The Journal of the American Oil Chemists' Society

Volume 27 AUGUST, 1950 No. 8

Comparative Value of Fatty Acids and Resin Acids of Tall Oil in Soaps[1]

FOSTER DEE SNELL and IRVING REICH, Foster D. Snell inc., New York City

THE production of tall oil in the United States increased to over 200 million pounds annually during the recent war. Today the low cost of this product makes it an attractive raw material for the manufacture of special soaps and the extending of commercial brown laundry bar. Saponification of tall oil proceeds very rapidly, even with relatively weak alkalies such as soda ash, requiring only neutralization of the fatty acids and resin acids present, because there is no appreciable content of esters (1). Tall oil soaps are especially useful for cleaning oily or greasy surfaces (2). Data on sensitivity of tall oil soaps to hardness in water are available but none on detergent performance.

Tall oil consists of roughly equal proportions of fatty acids and resin acids, plus a few per cent of sterols and hydrocarbons as unsaponifiables. The fatty acid fraction shows, by iodine value, an average unsaturation equal to about 1.5 double bonds per molecule and is essentially a mixture of oleic and linoleic acid, with a small percentage of linolenic acid (3, 4). When saponified, this fraction should yield a soap substantially equivalent to soaps furnished by vegetable oils of the same degree of unsaturation. The resin acid fraction consists largely of isomeric abietic acids and should form a soap with the general properties of rosin soaps.

Wash-tests run with straight rosin soap have indicated poor detergency, using a soiled cloth which was not easily scoured (5). In view of the present day market situation, it appeared desirable to answer the following questions:

1. How effective a detergent is tall oil soap as compared with rosin soap on the one hand and with sodium oleate on the other?
2. What is the effect of the unsaponifiable content of tall oil on the detergent value of the soap?
3. How does tall oil soap vary in detergent value with ratio of fatty acids to resin acids?

In order to determine the effect of fatty-acid-resin-acid ratio, tall oil fatty acids were separated from resin acids, sodium soaps were prepared from each, and these were combined in varying proportions. This permits plotting detergency results against percentages of resin-acid and fatty-acid soaps over the range 0-100%. Parallel determinations on sodium rosinate, sodium oleate, and their mixtures permitted evaluation of soaps of tall oil fatty acids as compared with those of oleic acid, soaps of tall oil resin acids as compared with rosin soap, and the soap of any tall oil acid mixture as compared with the corresponding oleic acid-rosin mixtures.

Preparation of Soaps

Sodium oleate was prepared by neutralizing "Low-Titre White Elaine" of the grade shown in Table I with C. P. sodium hydroxide in methanol, distilling off most of the methanol, then drying under vacuum.

Sodium rosinate was prepared by neutralizing "Wyte" wood rosin of the grade shown in Table I with C. P. sodium hydroxide, using enough alkali to saponify the small proportions of esters present. The reaction was carried out in methanol, which was then removed by distillation and vacuum-drying.

TABLE I

Constants of Materials Used for Preparing Soaps

	Manufacturer's Specification	Found
Oleic Acid (Emery Industries Low Titre White Elaine, 0-21)		
Acid number	195-199	197
Color (Lovibond)	15Y, 1½R (5¼")	......
% Unsaponifiables (15Y 1½R)	<2%	
Wood Rosin (Newport Industries "Wyte" Grade)		
Acid number	168 (Av.)	166
Saponification number	172 (Av.)	167
% Resin acids	92 (Av.)	88
% Unsaponifiables	7.2 (Av.)	......
Tall Oil (Union Bag and Paper Corporation Unitol R)		
Acid number	160-170	165
Saponification number	165-175	169
Iodine number	160-170	......
% Resin acids	46-54	49.5
% Fatty acids	40-48	43.7
% Unsaponifiables	6-7	6.8
Color (ASTM-Hellige Comparator)	4.0-5.0	......
Unitol R Resin Acids Fraction		
Acid number	163	
% Resin acids	94.0	
% Fatty acids	6.0	
% Unsaponifiables + Esters	None	
Unitol R Fatty Acid Fraction		
Acid number	184	
% Resin acids	6.6	
% Fatty acids	93.4	
% Unsaponifiables + Esters	None	

Sodium tall oil soap was prepared in the same manner as the sodium rosinate. Specifications for the tall oil are in Table I.

Sodium soaps of tall oil resin acids and tall oil fatty acids were prepared by preferential esterification of tall oil with methanol (3). The objective set was better than 90% purity in each fraction.

A batch of 150 grams of tall oil was mixed with 100 grams of absolute methanol containing 5 grams of sulfuric acid. The mixture was refluxed for one hour, cooled, and diluted with about 500 ml. of water. Under these conditions the fatty acids are preferentially esterified. The mixture of unesterified acids, methyl esters, and unsaponifiables was dissolved in 750 ml. of ethyl ether, and the ether solution was

---

[1] Presented at 113th meeting of the American Chemical Society, Chicago, Ill., April 14-23, 1948.

[EDITOR'S NOTE: This paper should have preceded "Physical-Chemical Properties of Tall Oil Soap Solutions" by Snell and Reich, which was published in the March 1950 issue.]

TABLE II

Launderometer-Evaluation Conditions

Machine	Atlas launderometer, holding 20 1-pint Mason jars
Amount of solution per jar	100 ml.
Speed of rotation	40 ± 1 r.p.m.
Mechanical washing assistants	10 ¼" Monel metal balls per jar
Temperature	60°C.
Time of washing	15 minutes
Rinsing procedure	Pour off detergent solution, rotate in machine 1 minute with 100 ml. of water of same hardness as in detergent solution, at 60° C. Pour off water and rinse a second time.
Soiled fabric per jar	1 strip 2 x 4 of standard soiled cotton cloth No. 26 supplied by the General Dyestuff Corporation.
Reflectometer	Pfaltz and Bauer Gloss Meter set to read disperse reflection and adjusted to read 100 units on the unsoiled portion of the standard cotton fabric.

washed with one liter of 5 per cent sodium hydroxide solution in a 2-liter separatory funnel. The free acids —principally resin acids—are saponified and enter the water phase. The water layer containing soaps plus excess sodium hydroxide was drawn off and diluted to about 1,500 ml. to avoid troublesome emulsions later. The water solution was washed 6 times with 100-ml. portions of ethyl ether to remove any remaining methyl esters. It was then acidified with hydrochloric acid and the liberated acids extracted with ethyl ether. After removing moisture with anhydrous sodium sulfate and evaporating the ether, the crude resin acids were dried at 110° for 5 hours. By the ASTM method, they gave a resin-acid value of 158, or 85% of resin acids calculated as abietic acid.

Further purification of the crude resin acids was accomplished by a second esterification, alkali extraction, and acidification, using the same proportions of materials. The repurified acids had a resin-acid value of 174, corresponding to 94% of resin acids calculated as abietic acid. This product was the tall oil resin-acid fraction used in subsequent work. Its chemical constants are listed in Table I.

The sodium soap was made by neutralizing the resin acids exactly with sodium hydroxide in methanol, drying, and extracting any remaining traces of methyl esters or unsaponifiables with petroleum ether.

The tall oil fatty-acid fraction was prepared by treating the ether solution of methyl esters from the first esterification as follows: The ether solution was washed with six 100-ml. portions of 5% sodium hydroxide solution, and finally with water until free of alkali. Thus any remaining traces of free acids were removed. After drying with anhydrous sodium sulfate and evaporation of the ether, the methyl esters were saponified with an excess of 50% aqueous potassium hydroxide, diluted with water, and extracted with ethyl ether to remove the unsaponifiables. The remaining soap solution was acidified and extracted with ether to recover the fatty acids. The ether was removed by evaporation. The dried acid had a resin acid value of 12.3, corresponding to 6.6% of resin acid calculated as abietic. This product was the tall oil fatty-acid fraction used in subsequent work. Its chemical constants are listed in Table I.

The sodium soap was prepared by exactly neutralizing the fatty acids with sodium hydroxide in methanol, drying, and extracting any remaining traces of unsaponifiables with petroleum ether.

From the acid numbers of the unsaponifiable-free tall oil fractions and the percentage composition of the tall oil listed in Table I, the acid number of the original tall oil is calculated to be 161. This is in satisfactory agreement with the value actually found, 165, when allowance is made for the probable error in determinations of resin acids.

The detergent performance of the tall oil fatty-acid soap and of the tall oil resin-acid soap could be altered only slightly by the small percentage of soap of the other acid present. The two soaps are referred to as though they were pure soaps. This is less serious than the complications of calculating on the basis of the true compositions of these two soaps. The tall oil fatty acid and resin acid soaps as prepared are free from unsaponifiables.

Launderometer Results

Determinations were made in triplicate according to the conditions of Table II on each of 12 soaps and soap-mixtures at each of the following concentrations:

0.1% soap in distilled water
0.2% soap in distilled water
0.3% soap in distilled water
0.3% soap in 15-grain water.

Experience indicates that samples run simultaneously, using soiled fabric from the same batch, usually check to 0-1 reflectance unit, occasionally 2 units, rarely more. Separate runs using the same batch of soiled cloth with care to maintain temperature, time, and rinsing constant, may nevertheless vary considerably in absolute values although relative values remain about the same. Hence all soaps were compared in parallel by a launderometer run at a single concentration. The run was repeated twice more, the whole procedure forming a group experiment.

The procedure was repeated for each soap concentration. Each of Figures 1-4 lists results for the series of soaps at a single concentration, hence for one integrated group of launderometer runs. Comparison of readings at different concentrations is not as justifiable as at the same concentration because they refer to different sets of launderometer runs and could be subject to systematic variations.

The probable error was calculated for each average of three replicate determinations on the same solution, as follows:

$$E = \frac{0.845 \sum_{i=1}^{n} di}{n \sqrt{n-1}}$$

Where E = probable error

$\sum_{i=1}^{n} di$ = sum of deviations from mean

n = number of observations (three).

Altogether 48 averages and 48 probable errors were calculated, representing the 12 soaps and soap mixtures at three concentrations in distilled water and one concentration in hard water. The average probable error was 0.65 unit. Of the probable errors, three were smaller than 0.3, 40 were between 0.3 and 0.9, and 5 were greater than 0.9.

It should be noted that these probable errors are measures of the deviation of non-grouped runs. They apply to data taken from three different runs rather than the same run. In studying individual curves which compare different soaps, relative errors will be smaller because of the group design of the experiments, whereby uniform errors associated with entire runs cancel out.

At 0.1% concentration in distilled water, as shown in Figure 1, straight sodium oleate reads 88.7 while straight sodium rosinate reads 76.6. The former reading represents good detergency. The latter is poor. Mixtures of the two soaps give intermediate readings, the value varying linearly with the proportion of oleate. Tall oil fatty-acid soap reads 85.7, 3 units below sodium oleate but 9.1 units above sodium rosinate. Tall oil resin-acid soap reads 75.3, 1.3 units below rosin soap. Although oleate and resinate soaps respectively are better than tall oil fatty-acid and resin-acid soaps, mixtures of the latter pair are better than corresponding mixtures of the former pair, over the range of 20-85%. So tall oil fatty-acid and resin acid soaps appear to have a synergistic effect. As the proportion of resin-acid soap is increased from 0 to 25%, the reading rises from 85.7 to 87.3, and only when the resin acid reaches 42.5% has the reading declined to 85.7 again.

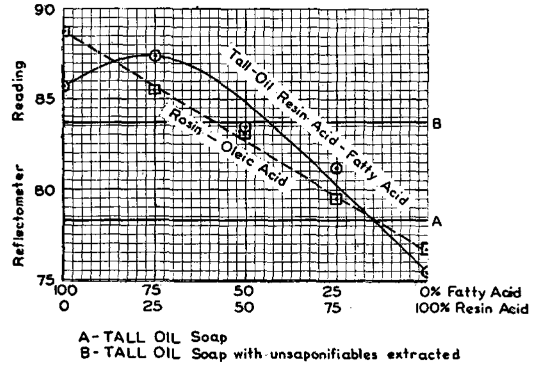

FIG. 1. Cotton-washing tests using 0.1% soap solutions in distilled water at 60°.

Tall oil soap containing unsaponifiables reads 78.2, equivalent to a mixture of 14% oleate and 86% rosinate soap. With unsaponifiables removed, the tall oil soap becomes a mixture of 54% resin-acid soap plus 46% fatty-acid soap. The detergency reading of this soap interpolated from Figure 1 at 54% resin acid, is 83.8. This equals the performance of 60% sodium oleate plus 40% sodium rosinate. Thus removal of the unsaponifiable matter improves detergent performance markedly.

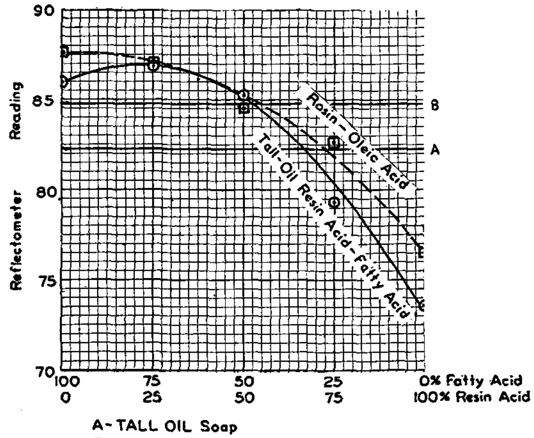

FIG. 2. Cotton-washing tests using 0.2% soap solutions in distilled water at 60°.

At 0.2% solution in distilled water, Figure 2, the oleate-rosinate curve is no longer a straight line. As before tall oil fatty- and resin-acid soaps are somewhat lower in detergency than oleates and rosinates, but mixtures of the tall oil soaps in the range 50% to 75% fatty acid are as good as the corresponding oleate-rosinate.

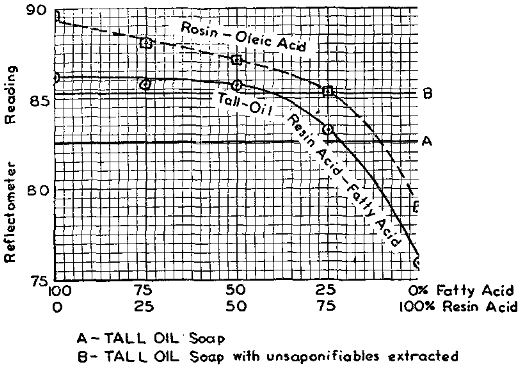

FIG. 3. Cotton-washing tests using 0.3% soap solutions in distilled water at 60°.

At 0.3% concentration, Figure 3, the oleate-rosinate soap mixtures are always better than the tall oil soap mixtures although here also the differences are smaller for fatty acid-resin acid soaps than for the straight rosin or the straight fatty-acid soaps.

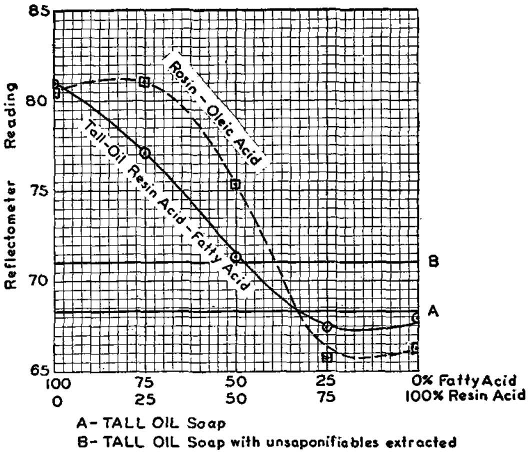

FIG. 4. Cotton-washing tests using 0.3% soap solutions in 15-grain hard water at 60°

Figure 5 is a composite of the results obtained in distilled water at 0.1%, 0.2%, and 0.3%, so that each point represents the average of 9 determinations covering the typical use concentration range in soft water. Sodium oleate is good, reading 88.6. Sodium rosinate is poor, reading 77.3. Tall oil fatty-acid soap reads 85.9 and is lower than the oleate but much higher than the rosinate. Tall oil resin-acid soap is lower than rosinate, reading 74.9.

When tall oil resin-acid soap is added to tall oil fatty-acid soap, detergency is not reduced until the proportion of resin soap exceeds approximately 40%.

Tall oil soap reading 81.0 is significantly better than sodium rosinate reading 77.3. It equals 16% oleate plus 84% rosinate. Tall oil soap with unsaponifiable matter removed is in turn better than straight tall oil soap. It reads 84.3, which is equivalent to a mixture of 43% of oleate plus 57% of rosinate.

TABLE III

Foaming Values of Soap Solutions

Agent	Height of Foam in cm. After Indicated Time in Minutes															
	Solutions in Distilled Water															
	At 30°								At 60°							
	0.2%				0.05%				0.2%				0.05%			
	0 min.	1 min.	5 min.	10 min.	0 min.	1 min.	5 min.	10 min.	0 min.	1 min.	5 min.	10 min.	0 min.	1 min.	5 min.	10 min.
Sodium Soap of Tall Oil Resin Acids	10	8	3	1	2	1	....	....	7	5	1	....	0.5	....	....	....
75% Soap of Tall Oil Resin Acids 25% Soap of Tall Oil Fatty Acids	13	12	11	9	5	3	2	2	21	18	14	5	8	7	1	1
50% Soap of Tall Oil Resin Acids 50% Soap of Tall Oil Fatty Acids	22	18	16	11	9	7	6	6	23	21	21	9	17	15	6	3
25% Soap of Tall Oil Resin Acids 75% Soap of Tall Oil Fatty Acids	23	20	18	11	18	15	14	13	23	21	20	5	20	18	5	4
Sodium Soap of Tall Oil Fatty Acids	24	21	19	15	21	17	17	15	25	22	21	17	14	12	6	1
Sodium Rosinate	1	1	....	....	nil*	....	....	....	7	4	1	....	1	....	....	....
25% Sodium Oleate 75% Sodium Rosinate	17	15	14	12	6	5	4	4	22	19	13	9	11	9	1	....
50% Sodium Oleate 50% Sodium Rosinate	22	18	17	16	13	11	9	9	23	21	20	18	19	17	15	3
75% Sodium Oleate 25% Sodium Rosinate	23	19	18	17	12	11	10	9	26	21	20	20	20	18	16	5
Sodium Oleate	23	21	18	15	19	16	15	15	26	21	21	19	21	20	18	8
Sodium Soap of Tall Oil	13	11	9	7	3	2	1	....	21	19	6	1	3	2	1	....

* Foam breaks at once.

In Figure 4 results for soap solutions at 0.3% concentration in 15-grain water are listed as typical of a hard water. The hard water contained 0.698 gram of anhydrous calcium chloride and 0.425 gram of magnesium chloride hexahydrate per gallon of New York City tap water, which already has a hardness of 2 grains per gallon. Hardness of 15 grains per gallon and greater is encountered in some sections of the United States.

Straight oleate soap at 0.3% concentration reads 89.5 in distilled water, and 80.6 in hard water. The 15 grains of calcium carbonate per gallon is stoichiometrically equivalent to 0.15% of sodium oleate. Therefore, only half of the 0.3% of the soap would be converted to insoluble oleates. The remaining 0.15% might have been expected to give a comparatively high reading since in distilled water 0.1% reads 88.7 and 0.2% reads 87.7. It is thus seen that the insoluble calcium and magnesium soaps exert a harmful effect on detergency over and above the stoichiometrically calculated loss of soluble soap. This is not surprising. The insoluble calcium and magnesium soaps must be dispersed and suspended by the remaining sodium soap, thereby sorbing some of the soap, so that a considerable portion of the latter is not available for ordinary detergent action. Further, some of the insoluble soaps may deposit on the soiled fabric and hinder soil removal. To match the readings obtained with distilled water, a soap concentration of 0.5-0.6% would probably be required.

A 75 oleate-25 rosin soap is roughly as good as the straight oleate soap at 0.3% concentration in hard water. The detergency then drops rapidly with increasing proportion of rosinate. The corresponding curve in distilled water begins to decline rapidly only when the rosinate has reached 75%.

Tall oil fatty-acid soap in hard water reads substantially the same as sodium oleate. So tall oil fatty-acid soap is less sensitive to the effect of hardness than oleate. This is logical since the unsaturated acids in tall oil would yield more soluble soaps. Similarly tall oil resin-acid soap is less sensitive to hardness than sodium rosinate and is superior to the latter in the 15-grain water. The synergistic effect noted in distilled water is not in evidence here. Readings decline steadily as the proportion of resin soap is increased, and the oleate-rosinate mixtures are superior to the corresponding tall oil fraction soaps through most of the range of ratios.

Tall oil soap in hard water reads 68.3, matching 32.5% oleate plus 67.5% rosinate. Tall oil soap with unsaponifiables removed reads 71.0. This is equivalent to 40% sodium oleate plus 60% sodium rosinate.

Foaming Values

Foaming power has been considered loosely as an index of detergent power. Frequently there is correlation, but good foaming agents can be poor detergents, and vice-versa. Foaming is of psychological importance because housewives and laundry foremen often judge a detergent largely on its foaming properties. Numerous methods for measuring foaming-power have been described in the literature. The technic of Ross and Miles (6) involves allowing 200 milliliters of solution to fall through a special orifice into a standard cylinder which already contains 50 milliliters of the same solution. The height of the foam layer thus generated is measured immediately after pouring and after 1, 5, and 10 minutes.

In Table III foam heights of soap solutions at 0.2% and 0.05% at 30°C. and 60°C. in distilled water are listed. Values at 0.2% in 10-grain water were also determined. All determinations were run in duplicate. Differences between check determinations were generally 1 cm. or less, sometimes as great as 2 cm. and over 2 cm. only in 2% of the determinations. The average of all differences between check determinations is 0.6 cm., which makes the average value for average deviations from the mean 0.3 cm. Hence a difference of as much as 2 cm. in foam height is very probably significant.

Since the large number of values in this table make it difficult to follow trends, a cumulative summary is provided in Table IV. Each value in Table IV is the sum of the 0-, 1-, 5-, and 10-minute values listed separately in Table III. These values depend on both the amount of foam generated during the pour and the stability of that foam. Both are involved in the concept of foaming power. Table IV also includes summaries of values in 10-grain water. Only the values in Table IV will be considered in further discussion.

Figure 6 shows the cumulative results for the soaps in distilled water—the sums of all values at both temperatures and both concentrations as listed in the fifth column of Table IV. They furnish a statistical measure of general foaming power.

Let us consider a washing machine or other device which generates foam continuously. While operating, it will generate foam at an approximately constant rate, K_g. Foam will be destroyed, not at a continuous rate but at a rate approximately proportional to the amount actually present. The rate of destruction is thus the product of a destruction-constant and the amount of foam present, K_dF.

At the start, $F = 0$, hence the rate of destruction is zero. As foam is generated, K_dF increases until it is eventually equal to the rate of generation. At this dynamic equilibrium point, $K_dF = K_g$ or $F = \frac{K_g}{K_d}$ and so the amount of foam depends on both constants.

Both rosin soap and tall oil resin soaps are very poor foamers although the tall oil resin soap is slightly better. The small percentage of fatty acid soap present probably accounts for that. Oleate soap is very good, tall oil fatty-acid soap slightly poorer. Over most of their ranges the curves for the two soap series parallel each other.

Tall oil soap shows appreciable foaming power. Tall oil soap with unsaponifiable matter extracted is very substantially better than when unsaponifiables are present.

The data for the soaps at 0.05% and 0.2% at 30° show that in both series of soaps, foaming values drop more rapidly with increasing proportion of resin acids at the lower concentration. This parallels launderometer readings. Foaming of tall oil resin-acid soap becomes almost nil at 0.05% concentration. Rosin soap is practically nonfoaming at either concentration. The fatty-acid soaps foam only moderately less at 0.05% than at 0.2%. Tall oil soap practically loses its foaming power at the lower concentration, but with unsaponifiables removed it foams moderately.

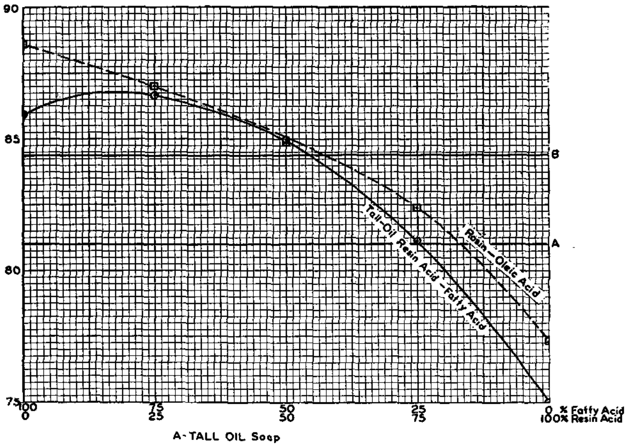

FIG. 5. Cotton-washing tests. Averaged results for 0.1%, 0.2%, and 0.3% soap solutions in distilled water at 60°.

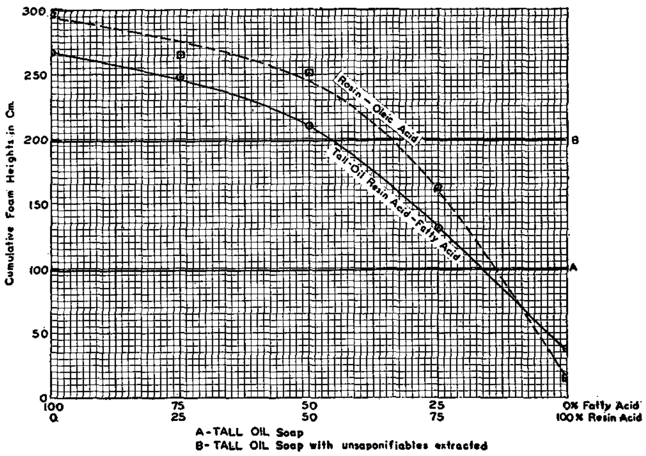

FIG. 6. Cumulative foam-heights. Averaged results for 0.05% and 0.2% soap solutions at 30° and 60° in distilled water.

At 30°C. and 60°C. with 0.2% concentration, the higher temperature causes a limited increase in foaming power for both series of soaps and a relatively smaller increase for straight tall oil soap.

Reducing the concentration from 0.2 to 0.05% at 60° reduced foaming of the oleate-rosinate soap series roughly by the same amount at 60° as at 30°.

The reduction for tall oil fatty-acid soaps and mixtures rich in them is much more severe at 60°. Hence these mixtures, and also tall oil soap, are low in foaming power as compared with oleate-rosinate soaps under these conditions. Tall oil soap is considerably better in foaming properties in distilled water than rosin soap, particularly when unsaponifiable matter is removed.

In hard water the foaming powers of the resin soaps at 0.2% concentration and 30° are practically nil. The tall oil soaps show no foaming values since they are too low in fatty acid content to foam in hard water at those soap concentrations. The fatty acid soaps foam moderately, tall oil fatty acid soap being about equal to oleate. At 60° none of the soaps shows appreciable foaming power.

Effect of Unsaturation

Soaps of highly unsaturated fatty acids are, in general, of lower detergency than more saturated compounds. The generally lower detergency of tall oil fatty-acid soap than of sodium oleate can be ascribed to the greater unsaturation of the former. To demonstrate the effect of degree of unsaturation on detergent performance of soaps, Table V shows a series of launderometer readings on soaps of varying degrees of unsaturation. The iodine values are manufacturers' specifications.

Detergency decreases steadily with increasing unsaturation, with the greatest differences at 0.05%. Tall oil fatty-acid soap falls between oleic acid and linseed oil soaps, as would be predicted from the degree of unsaturation.

General Discussion

The launderometer and foaming results show the marked superiority of tall oil soap to rosin soap. As a first approximation, it appears proper to consider

TABLE IV

Cumulative Foam Heights After 10 Minutes; Condensed From Table III

Agent	Solutions in Distilled Water				Summation of All Values in Distilled Water	Solutions in 10-Grain Hard Water	
	At 30°		At 60°			At 30°	At 60°
	0.2%	0.05%	0.2%	0.05%		0.2%	0.2%
Sodium Soap of Tall Oil Resin Acids	22	3	13	0.5	38.5	0.5	7
75% Soap of Tall Oil Resin Acids 25% Soap of Tall Oil Fatty Acids	45	12	58	17	130	0	0
50% Soap of Tall Oil Resin Acids 50% Soap of Tall Oil Fatty Acids	67	28	74	41	210	1	0
25% Soap of Tall Oil Resin Acids 75% Soap of Tall Oil Fatty Acids	72	60	69	47	248	17	0
Sodium Soap of Tall Oil Fatty Acid	79	70	85	33	267	52	2
Sodium Rosinate	2	0	12	1	15	0	2
75% Sodium Rosinate 25% Sodium Oleate	58	19	63	21	161	0	0
50% Sodium Rosinate 50% Sodium Oleate	73	42	82	54	251	1	0
25% Sodium Rosinate 75% Sodium Oleate	77	42	87	59	245	29	0
Sodium Oleate	77	65	87	67	276	46	7
Sodium Soap of Tall Oil	40	6	47	6	99	0	0
Sodium Soap of Tall Oil with Unsaponifiables Removed	62	25	68	38	198	....	....

soap made from acid-refined tall oil without unsaponifiables as the equivalent of a mixture of rosin soap corresponding to the resin-acid content and oleic-acid soap corresponding to the fatty-acid content. Unsaponifiable matter can make tall oil soap poorer than such a rosin-oleate soap mixture, although still decidedly better than rosin soap. At low concentrations tall oil soap without unsaponifiables is much more efficient than would be predicted from results on fatty and resin soaps alone, due to the synergistic cooperation.

A complete prediction of performance of tall oil and rosin soaps as fractional constituents of tallow bars cannot be made from these data. The marked superiority to the tall oil soap to rosin soap indicates strongly that tall oil would be a superior additive. This is logical in view of the fatty-acid content of tall oil.

Differences in launderometer readings become most pronounced at low effective soap concentrations. However a concentration of 0.3% in hard water may be effectively as low as 0.05% in distilled water. Not only the soap precipitated by the metal salts but also the soap sorbed by that precipitate must be considered as lost.

Many detergents differ widely in effectiveness at low concentrations but reach approximately the same maximum value at higher concentrations. Tests run at higher concentrations may thus fail to demonstrate differences which can be very important economically. To take a simple example, a straight tallow soap would yield approximately the same washing test value as a mixture of 80% soap and 20% sand, if both were used at 0.3% concentration. This is simply stating that there is little difference between 0.3% soap solution and a 0.24% solution. Yet, if both were used at 0.05% concentration, a difference would be noted.

Even when soap is used at a high concentration, the final concentration under practical conditions may be quite low. Some soap is precipitated by hardness in the water, some is sorbed by the soil and by the fabric. Overall efficiency of the washing process after loosening of the soil depends on ability of the soap solution to keep soil dispersed and suspended to the end, bearing in mind that the soap solution is further diluted during the rinsing stage while some soil is still present.

At 0.2% and 0.3% concentrations, the effectiveness of sodium oleate does not appear to be impaired by replacing substantial fractions of it with sodium rosinate. At 0.1% concentration, detergency falls off rapidly as rosin is added. The analogy with the soap-sand situation suggests itself.

Thus the tall oil studied is a detergent falling approximately midway between the high performance level of oleates and the low performance level of rosinates. This is accounted for by its composition and by an apparent synergistic cooperation between the fatty and resin soaps.

Acknowledgment

This study was made under a grant from The Union Bag and Paper Company.

Summary

A study has been made of the detergency and foaming power of soaps made from a typical acid-refined American tall oil. Sodium soap of tall oil, straight

TABLE V

Launderometer Results for Sodium Soaps Varying in Saturation; Averaged Reflectance Values for Washed Soiled Cotton Fabric (Unsoiled = 100)

Fatty Acid	Commercial Designation	Iodine Value	Launderometer Reading of Sodium Soaps	
			0.2%	0.05%
Stearic Acid	Neo-Fat 1-65 Armour & Co.	3	87.3	85.5
Oleic Acid	Water White Elaine 0-21, Emery Industries, Inc.	93	87.0	84.0
Tall Oil Fatty Acids	Prepared from Unitol R	125-140	86.3	82.0
Linseed Fatty Acids	Wecoline L, E. F. Drew & Co. inc.	175-186	86.0	81.0

tall oil fatty-acid soap, and straight tall oil resin-acid soap were evaluated. The effect of fatty acid-resin acid ratio was determined by using mixtures of those soaps. Sodium rosinate, sodium oleate, and mixtures of these soaps were used as comparison standards. Curves plotted show wash-test data and foaming values as functions of the ratio of fatty soap to resin soap.

The data indicate in terms of detergency: a) tall oil soap has a higher value than sodium rosinate; b) sodium oleate is better than tall oil fatty-acid soap, but the latter is approximately equivalent to soaps from various unsaturated vegetable oils; c) both tall oil resin-acid soap and rosin soap have low detergency on cotton; d) the detergency of most mixtures of tall oil fatty-acid and resin-acid soaps at lower concentrations is greater than would be predicted from the individual soaps, indicating a synergistic effect.

As a rough approximation, tall oil soap without unsaponifiables is equivalent to a corresponding mixture of sodium oleate and sodium rosinate. The presence of unsaponifiables lowers both detergency and foaming. Tall oil soap is somewhat less sensitive to hard water than sodium oleate.

Significant differences between detergencies of soaps, and especially between soap mixtures, are obscured when launderometer tests are run at moderate soap concentrations. These differences are readily detected at lower concentrations.

REFERENCES

1. Hastings, R., Pollack, A., and Wafer, J. M., Soap and Sanitary Chemicals *20*, 24-27, 70 (1943).
2. Treffler, Andreas, Soap and Sanitary Chemicals *20*, 29, 30, 63 (1944).
3. Anderson, R. H., and Wheeler, D. H., Oil and Soap *22*, 137-141 (1945).
4. Browning, B. L., and Calkin, John B., Paper Trade Journal *123*, No. 26, 45-47 (1946).
5. Borglin, J. N., Mosher, P. R., Noble, Barbara, and Pushon, T. Oil and Soap *20*, 77-84 (1943).
6. Ross, John, and Miles, Gilbert D. *18*, 99-102 (1941).

[Received December 30, 1949]

Characteristics of Solvent-Extracted and Hydraulic-Pressed Okraseed Oils

S. A. HUSSAIN, State of Hyderabad, India, and F. G. DOLLEAR, Southern Regional Research Laboratory,[1] New Orleans, Louisiana

THE okra plant, *Hibiscus esculentus* L., may be grown throughout most of the cotton belt of the United States. Research has recently been directed towards breeding non-shattering varieties of okra with seed adapted to mechanical harvesting and having a higher oil content than those usually grown for edible purposes. Although okraseed is not at present a very desirable seed for oil and meal production, research may be expected to yield improved strains which may take their place with or possibly replace cottonseed as an oilseed crop in some areas of the South.

The production of okra for industrial uses has been discussed by Edwards and Miller (1). In processing this seed, the problem of decortication requires more attention since the present methods are not effective in separating the kernels from the hulls (2). Edwards and Miller (1) reported that okraseed oil could be refined, bleached, and deodorized by the usual methods without any serious problems. They found that the okraseed meal is comparable to other meals now in commercial use for feeding livestock.

Analyses of okraseed and extracted meal have been reported by Kilgore (3), Halverson and Naiman (4), Edwards and Miller (1), Markley and Dollear (2), and Clopton *et al.* (5). The characteristic properties and composition of okraseed oil reported by Jamieson and Baughman (6) and others (2, 5), have been compared with those of cottonseed and peanut oils. The reported composition of okraseed oil determined by chemical methods is approximately, 25.5-29.7% linoleic acid, 41.5-41.9% oleic acid, and 28.8-29.7% saturated acids. However the fact that discrepancies have been observed between these results and composition as determined by the spectrophotometric method has been reported by Edwards and Miller (1) and Clopton *et al.* (5). The amount of linoleic acid spectrophotometrically determined by Clopton *et al.* was 13.2% although calculation from the iodine and thiocyanogen values and calculation from iodine and saponification values of the distilled methyl esters, gave 27.1% and 26.1% linoleic acid, respectively. The reported linoleic acid content of 27.1% calculated from the reported iodine and thiocyanogen values appears to be too low, probably because of an error in the calculations. The present authors have recalculated the composition of this okraseed oil using the equations adopted by the American Oil Chemists' Society (7) and the iodine value (Wijs) and thiocyanogen values reported by Clopton *et al.* (5). When the factor 1.046 is used to convert the results from a glyceride to acid-in-oil basis and the saturated acids are corrected by subtracting the percentage of unsaponifiable matter, the content of fatty acids in the oil is 37.1% linoleic acid, 25.7% oleic acid, and 31.6% saturated acids.

No processing data for okraseed oil have been reported in the literature, and the data with respect to the fatty acid composition determined by various analytical methods are not consistent. In the present communication the results of a comprehensive investigation on the production, characteristics, composition, and stability of solvent-extracted and hydraulic-pressed okraseed oils and their hydrogenated products are reported.

Experimental

Material. The okraseed used in this investigation was of the Louisiana Green Velvet variety, grown at the Louisiana State Penitentiary, Angola, La., in 1947. The samples of cracked seed, hydraulic-pressed oil, and press cake were obtained during a mill scale processing test at the Southern Cotton Oil Company's oil mill, New Roads, La. The composition of the seed used for solvent extraction and hydraulic pressing is given in Table I.

---

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.