadecadienoic acid, $C_{17}H_{31}COOH$

linolenic acid

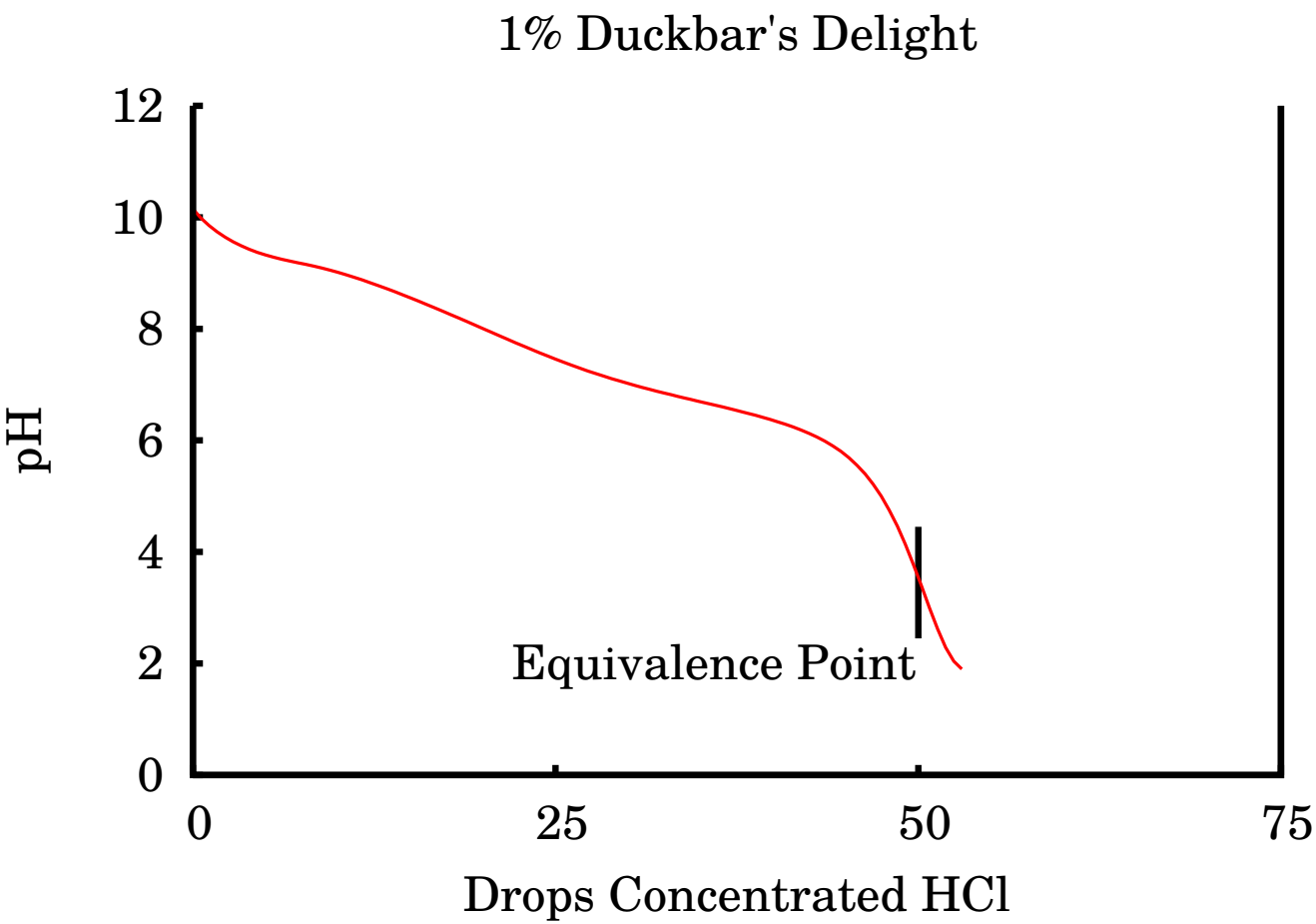


278.44 g/mol 9,12,15-octadecatrienoic acid, $C_{17}H_{29}COOH$

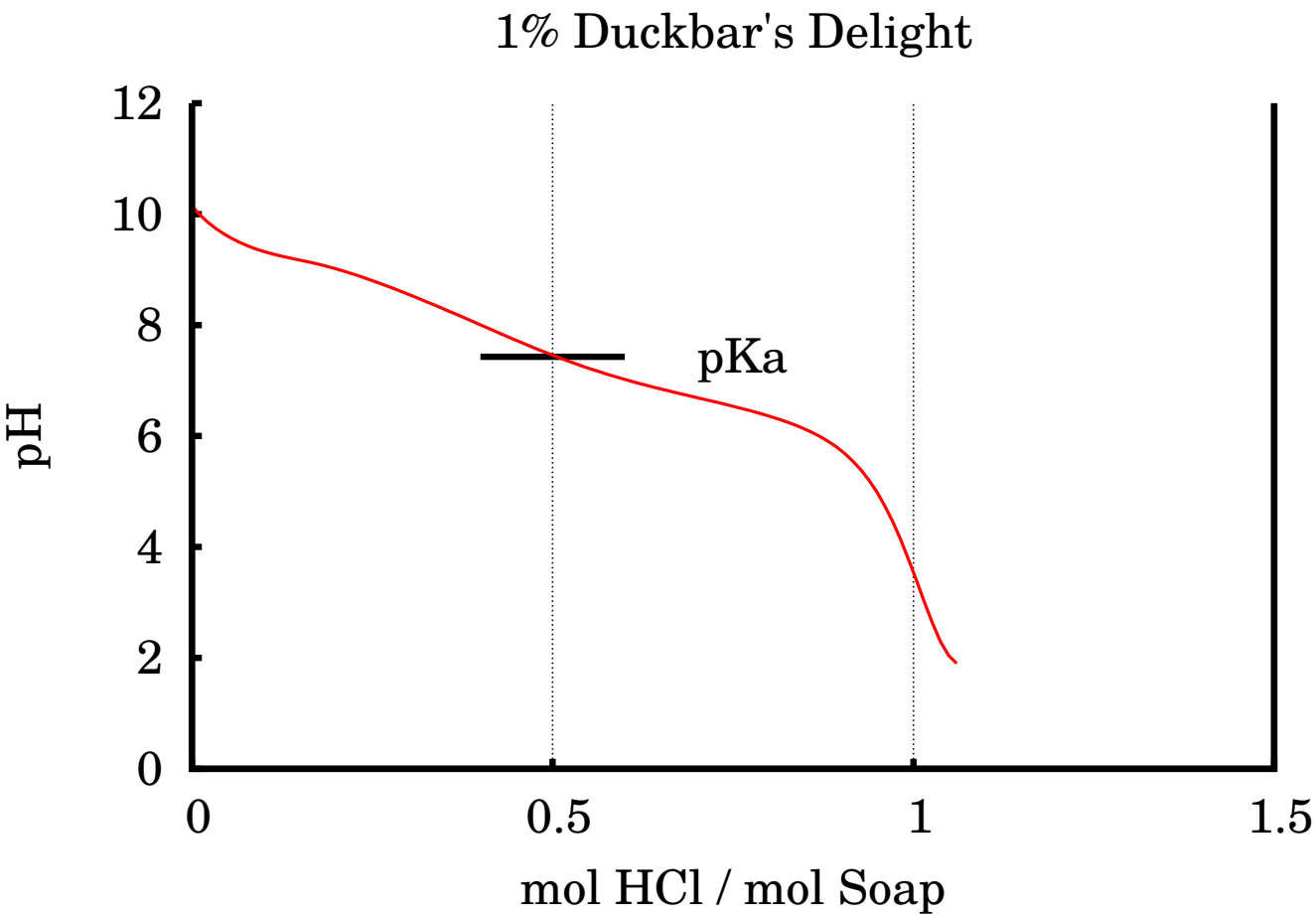
Soap Titration

- Dissolve 1 gram of soap in 100 grams of distilled water.
- Place a calibrated pH probe in this solution.
- Add concentrated hydrochloric acid one drop at a time.
- Record the pH after each drop is added.

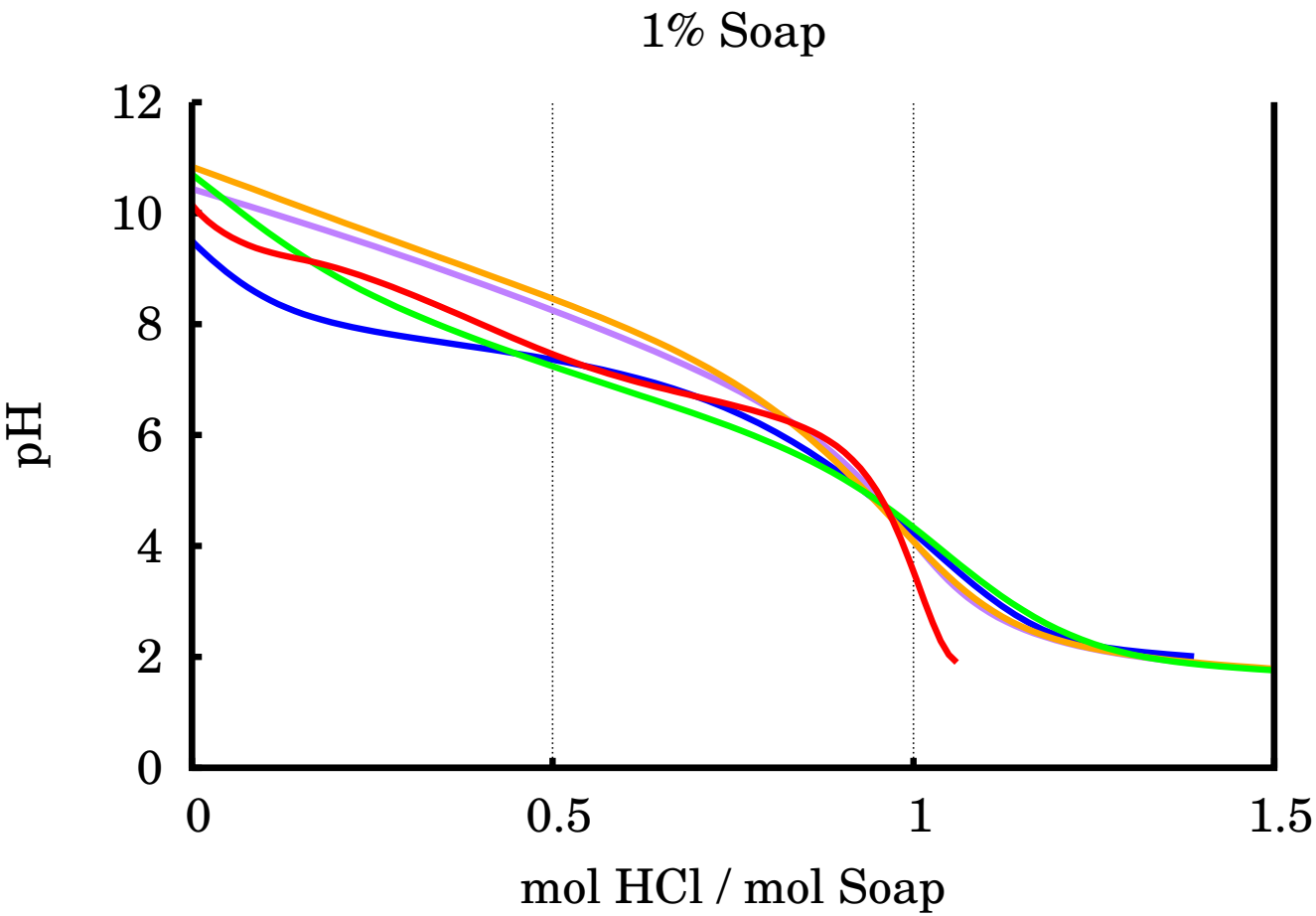
Soap Titration



Soap Titration



Soap Titration



pH Ranges for Fatty Acids/Soaps

Fatty Acid	pKa	pH*	Soap
Lauric Acid	7.5	10.1	Sodium Laurate
Myristic Acid	8.2	10.4	Sodium Myristate
Palmitic Acid	8.8	10.7	Sodium Palmitate
Stearic Acid	10.2	11.4	Sodium Stearate
Oleic Acid	9.9	11.2	Sodium Oleate
Linoleic Acid	9.2	10.9	Sodium Linoleate
Linolenic Acid	8.3	10.4	Sodium Linolenate

* pH for 1% solution of pure soap in water.

Kanicky *et al, Langmuir,* 2000, 16(1), pp. 172-177. Kanicky *et al, Journal of Colloid and Interface Science,* 2002, 256, pp. 201-207.

pH Ranges for Real-World Soaps

Fatty Acid	pKa	pH*	Soap
Coconut Acid	7.2	9.7	Sodium Cocoate
Castor Acid	7.5	9.5	Sodium Castorate
Palm Acid	8.2	10.3	Sodium Palmate
Olive Acid	8.4	11.0	Sodium Olivate
Delight Acid	7.4	10.2	Sodium Delightate

* pH for 1% solution of pure soap in water.

When pH is below pKa, there is more fatty acid present than soap.

Forced Acidification of CP Soap

Can we practically lower the pH of cold process soap?

We made a bar of Duckbar's Delight and cut it into four pieces. The first piece was stored in a sealed bag. The second was allowed to cure in air. The third was stored in a bag filled with carbon dioxide gas. The fourth was stored in a bag that contained a cup of household vinegar.

Forced Acidification of Coconut Oil Soap

Atmosphere	Start pH	End pH
Sealed	10.1	9.9
Air	10.1	9.9
CO_2	10.1	9.6
Vinegar	10.1	9.6

Forced Acidification of Castor Oil Soap

Atmosphere	Start pH	End pH
Sealed	9.5	9.5
Air	9.5	9.4
CO_2	9.5	9.2
Vinegar	9.5	8.8

Forced Acidification of Palm Oil Soap

Atmosphere	Start pH	End pH
Sealed	10.3	10.2
Air	10.3	10.2
CO_2	10.2	10.1
Vinegar	10.3	9.9

Forced Acidification of Olive Oil Soap

Atmosphere	Start pH	End pH
Sealed	11.4	10.3
Air	11.4	10.3
CO_2	11.4	10.3
Vinegar	11.4	9.9

Forced Acidification of CP Soap

We were unsuccessful in significantly lowering the pH of CP soap. The best prospects for future work remain with HP and liquid soaps, which can be acidified after saponification is complete. It might then be practical to lower pH down to the neighborhood of pKa. Potential acidifiers would include vinegar, citric acid, and fatty acids.

Why Lower the pH of Soap?

- The skin is slightly acidic.
- Washing with soap makes skin temporarily alkaline.

Correlation Between pH and Irritant Effect of Cleaners Marketed for Dry Skin

Baranda, et. al. published this report in the *Intrnational Journal of Dermatology,* 2002, 41, 494-499. They placed 8% soap emulstions on the forarms of 30 test subjects for *5 consecutive days* and rated the skin irritation by a variety of techniques. The products remained on the skin for 24 hrs the first day and 6 hours for each consecutive day.

Correlation Between pH and Irritant Effect of Cleaners Marketed for Dry Skin

They found that all the cleaning products were irritants under these conditions. The least irritating products were low pH syndet formulations (pH 5.2 to 7.7). The true soaps all had pH between 9.9 and 12.4. The irritancy of high pH soaps and detergents were similar to one another.

A Comparative Study of the Effects on the Skin of a Classical Bar Soap and a Syndet Cleansing Bar in Normal Use Conditions and in the Soap Chamber Test

Baren, et. al. published this report in *Skin Research and Technology,* 2001, 7, 98-104. They had 50 women wash with either soap or a syndet bar under real world conditions for 10 consecutive weeks. Measurements of skin irritation showed no difference between the soap and the syndet bar.

A Comparative Study of the Effects on the Skin of a Classical Bar Soap and a Syndet cleansing Bar in Normal Use Conditions and in the Soap Chamber Test

In contrast, when both products were tested in the traditional "soap chamber," the soap was found to be significantly more irritating than the syndet bar. They conclude that continuous contact with skin for multiple days at a time is an exaggerated and unrealistic measure of its irritancy.

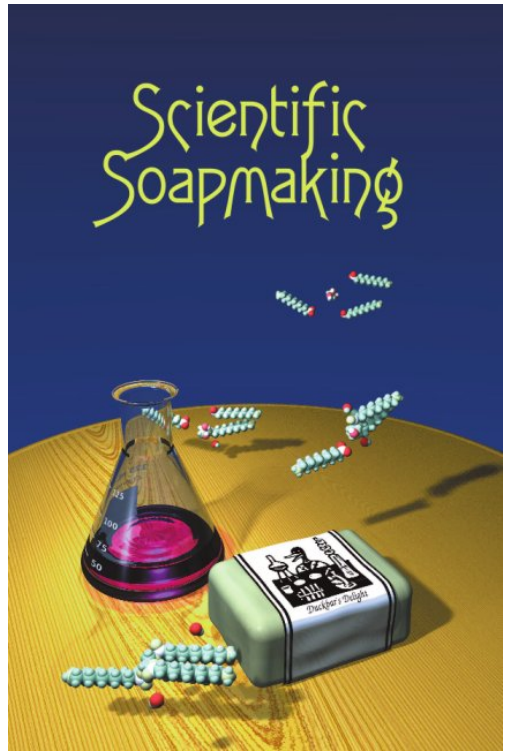
Why Let Soap Remain Alkaline?

- It is hard to lower the pH significantly.
- High pH soaps (12) were not found to be more irritating than low pH soaps (10) when used in the soap chamber.
- Soap (pH 9.6) was not found to be more irritating than a syndet bar (pH 6.9) under normal use conditions.

Summary

- Caustic soda should be protected from moisture.
- Caustic soda contaminated with moisture can cause soap to be soft.
- Soapmakers can test their caustic soda for moisture contamination.
- Caustic soda contaminated with water can still be used to make soap if you correct for it.
- CP soap is very resistant to changes in pH.

Scientific Soapmaking



Keep asking questions!