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The "Water Discount"

by Kevin M. Dunn

All soapmakers are familiar with the notion of a lye discount. In order to prevent the possibility of excess lye in the finished soap, less lye is used than would be needed for complete saponification. This is most frequently expressed as a percentage. If, for example, a mixture of oils requires 100 g of sodium hydroxide for complete saponification, we might choose to use 95 g instead (a 5% discount).

The notion of a discount implies we know how much sodium hydroxide is required for compete saponification. We use a lye calculator or a table of saponification values to determine this amount. Ultimately, these calculations rest on the saponification values measured by someone, somewhere, on a particular sample of oil. Because saponification values vary from one sample to the next, the oil you are using might be slightly different from the one that was used to make the table and largely because of this uncertainty, we choose to discount lye.

The notion of a discount implies that there is a normal, correct, or standard value to be discounted. While you might not know the exact saponification value of a particular sample of oil, it does, in fact, have a saponification value that could be measured if you chose to do so. Saponification values exist because saponification is a reaction between an alkali (e.g. sodium hydroxide) and an oil:

$$\text{Oil} + 3\ NaOH = \text{Glycerol} + 3\ \text{Soap}$$

Each oil molecule requires three molecules of sodium hydroxide for complete saponification. Anything less than this results in incomplete saponification, a price we are willing to pay to avoid the possibility of excess alkali in the finished soap. Thus, there is a normal, correct, standard amount of sodium hydroxide and it makes sense to talk about a discount from that amount. The same cannot be said of water.

Water does not appear in the saponification reaction. There is no fixed relationship between the number of molecules of water needed for a molecule of oil. Water is simply used to dissolve the sodium hydroxide so that it can react with the oil.

Where, then, do we get the notion that there is a normal, correct, or standard value for the amount of water to be used in a soap formula?

I surveyed the soap recipes from four books in my collection. The earliest, Ann Bramson's *Soap: Making It, Enjoying It* [1] may be considered the founding document of the handcrafted soap movement and has introduced countless soapmakers to the craft. Published in 1972, it lacks any discussion of the chemistry of saponification, but the recipes imply that there are correct amounts of both sodium hydroxide and water. While an examination of the recipes shows that they were correctly formulated with regards to sodium hydroxide, the book does not show how these amounts were determined. The amount of water in the recipes resulted in lye solutions which ranged from 25% - 27% sodium hydroxide, the average being 26%.

Susan Cavitch's 1997 *The Soapmaker's Companion*[2] includes an extensive discussion of chemistry, including the use of saponification values. Cavitch also discusses the amount of water to be used and understands that the amount may be varied, depending on circumstances such as the mixing temperature. She recommends a starting value of 30%. In her recipes, however, she tends to be somewhat lower, ranging from 26-29%, with an average concentration of 27%. In fact, 21 of the 26 recipes use lye concentrations of exactly 27%. Both Bramson and Cavitch adopt concentrations of 26-27% and this may be the reason that many lye calculators use 27% as the normal, correct, standard lye concentration.

Later books have trended toward higher lye concentration. Robert McDaniel's 2000 *Essentially Soap*[3] uses concentrations between 33% and 38%, with an average of 34%.

Anne Watson's 2007 *Smart Soapmaking*[4] uses concentrations between 30% and 37%, with an average of 33%.

Watson briefly discusses the choice of concentration, claiming that saponification and curing are faster when less water is used. She also says that it is harder to dissolve the lye at higher concentrations and that the solution may give off more fumes.

Experimental Soap Processing

I have undertaken to explore the effect of lye concentration on the saponification process. I made a series of soaps which were processed identically except for the lye concentration and then measured their weight, hardness, alkalinity, and moisture content over an 8-week curing period. I made single-oil soaps from coconut, palm, and olive oils. I also made a four-oil soap from a blend of coconut, palm, olive, and castor oils.

All soaps were prepared using a 50% sodium hydroxide solution, with extra water added to some soaps to bring the sodium hydroxide concentration to 33.33% and 25%. The soaps consequently span a range of lye concentration from 50% (higher than most soapmakers use) to 25% (lower than most soapmakers use).

All of the soaps in this study were prepared identically except for the lye concentration. 50% lye was prepared by mixing equal weights of sodium hydroxide and distilled water. The lye was prepared in advance and used as needed. Each bar of soap was prepared from 100 g of oil and a standard weight of 50% lye.

For each oil or oil blend, three bars of soap were produced. The first contained no additional water and so the effective lye concentration was 50%. I added water to the second bar equal to half the lye weight, resulting in an effective lye concentration of 33.33%. I added water to the third bar equal to the lye weight, resulting in an effective lye concentration of 25%. Thus all three bars contained exactly the same proportion of sodium hydroxide to oil, but varied in their moisture content.

The composition of each bar may be expressed as a formula giving the relative proportions of oil, lye, and water. The three coconut oil soap, for example, had formulas:

Coconut1000Lye348 (low-water)
Coconut1000Lye348Aq174 (medium-water)
Coconut1000Lye348Aq348 (high-water)

For each soap, the lye weight was 0.348 times the oil weight. The first of these had an effective lye concentration of 50%, the second 33.33%, and the third 25%. These soaps will be described as low-water, medium-water, and high-water, respectively.

For each bar of soap, 100 g of oil was weighed into a 500-mL polypropylene bottle. This was followed by the water, if needed, and then the lye. The lid was screwed onto the bottle and was placed on a modified electrical paint shaker, where it was shaken vigorously for 15 seconds. The bottle was then gently swirled as the soap thickened for a period of 2 - 5 minutes, depending on the rate of thickening. The soap was poured into a singlebar mold from Upland Soap Factory and placed into a roaster oven set to 60±C (140±F) for four hours. This time and temperature had been previously determined to be sufficient for complete saponification.

The day after mixing, each bar was removed from the mold and tested for alkali concentration, expressed as part per thousand (ppt) of NaOH. This was determined by dissolving 1 - 2 g of soap in ethyl alcohol and titrating with a standard citric acid solution, using phenolphthalein as an indicator. Some soaps were found not to be alkaline and were titrated with a standard KOH solution to determine the amount of acid (presumably fatty acid) present. This was expressed as a negative alkali concentration, expressed as ppt NaOH for consistency with the other alkali measurements. An alkali concentration less than 1 ppt should be considered safe for use and most soaps eventually had negative alkali concentrations, meaning that they contained more fatty acid than free alkali. For each bar, the alkali concentration at the top and bottom of the bar were measured independently to check for possible separation of the soap.

Each soap was then weighed about once per week for a period of at least 8 weeks. In addition, the hardness of each bar was measured using a soil penetrometer. This penetrometer has a spring-loaded foot with a diameter of 0.25 inch. The penetrometer foot is pressed into the soap to a depth of 0.25 inch and the hardness can then be read from a scale which records the force used to press the foot into the soap. The hardness ranges from 0- 4.5 kg/cm2. For harder soaps, I devised a 0.125 inch foot that slips over the standard foot. From measurements on numerous soaps, I determined a scale factor of 2.9 to convert measurements from the smaller foot to the larger one. Thus I was able to measure soap hardness from 0-13 kg/cm2.

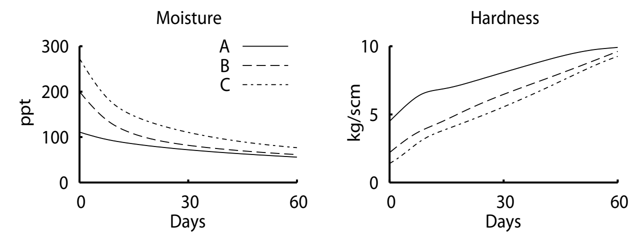
The soap cured on a chrome-plated rack and lost weight as water evaporated. Since I knew the initial moisture content and the weight of the water lost to evaporation, it was possible to calculate the moisture content of each bar from week to week without removing additional samples. At the end of the curing period, the alkali concentration was determined at the top and bottom of the bar for comparison with the initial values. The final alkali test marked the end of the study for each bar.

Palm Oil Soap

Palm oil was the first oil I investigated. Figure 1 shows the data for three palm oil soaps, each containing an identical amount of sodium hydroxide but different amounts of water. Soap A was the low-water soap, B the medium-water soap, and C the high-water soap.

Figure 1. Palm Oil Curing

Batch Code KMD2007.12.27		Moisture/ppt		Alkali/ppt NaOH			
		Initial	Final	Initial		Final	
				Top	Bottom	Top	Bottom
A	Palm$_{1000}$Lye$_{286}$	111	54	1.8	4.9	0.3	0.9
B	Palm$_{1000}$Lye$_{286}$Aq$_{143}$	200	60	1.8	1.4	-1.7	-0.2
C	Palm$_{1000}$Lye$_{286}$Aq$_{286}$	273	74	0.5	0.3	-1.7	-0.1



The low-water soap had the least amount of moisture, both at the beginning and at the end of the 60-day study period. The low-water soap had an initial moisture concentration of 111 ppt. The medium-water soap cured for 14 days and the high-water soap for 31 days before reaching this concentration. As shown in the first graph, however, the moisture decreased steadily over this period and it would appear that eventually all three soaps will contain the same amount of moisture. If you were to make medium-water soap rather than high-water soap, you would save about 2 weeks of curing time. If you were to make low-water soap, you would save another 2 weeks.

As the moisture concentration decreased, the hardness increased. The low-water soap had an initial hardness of 4.5, and it took the other two soaps 16 and 25 days, respectively, to attain this hardness. While the low-water soap was initially much harder than the other two, by the end of the study period the gap had closed to the point that all three soaps were very hard indeed. As in the case of moisture, it would appear that eventually they will have the same hardness. And it would appear that using less water saves about 2 weeks of curing from one soap to the next.

All three of the soaps were alkaline when removed from the mold 1 day after mixing. The bottom of the low-water bar was most alkaline, but after 60 days all three bars had acceptable alkali concentrations on the top and bottom of each bar. The medium- and high-water bars, in fact, had negative alkali concentrations, meaning that they were more acidic than the phenolphthalein indicator. The low-water palm bar was the only one to remain alkaline after 60 days. In retrospect, it may be that less lye should have been used, but even for this bar the total alkali concentration was lower than the recommended threshold (1 ppt) given by many industrial soap books.

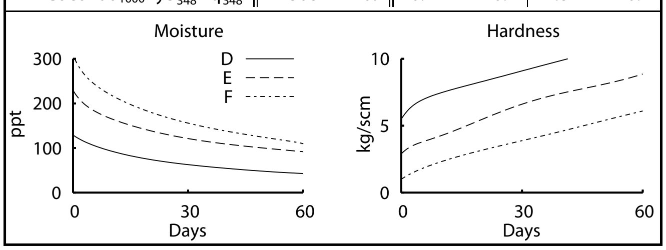
In the case of palm oil, the amount of water used to make soap has the greatest impact on the time required for curing. Less water at the beginning translates into a harder bar containing less moisture. There appears to be no danger in using less water, though it may be that for this oil less water translates into a slightly more alkaline bar.

Coconut Oil Soap

Many of the observations on palm oil soap carry over to coconut oil (Figure 2). The low-water soap was harder and contained less moisture and more alkali than the other two. The coconut oil soaps lost moisture less rapidly, however, than the palm oil soaps, even though they were cured on the same rack over approximately the same time period. The medium- and high-water soaps remained significantly softer than the low-water soap, even after 60 days. It took 25 and 46 days, respectively, for the medium- and high-water soap to attain the initial moisture concentration of the low-water soap. It took 19 and 52 days for them to attain the initial hardness of the low-water soap. The time savings that follows from using less water is more evident for coconut oil soaps than for palm oil soaps.

Figure 2. Coconut Oil Curing

Batch Code KMD2008.1.8		Moisture/ppt		Alkali/ppt NaOH			
		Initial	Final	Initial		Final	
				Top	Bottom	Top	Bottom
D	Coconut$_{1000}$Lye$_{348}$	129	41	0.4	0.5	-0.6	-0.3
E	Coconut$_{1000}$Lye$_{348}$Aq$_{174}$	229	88	-0.1	-0.2	-1.7	-1.0
F	Coconut$_{1000}$Lye$_{348}$Aq$_{348}$	308	109	0.1	0.2	-1.8	-0.4



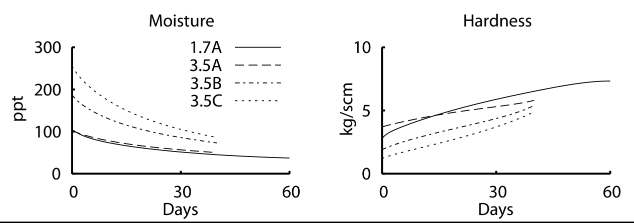
All of the coconut oil soaps contained less then 1 ppt alkali 1 day after mixing. By the end of the study period, they were all more acidic than the phenolphthalein indicator and were safe for use. Because coconut oil soaps take longer to lose moisture than do palm oil soaps, the advantages of using less water are more pronounced for these soaps.

Olive Oil Soap

My initial tests of olive oil soaps ran into trouble. While the low-water soap reached trace within a few minutes, the medium- and high-water soaps did not. Eventually, I got tired of waiting and processed them as usual, but these two soaps separated in the mold and were obviously unsatisfactory. A chalky, lye-heavy soap settled to the bottom of each mold and unsaponified oil rose to the top. Rather than give up on these soaps, I decided to accelerate trace by adding 1 gram of clove oil to each soap. This produced solid bars for all three moisture levels, but there was still some obvious separation of the high-water soap. The original clove-free, low-water soap is included in Figure 3 for comparison.

Figure 3. Olive Oil Curing

Batch Code KMD2008		Moisture/ppt Initial	Moisture/ppt Final	Alkali/ppt NaOH Initial Top	Initial Bottom	Final Top	Final Bottom
1.7A	Olive$_{1000}$Lye$_{264}$	104	36	0.3	0.2	-3.2	-0.4
3.5A	Olive$_{990}$Clove$_{10}$Lye$_{259}$	103	50	-0.4	-0.7	0.0	0.0
3.5B	Olive$_{990}$Clove$_{10}$Lye$_{259}$Aq$_{130}$	187	73	-0.4	-0.4	-0.0	-0.0
3.5C	Olive$_{990}$Clove$_{10}$Lye$_{260}$Aq$_{260}$	256	86	-0.7	6.2	-0.0	-0.0



The olive oil soaps followed the usual trends in hardness and moisture concentration. It took 19 and 32 days for the medium- and high-water soaps to reach the initial low-water moisture level. It took 12 and 19 days for them to catch up in hardness. The two low-water soaps, with and without clove oil, were almost identical in moisture and very close to one another in hardness.

Only the high-water soap had an unacceptably high alkali concentration when removed from the mold, a consequence of its partial separation. At the time of writing, 60 days have not passed since the clove-oil soaps were mixed and so the final alkali concentrations remain to be determined.

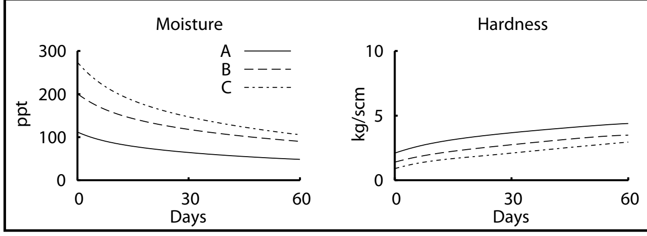
Four-Oil Soap

The single-oil soaps may give us some insights into the role of water in saponification and curing, but handcrafted soap is generally made from a blend of oils. To complete the study, I chose a blend of olive, palm, coconut, and castor oils modeled after the "SoapQuick" blend from Mission Peak Soap [5]. My blend contained olive oil in place of high-oleic canola oil and for brevity in the formula, I named it Delight. Delight consists of 39% olive oil, 28% palm oil, 28% coconut oil, and 5% castor oil.

The moisture concentration of the three Delight soaps followed the usual pattern. While the hardness increased as expected, the Delight soaps started and remained softer even than the olive oil soaps. This is not to say that they were soft, just softer, and had a consistency typical of what I expect of handcrafted soap. It took 36 and 57 days for the medium- and high-water soaps to reach the initial low-water moisture level. It took 12 and 36 days for them to catch up in hardness. As in the case of the single-oil soaps, time may be saved in curing this soap by using less water at the beginning.

Figure 4. Delight (4 oil) Curing

Batch Code KMD2008.2.17		Moisture/ppt Initial	Moisture/ppt Final	Alkali/ppt NaOH Initial Top	Initial Bottom	Final Top	Final Bottom
A	Delight$_{1000}$Lye$_{288}$	112	48	-0.2	0.2	-1.0	-0.4
B	Delight$_{1000}$Lye$_{288}$Aq$_{144}$	201	89	-0.4	0.3	-3.1	-0.9
C	Delight$_{1000}$Lye$_{288}$Aq$_{288}$	274	104	-0.9	0.9	-3.7	-1.3



While all three Delight bars were solid, there was noticeable separation of the high-water soap. The surface of this soap was oily and upon further investigation, this oil was identified as olive oil, which had separated in the mold. While not as pronounced as in the pure olive-oil soap, the separation is evident in the initial alkali concentration: acidic on the oily top of the bar and alkaline at the bottom of the bar. By the end of the study period, all three soaps were more acidic than the phenolphthalein indicator, but the difference in alkalinity remained evident between the top and bottom of the high-water bar. For this oil blend we can save time in curing by using less water. Using too much water may result in separation of the soap.

Conclusion

As I began this study I expected that low-water soaps would start out harder than high-water soaps, but that they might eventually reach the same hardness. This expectation was born out in all of the soaps studied. I worried that perhaps the low-water soaps might not have enough water to ensure that the oil was thoroughly saponified. This fear was not born out in practice; all of the soaps were low in alkali, most of them immediately upon unmolding. What I did not expect was that there might be such a thing as "too much" water. When olive oil was present, it tended to separate from high-water soaps, leaving the bar underneath more alkaline than it would otherwise have been. I also found that saponification and curing are not synonymous, and take place on very different time scales. Most of the saponification occurred in the first 24 hours for all of these soaps; most of them were continuing to lose moisture even after 60 days.

I am not about to recommend that all soap should be made with 50% sodium hydroxide solutions. I am suggesting that you may use such a concentration if you wish. Starting with this lye solution, you are then free to add additional water or milk to increase the initial moisture concentration. A low-water bar can be expected to be initially harder than a high-water bar, which would be helpful in removing soaps from cavity molds. A high-water formula would be more appropriate for soap that must be cut into bars. A low-water soap generally traces faster and is more resistant to separation than a high-water soap. If you have a problem with slow trace or separation, reducing the amount of water may solve your problem. In none of my experiments did I find that the low-water soap was dangerous. I believe that you can safely experiment with low-water soaps up to and including lye concentrations of 50%. As usual when developing a formula, start out with relatively small batches and increase your batch size as you gain experience with the new formula.

Acknowledgements

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References:

[1] Ann Bramson, Soap: Making it, Enjoying it, 1972, ISBN 0-911104-57-7.

[2] Susan Cavitch, The Soapmaker's Companion, 1997, ISBN 0-88266-965-6.

[3] Robert McDaniel, Essentially Soap, 2000, ISBN 0-87341-832-8.

[4] Anne Watson, Smart Soapmaking, 2007, ISBN 978-0-938497-42-4.

[5] Mission Peak Soap, (www.MissionPeakSoap.com).

[6] Columbus Foods, (www.SoapersChoice.com). All soapmakers are familiar with the notion of a lye discount. In order to prevent the possibility of excess lye in the finished soap, less lye is used than would be needed for complete saponification. This is most frequently expressed as a percentage. If, for example, a mixture of oils requires 100 g of sodium hydroxide for complete saponification, we might choose to use 95 g instead (a 5% discount).

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