Water-Softening Characteristics of Tallow, Soybean, Coconut Oil, and Rosin Soaps[1]

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INSOLUBLE calcium and magnesium soaps are formed upon the addition of soluble soaps of fatty acids or rosin to hard water containing soluble calcium and magnesium salts. Upon continued addition of the soluble soaps, with suitable agitation, a point is reached at which a reasonably permanent lather appears and the water is then said to be "softened."

The housewife is guided in the addition of soap to washing solutions by the development of suds and customarily adds soap gradually with agitation until the water is softened and a suitable layer of suds is obtained. The effectiveness of a commercial soap in softening water is, therefore, of immediate interest to the consumer because most domestic waters contain a certain amount of hardness, the average for the United States approximating 100 p.p.m. as $CaCO_3$. Soaps made from certain stocks are more effective in softening water than are those from others and, hence, smaller amounts are required to yield adequate suds. The general use of mixtures of fats in commercial soaps, as well as the wartime necessity of substituting available stocks for those temporarily scarce or unobtainable, enhances interest in data on the comparative water-softening capacity of soaps derived from various soap making stocks. In the present paper data on the relative amounts of the sodium soaps of fatty acids derived from tallow, coconut oil, soybean oil, and of WW gum rosin required to soften water are reported.

In the experimental study a definite volume of artificially prepared hard water was titrated with the appropriate soap solution, and the volume required to produce a stable lather was determined. Results are expressed as milligrams of fatty acids or rosin in the form of soap required to soften 50 milliliters of 50 p.p.m. hard water.

All of the fatty acid soap solutions contained one gm. of fatty acid per 100 ml. The rosin soap solution was adjusted to five grams of rosin per 100 ml. in order to maintain the rosin soap solution addition at approximately the same volume as that of the fatty acid soaps. The solutions were prepared by dissolving one gm. of fatty acids or five grams of rosin in 25-50 ml. alcohol, then titrating to phenolphthalein with alcoholic sodium hydroxide, adjusting with alcohol to 60 ml. and subsequently diluting to 100 ml. with distilled water. The artificial hard waters were prepared in the desired ratios of calcium to magnesium by diluting carefully analyzed solutions of calcium chloride and magnesium sulphate of approximately 10,000 p.p.m. as $CaCO_3$ to a concentration of 50 p.p.m. as $CaCO_3$.

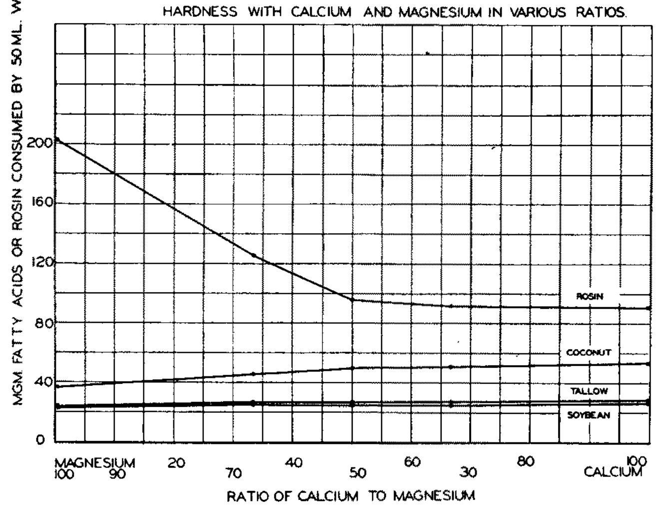
The softening tests were made by titrating slowly in a glass stoppered 8-ounce narrow mouth bottle with intermittent shaking, 50 ml. of the hard water previously neutralized to phenolphthalein, with soap solution until a lather was obtained which was stable for five minutes when the bottle was shaken and placed on its side. In order to avoid the possibility of confusing the "false" magnesium end point with the true end point after complete softening, additional soap solution was added and the permanency of the lather after further standing was confirmed. All titrations were made at room temperature since experiments indicated that up to 125°F. there were no significant changes in water softening capacity. Results are summarized in Table I and are shown graphically in Figure 1.

TABLE I

Effect of Variation of the Calcium: Magnesium Ratio in the Water Hardness on the Amount of Soap Required to Soften

Type of Hardness	Mgm. Fatty Acids and Rosin to Soften 50 Ml. of 50 p.p.m. Water			
	Tallow	Soybean	Coconut	WW Gum Rosin
All Ca	24.0	23.5	36.7	203.0
2/3 Ca - 1/3 Mg	27.5	25.5	46.0	126.0
1/2 Ca - 1/2 Mg	27.0	25.0	50.0	96.0
1/3 Ca - 2/3 Mg	27.5	25.0	51.0	92.0
All Mg	29.0	26.8	53.8	91.0

FIGURE 1—COMPARISON OF SODIUM SOAPS OF TALLOW, SOYBEAN OIL, COCONUT OIL, AND WW GUM ROSIN IN WATER AT 50 PPM HARDNESS WITH CALCIUM AND MAGNESIUM IN VARIOUS RATIOS.



There is a rather extensive literature on the detergent characteristics of rosin, but apparently no attention has been paid to the water-softening properties of rosin soaps alone, or of tallow-rosin soap mixtures. The large amounts of rosin soap required to soften 50 p.p.m. water (Table I) suggested that tallow-rosin soaps might be deficient in water softening capacity. Accordingly, tests were made on soaps of this type at various ratios of tallow fatty acids to rosin. The mixed soap solutions employed contained a total of one gram fatty acids and rosin per 100 ml.

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up to and including 70% rosin, 30% tallow. Above 70% rosin the concentration was adjusted to 5 gm. of the mixed soap stock per 100 ml. The tests were limited to 50 p.p.m. hard water at a single calcium-magnesium ratio of two-thirds Ca, one-third Mg. This is approximately the average ratio of Ca to Mg in domestic waters in the United States.

IT WAS of interest to compare the theoretical amounts of the rosin-tallow soaps of varying ratios, calculated from the quantities of each pure soap necessary to soften, with the actual quantities required. The theoretical weights of any soap containing n components—present in known percentages—to soften a given volume of given hardness water, provided the weight of each pure component to soften the water is known, may be calculated as follows:

Let S_x = weight of mixed soap to soften.
and $S_1, S_2, \text{---------} S_n$ = weight of each individual component required to soften the water completely.

Then $\frac{1}{S_1}, \frac{1}{S_2}, \text{---------} \frac{1}{S_n}$ = portion of total hardness softened by a unit weight of each soap.

Let $F_1, F_2, \text{---------} F_n$ = fractional part of each component in the mixed soap.

Then it follows that

$\frac{F_1}{S_1} + \frac{F_2}{S_2} + \text{---------} \frac{F_n}{S_n}$ = fraction of total hardness softened by a unit weight of mixed soap.

$$\text{therefore } \frac{1}{S_x} = \frac{F_1}{S_1} + \frac{F_2}{S_2} + \text{---------} \frac{F_n}{S_n}$$

$$\text{or (1)} \quad S_x = \frac{1}{\frac{F_1}{S_1} + \frac{F_2}{S_2} + \text{---------} \frac{F_n}{S_n}}$$

Applying formula (1) to the two-component mixture tallow F.A.-rosin, and substituting values for S_1 and S_2 found experimentally,

S_1 = mgm. tallow F.A. required as soap to soften 50 ml. of 50 p.p.m. water = 27.5.
S_2 = mgm. rosin required as soap to soften 50 ml. of 50 p.p.m. water = 126.0.
F_1 = fractional part of tallow F.A. in the stock mixture.
F_2 = fractional part of rosin in the stock mixture.
and (1) becomes
S_x = mgm. of tallow F.A. plus rosin to

$$\text{soften} = \frac{1}{\frac{F_1}{27.5} + \frac{F_2}{126}} = \frac{126 \times 27.5}{126F_1 + 27.5F_2}$$

The actual and the calculated values are recorded in Table II.

TABLE II

Experimental and Calculated Quantities of Mixed Tallow and Rosin Soap Required to Soften

Composition of Mixed Stock, %		Total Weight in Mgm. of Tallow Fatty Acids and Rosin as Soap to Soften 50 ml. of 50 p.p.m. Water	
Tallow F. A.	Rosin	Calculated	Experimental
100	0	27.5	27.5
90	10	29.8	29.5
80	20	32.6	32.8
70	30	35.9	34.2
60	40	40.0	38.5
50	50	45.1	44.0
40	60	51.8	51.0
30	70	60.7	59.3
20	80	73.4	95.0
10	90	92.7	148.0
0	100	126.0	126.0

The results in Tables I and II were based entirely on laboratory scale experiments and, in addition, alcohol was present in the soap solution. This is a condition which does not exist in the practical use of a soap. In order to confirm the laboratory work, some practical water-softening tests were made on several built soaps prepared and spray dried on a plant scale.

The soaps were made from stocks consisting of 100% tallow and tallow with varying amounts of rosin up to 15% of the mixture The finished soaps contained 57% total fatty and rosin acids. Practical water-softening tests were made in a washing machine under conditions corresponding to domestic usage. Soap was added in small quantities to 15 gallons of 300 p.p.m. hard water at 125°F. under agitation in a washing machine until suds were formed which persisted for 45 seconds without agitation. The quantities of the several soaps required to soften are given in Table III.

TABLE III

Comparison of Laboratory Results With Practical Use Tests

Percentage Composition of Soap Stock		Ounces Required to Soften 15 Gal. of 300 p.p.m. Water	Percentage Increase in Rosin-Tallow Soap Consumption Over All Tallow	
Tallow	Rosin		Practical Tests	Lab. Tests from Fig. II
100	....	5.6	......	......
95	5	5.9	5.4	3.6
90	10	6.1	9.0	7.3
85	15	6.5	16.1	13.1

The figures in Table III for the percentage increase in rosin-tallow soap requirement as compared to all tallow soap for softening water under domestic conditions are in reasonably good agreement with the laboratory data and indicate, therefore, that the presence of alcohol and the other artificial conditions of the latter determinations did not materially influence the results. It may be concluded from these observations that laboratory tests of the type outlined will prove useful in predicting the behavior of commercial soaps.

Discussion

Tallow vs. Soybean. From inspection of Table I it might be concluded that sodium soybean fatty acids soap is very slightly more effective than sodium tallow soap in softening 50 p.p.m. water. This is probably not of any particular significance because both soybean oil and tallow vary somewhat in fatty acid composition, and undoubtedly the type and percentage of the individual fatty acids affect the water softening properties of the soap.

Tallow vs. Coconut Oil. It requires from one and one-half to about two times as much sodium coconut fatty acids soap as of sodium tallow soap to soften water of 50 p.p.m. hardness. The amount of coconut soap necessary to soften is materially influenced by the ratio of Ca:Mg in the water hardness and increases with increasing proportions of magnesium. Theoretically, smaller weights of coconut oil fatty acids soap than of tallow soap should be required to soften because of the lower mean molecular weight of the coconut oil fatty acids. The softening process, however, involves not only precipitation of hard-water soaps but also the formation of a permanent lather by soluble soaps in the solution. Calcium laurate is reported to be less soluble than calcium oleate, one investigator (1) finding 13 mgm. per 100 ml. at 50°C.

as compared to 32 mgm. for the oleate. Sodium laurate, however, yields a poor and relatively unstable lather. The higher molecular weight saturated fatty acid calcium soaps are undoubtedly less soluble than calcium laurate and tend to precipitate first leaving the solution richer in low molecular weight and poorer lathering soluble soaps. It is to be expected on this basis, therefore, that more coconut oil than tallow soap will be required to soften water. Further, judging from the water-softening results in all magnesium hardness water, it seems probable that the difference in solubility between the magnesium low- and high-molecular weight fatty acid soaps must be considerably greater than that of the calcium compounds.

Tallow vs. Rosin. Three to eight times as much sodium rosin soap as sodium tallow soap is required to soften 50 p.p.m. water, depending upon the calcium-magnesium ratio. Sodium rosin soap is least efficient in water in which calcium hardness predominates. On the other hand, fatty acid soaps are most efficient in all-calcium hardness water and least effective in all-magnesium hardness.

There is no obvious theoretical explanation for this behavior. The fact that many times the stoichiometric quantities of rosin soap are required to soften calcium hardness suggests that adsorption of the sodium resinate by the insoluble calcium soap may occur (Table IV). It is possible that the precipitated magnesium resinates also adsorb the sodium resinates, but to a lesser degree, because the same excess of sodium resinate in the aqueous phase should yield a permanent lather in either calcium or magnesium water.

TABLE IV

Comparison on Stoichiometric Basis of Actual and Calculated Amounts to Soften

Type of Hardness	Equivs. $CaCO_3$ x 10^5	Equivalents x 10^5 of Fatty Acids and Rosin as Soap to Soften 50 ml. of 50 p.p.m. Water			
		Tallow F. A. (Equiv. Weight = 293.7)		WW Gum Rosin (Equiv. Weight = 337.0)	
		Actual	Calculated	Actual	Calculated
All Ca	5.0	8.2	6.0	60.2	14.6
2/3 Ca, 1/3 Mg	5.0	9.4	6.0	37.4	14.6
1/2 Ca, 1/2 Mg	5.0	9.2	6.0	28.5	14.6
1/3 Ca, 2/3 Mg	5.0	9.4	6.0	27.3	14.6
All Mg	5.0	9.9	6.0	27.0	14.6
Zero Hardness	....	1.0	....	9.6	....

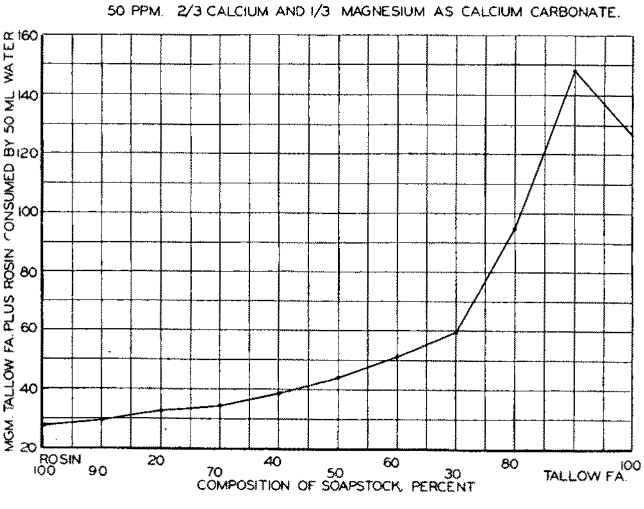
In an effort to throw some light on the reason for the difference between tallow and rosin soaps, the amounts of each required to produce a lather in zero hardness water were determined. The results are recorded in Table IV as equivalents $\times 10^5$. Likewise the data in Table I for tallow and for rosin soaps in water containing various ratios of calcium to magnesium have been recalculated to permit ready comparison of the equivalents of hardness in the water with the equivalents of soap necessary to soften.

The theoretical quantity of fatty acids or rosin soap required to precipitate the calcium and magnesium hardness in 50 ml. of 50 p.p.m. water is 5.0×10^{-5} equivalents. The quantity of tallow soap necessary to produce a lather in 50 ml. of zero hardness water was found experimentally to be 1.0×10^{-5} equivalents, and that of rosin soap 9.6×10^{-5} equivalents. It might be expected, therefore, that 5.0×10^{-5} plus 1.0×10^{-5}, or 6.0×10^{-5} equivalents of tallow soap, and 5.0×10^{-5} plus 9.6×10^{-5}, or 14.6×10^{-5} equivalents of rosin soap would be required to produce a lather under the conditions of the test.

It is evident from Table IV that about 37 per cent excess of tallow soap in all-calcium water, and about 55 per cent in all-magnesium hardness water was required to yield a permanent lather. In contrast, an excess of rosin soap ranging from 85 per cent in all-magnesium hardness water to 300 per cent in all-calcium hardness water was necessary. The substantial differences between the number of equivalents actually required and the theoretical quantities may possibly correspond to the sodium soap adsorbed on the insoluble soap. While mechanisms other than adsorption may also be postulated to explain the observations, any definite conclusion is impossible on the basis of the available information.

Tallow-Rosin Soap Mixtures. The water-softening properties of mixed sodium tallow soap and sodium rosin soap are additive at levels of rosin in the stock below roughly 70%. At 90% rosin, the effect of the tallow fatty acids is apparently detrimental since more of the mixture than of rosin alone is required to soften (Figure 2).

FIGURE 2- SOFTENING BY TALLOW-ROSIN SOAP MIXTURES. WATER HARDNESS 50 PPM. 2/3 CALCIUM AND 1/3 MAGNESIUM AS CALCIUM CARBONATE.



Inasmuch as rosin is generally limited to amounts below 40% in the stocks of commercial soaps, the abnormal softening behavior at the higher concentrations of rosin is of no practical interest.

BIBLIOGRAPHY

(1) Pohle, W. D., Oil and Soap *18*, 244 (1941).