Rosin — Use in Soap

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Rosin—Use in Soap

Rosin is the cheapest, high-molecular-weight organic acid available in dependably large quantities. There are two types of rosin: namely, gum rosin which is procured from the living tree, and wood rosin which is extracted from the dead wood such as stumps and top wood. Both rosins are derived from such pines as longleaf, loblolly, cuban, slash, etc., which grow in the states of Florida, Georgia, Alabama, Mississippi, Louisiana, and Texas.

Rosin is composed of about 85% resin acids, 10% resenes or unsaponifiable, and 5% esters. The unsaponifiable consists of hydrocarbons and high-molecular-weight secondary alcohols of the sterol type. The resin acid portion consists of abietic, *l*-pimaric, *d*-pimaric, and other resin acids of uncertain struc-

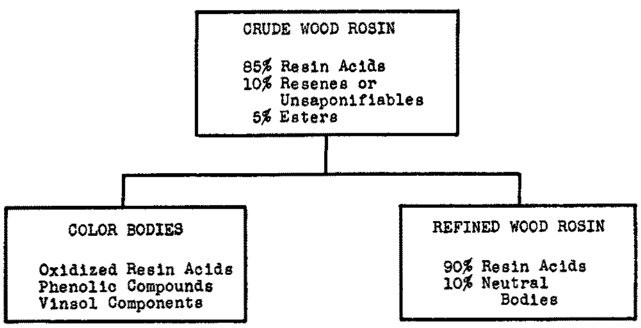


FIG. 1. Composition of crude wood rosin.

TABLE 1
Refined Wood Rosin Composition

91% Resin Acids		9% Neutral Bodies	
Abietic Acid	40%	Steam-volatile Material	0.3%
d-Pimaric Acid	10-15%	Esters, Hydrocarbons, etc.	8.7%
Noncrystalline Isomeric Acids	41-36%		

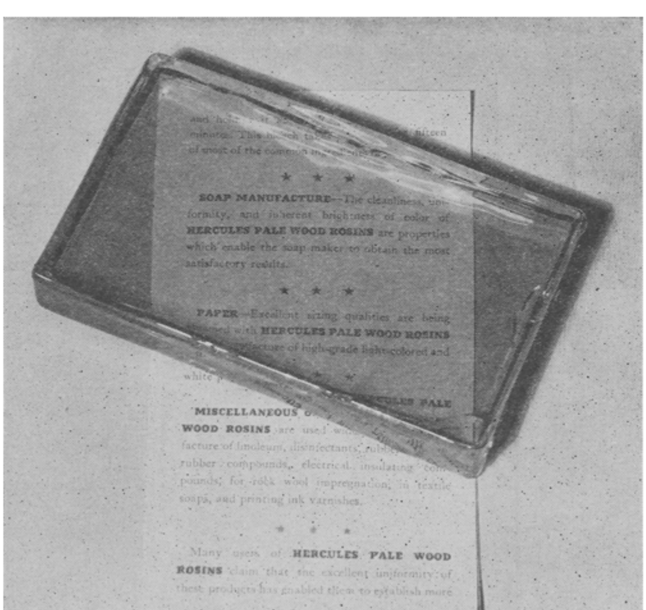
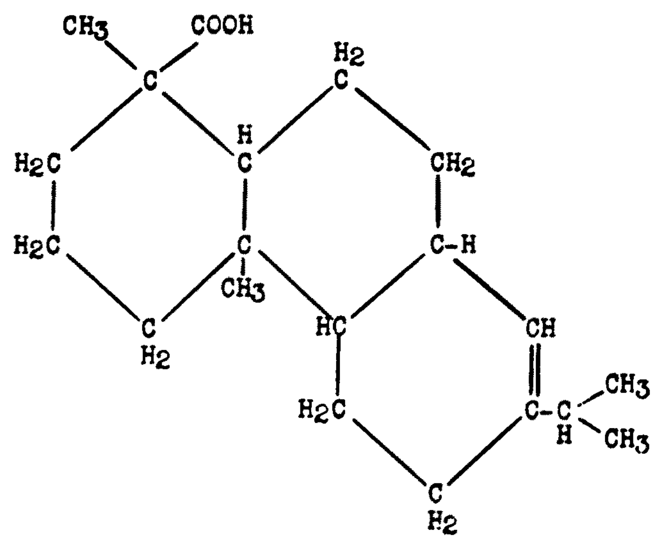
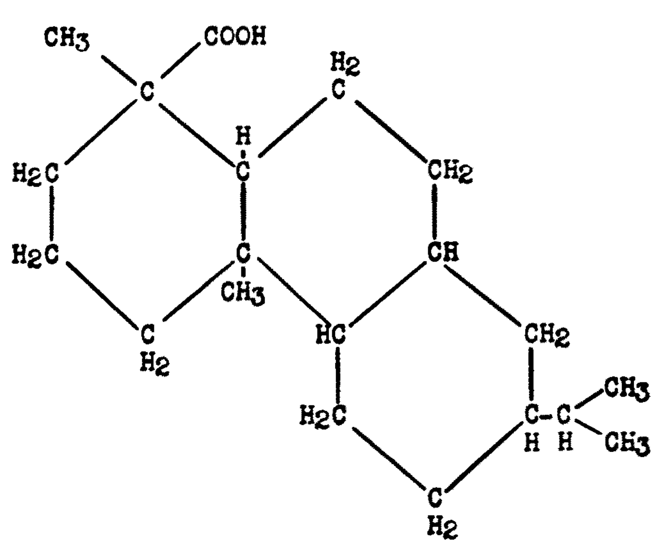


FIG. 2. This picture illustrates the uniform cleanliness and brilliance of refined wood rosin.



Dihydroabietic Acid

FIG. 3.



Tetrahydroabietic Acid

FIG. 4.

ABIETIC AND PIMARIC ACIDS

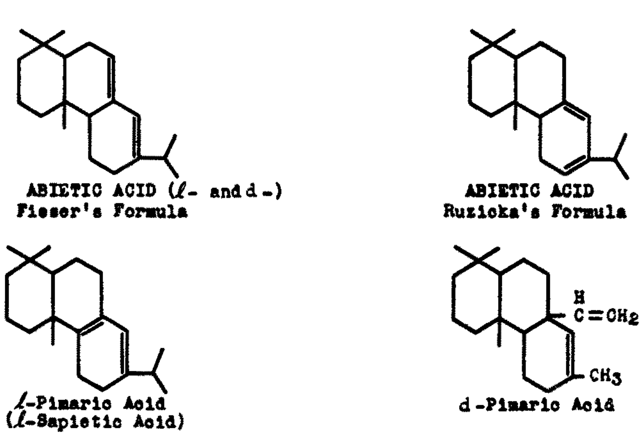


FIG. 5

HYDROGENATION OF RESIN ACIDS

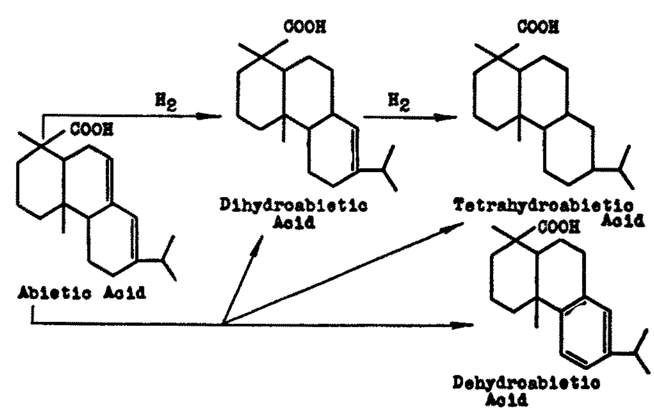
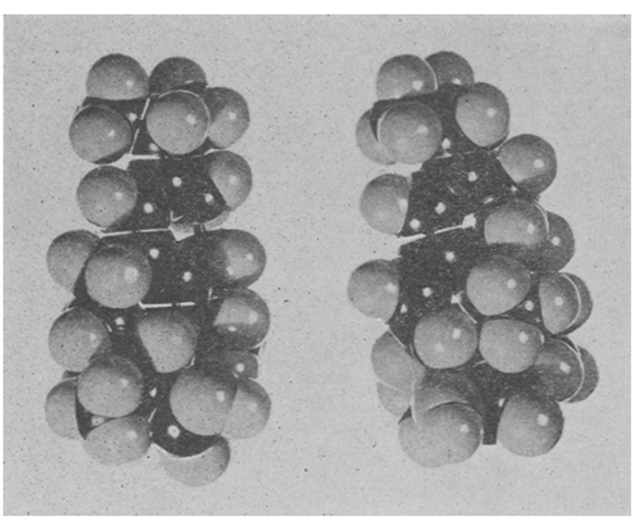


FIG. 7. Hydrogenation and Disproportionation of Rosin.

ture and properties. Contrary to general belief, abietic acid represents only a portion of the total resin acids and may be present to the extent of 0% to about 40% depending upon the history of the rosin.

The resin acids present in rosin are unsaturated and contain two double bonds. One of these double bonds is more reactive than the other. This unsaturation causes rosin to absorb oxygen or oxidize. For some purposes, this unsaturation is desirable while for other purposes it is detrimental. For the latter type of uses rosin can be markedly improved by hydrogenation or disproportionation.



l-Pimaric Acid   Abietic Acid

FIG. 6. Molecular Models.

TABLE 2

Properties of Staybelite and N Wood Rosin

	Staybelite*	N Wood Rosin
Acid Number	162	167
Melting Point (Drop Method)	167°F.	181°F.
Saponification Number	167	172
Unsaponifiable Matter	8.9%	6%
Specific Rotation	+26°	+12°
Petroleum Ether Insoluble	0.1%	0.1%
Gasoline Insoluble	0.015%	0.015%

* Hercules grade of hydrogenated rosin.

As can be seen from the following graph, wood rosin is somewhat more resistant to oxidation than is gum rosin. Moreover, hydrogenated rosin (Staybelite) is extremely resistant to oxidation. This oxidation resistance of hydrogenated rosin carries through to the various derivatives made therefrom. As will be seen (Figure 9), hydrogenated rosin soap is resistant to oxidation and consequent discoloration.

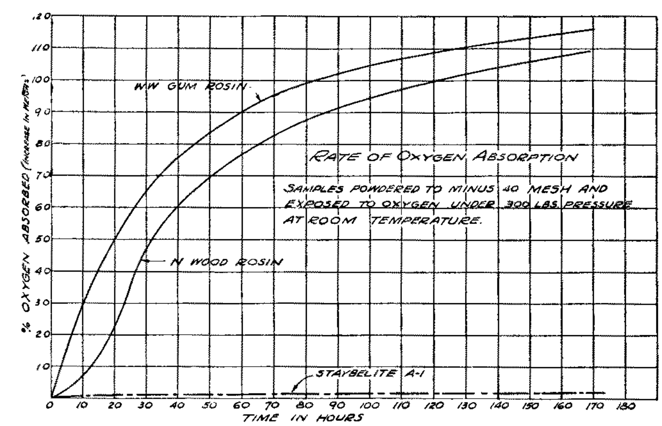


FIG. 8.

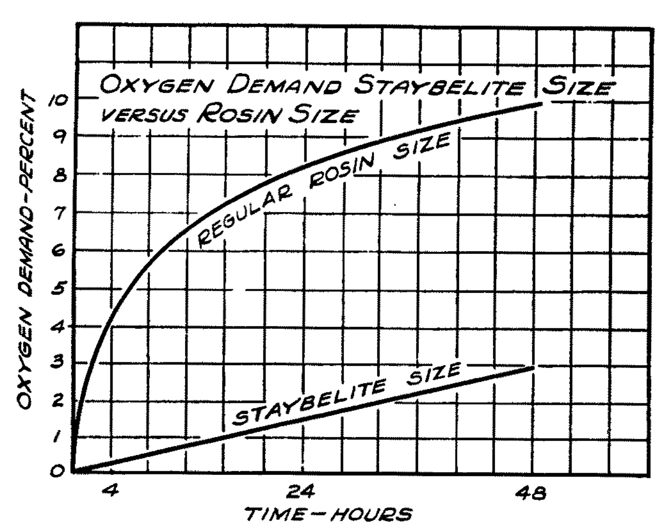


FIG. 9.

The versatility of rosin causes it to enjoy a large variety of uses. Suffice it here to point out that the major large-volume uses are in soap, paints, varnishes, synthetic resins, paper size, disinfectants, etc.

The use of rosin in soap manufacture began in the middle of the nineteenth century when it was used largely in high-tallow-content soaps. The presence of rosin was said to improve water solubility and sudsing.

In the past it has been the belief of many that rosin was of limited value for use in soap manufacture. According to this school of thought rosin serves primarily as a filler or extender. The work performed in this present investigation shows conclusively that the use of rosin imparts desirable properties which will be further discussed.

The advantages may be listed as follows:

1. Low price.
2. Dependable availability in large volume.
3. Quick and lasting suds.
4. Improved solubility.
5. No skin irritation.
6. Inhibits dusting of spray-dried soaps.

The heretofore believed disadvantages may be listed as follows:

1. Dark color of the original and aged soap.
2. Somewhat high unsaponifiable content as compared to fats.
3. Low solubility of lime soaps.
4. Reversion of the powdered rosin-containing soaps.
5. No by-product glycerin.
6. Odor is different from that of fatty acid soaps.
7. Poor detergent action.
8. Stickiness of soaps.

There has been much difference of opinion regarding the use of rosin in soap manufacture. Until recently no published data were available upon which a definite and accurate opinion or conclusion could be drawn. Hercules Powder Company therefore undertook an extensive research program to determine the true facts. This program was started several years ago and is still in progress. The results of this work have confirmed some of the opinions previously held but have also definitely made other beliefs no longer tenable.

A portion of the results of this research investigation will be briefly described. However, before going into details of this work, we wish to call attention to the work of W. D. Pohle and C. F. Speh of the Naval Stores Research Division, Bureau of Agricultural Chemistry and Engineering (Oil and Soap, July 1940, p. 150; Oil and Soap, December 1941, pages 244 and 247; Soap, February 1942, page 29), (W. D. Pohle and C. F. Speh, Oil and Soap, October 1940, page 214; Oil and Soap, May 1940, page 100). Also the work of L. D. Edwards (Soap, December 1941, page 65) who tested "The Action of Rosin Soaps on the Human Skin," and who stated that "it seems fair to conclude that rosin soaps and rosin acid soaps under the several conditions as outlined are relatively nonirritant to human skin."

The work of Pohle and Speh dealt largely with gum rosins and rosin acids. Tests were conducted with distilled water. In the work to be described, gum and wood rosins were used in order that the data obtained should be representative for all commercial rosins now available. Moreover, all of our tests were conducted using water of two different degrees of hardness, therefore more closely approaching the probable conditions under which soaps are actually used.

Rosins and Fats Used

The rosins and fats used in this work had the following analytical constants:

TABLE 3

Rosins and Fats Used

	Color	Softening Point °C.		Acid No.	Sapon. No.	Free Acidity
		Drop Method	Ring and Ball			
Staybelite	X (8A)	76	68	159	159	....
N Wood Rosin	N	85	80	167	174	....
H Gum Rosin	H	89	82	171	178	....
N Gum Rosin*	N	84	77	164	167	....
White Tallow	Prime	....	....	7	200	3.3
Brown Tallow	Brown	....	....	59	184	31.0
Coconut Oil	Prime	....	....	0	260	....

* Specially refined.

Preparation of Bar Soaps

The preparation of experimental soaps at the Hercules Experiment Station is by the full-boiled process which is the process used by industry for the bulk of its soap production.

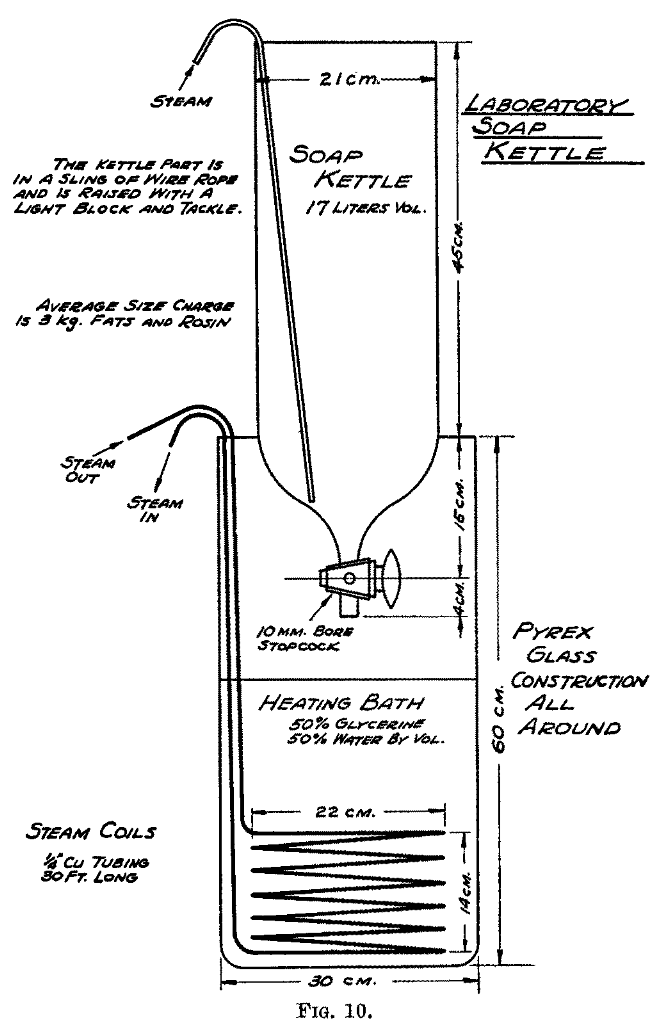


FIG. 10.

The apparatus used consists of a 17-liter Pyrex kettle (enabling full vision of all changes) slung in a wire rope harness, raised and lowered with rope and pulley, to permit easy siphoning off of a spent lye layer after a change. The soap after fitting and settling overnight at 90°C. is removed through the stopcock. The nigre, being considerably more fluid than neat soap, is easily removed in its entirety first if due care is used. This eliminates need of a swing-pipe and pump in the laboratory.

The technique used for soap boiling in our laboratory is essentially the same as that described by Dr. W. C. Preston of Procter and Gamble (entitled "Soap Boiling on a Laboratory Scale" in the J. Chem. Ed., October 1940, pages 476-8), and also described by R. E. Divine of the Soap Laboratory of Hooker Electrochemical Company (entitled "Laboratory Boiling of Soap in Glass" in Oil and Soap, **17**, 1940, pages 2-4). The change made lies in the use of rosin as a component of the soap.

Titre Value

The titre value of a soap stock is often considered as one of several criterions by which a raw material may be evaluated for use in soap manufacture. Fatty acids have a definite titre value, but rosin being amorphous has no titre and must necessarily be tested for titre value in conjunction with a fatty acid and the relative change in titre noted for each rosin. Using a high grade of white tallow fatty acid with gum and wood rosin, the following titre values were ascertained:

TABLE 4

	Titre
Tallow fatty acid soap stock only	47.8°C.
Tallow fatty acid soap stock + N gum rosin (50:50)	38.2
Tallow fatty acid soap stock + N wood rosin (50:50)	37.8

The titre values of the soap stocks used in the work here reported were as follows:

TABLE 5

	Titre Value
White tallow fatty acids alone	44.5
Brown tallow fatty acids alone	39.3
Coconut oil fatty acids	22.3
White tallow fatty acids with N wood rosin (50:50)	37.8
Brown tallow fatty acids with H gum rosin (50:50)	38.2

Sudsing Action

The apparatus used in the sudsing or foam test was described in detail with theory of operation in "An Apparatus for Comparison of Foaming Properties of Soaps and Detergents" by John Ross and Gilbert D. Miles in the May 1941 issue of Oil and Soap, pp. 99-102. The data obtained are illustrated in the following graph. These data show clearly that in moderately soft water (50 p.p.m. or 2.9 grains per gallon) the rosins in white or brown tallow-coconut oil base soap are quite effective in maintaining or improving the sudsing action. Refined wood rosin, however, was generally superior to gum rosin or Staybelite. This was true not only regarding the volume of suds developed but also in the stability of the suds. In moderately hard water (300 p.p.m. or 17.5 grains per gallon) all of the rosins were about equivalent. While

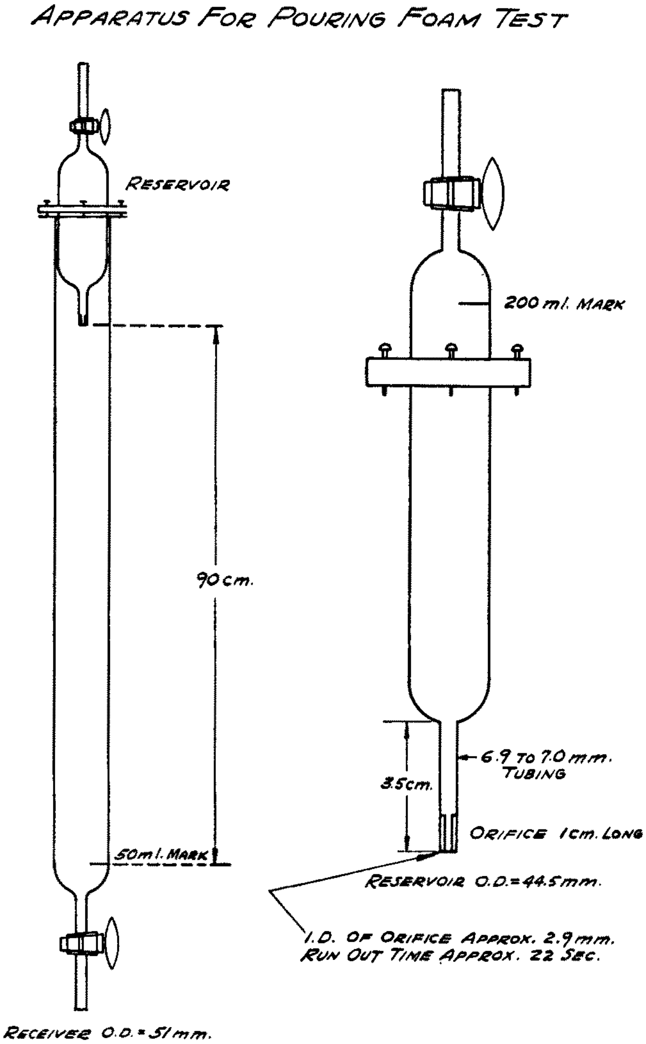


FIG. 11.

they did not enhance the suds volume or stability, they also did not detract from this desirable property of soap.

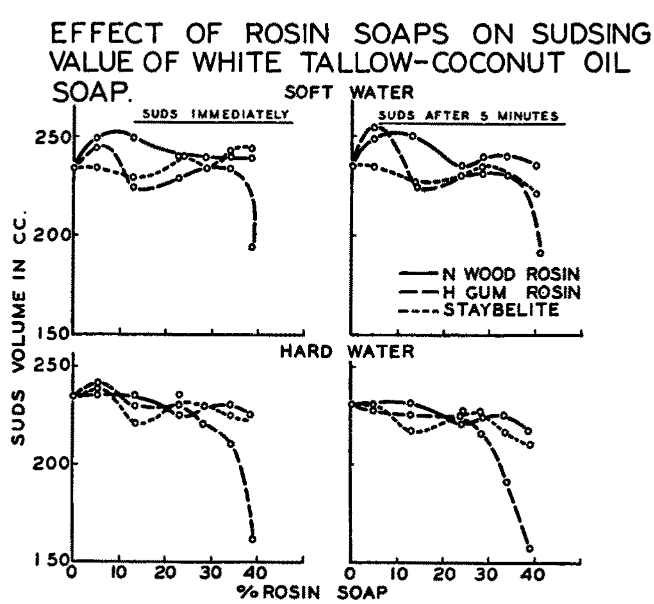


FIG. 12.

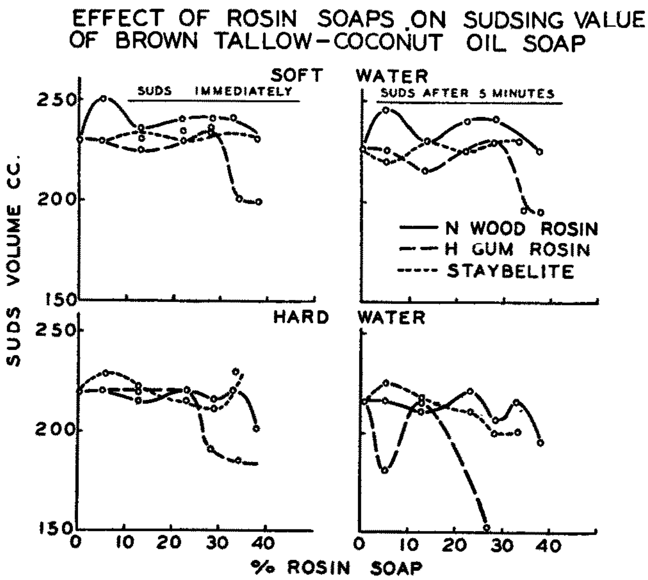


FIG. 13.

Detergent Action of Rosin-Containing Soaps

In determining detergent efficiency the standard washing test was used and comprised three steps; namely, (1) the soiling of a standard cotton cloth, (2) measuring the brightness of the cloth soiled with a vegetable oil, mineral oil and carbon black, and (3) washing the standard soiled cloth in a Launder-Ometer.

When used in conjunction with a white tallow-coconut oil base soap containing no builder, Hercules refined wood rosin, regular gum rosin, and Staybelite were about equivalent. Over the range of rosin concentrations normally used, these rosins not only maintained the high detergent action but actually enhanced this property of the base soap. The specially refined gum rosin was somewhat less effective. This was true when tested in water of moderately low hardness (50 p.p.m. or 2.9 grains per gallon). When harder water (300 p.p.m. or 17.5 grains per gallon) was used, Hercules refined rosin and regular gum rosin were substantially equivalent and maintained the detergent action of the base soap. Staybelite and specially refined gum rosin were equivalent and somewhat inferior to the previously mentioned rosins.

The use of rosins in brown tallow-coconut oil base soap gave a detergent action quite different from that in the white base soap. While all the rosins were somewhat less effective from the detergent viewpoint when used in the brown base soap, Hercules refined rosin and Staybelite were quite similar and superior to regular or specially refined gum rosins. This refers to evaluation in a moderately soft water (50 p.p.m. or 2.9 grains per gallon) and also a moderately hard water (300 p.p.m. or 17.5 grains per gallon).

While rosin-containing soaps are not so effective as fatty acid soap in hard water, this difference is not too great over the range of rosin concentrations normally used.

The above conclusions are based on the data from which the following graphs were plotted. It will be observed that according to these graphs rosin soaps possess substantially zero detergency when tested per se. It must however be kept in mind that a soiled cloth was used which was not easily scoured. Moreover, certain commercial laundry soaps which contained no rosin when tested with this soiled cloth also gave zero detergent action.

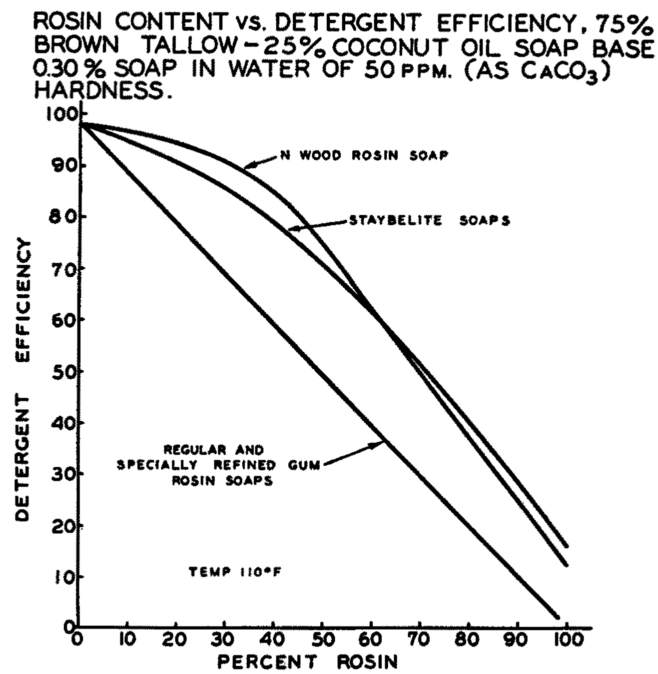


FIG. 14.

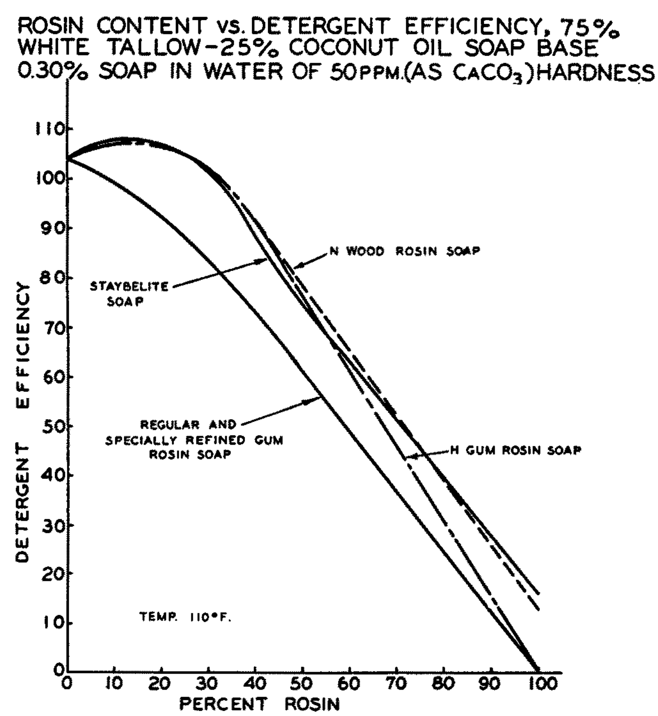


FIG. 15.

White tallow (high-titre) base soaps which contained 15 and 25% of K wood rosin possessed approximately the same detergent value in soft and hard water as did the tallow base soap.

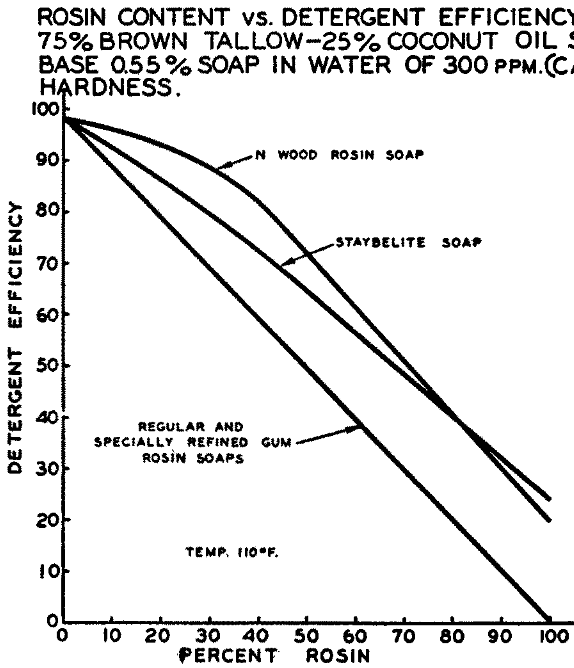


FIG. 16.

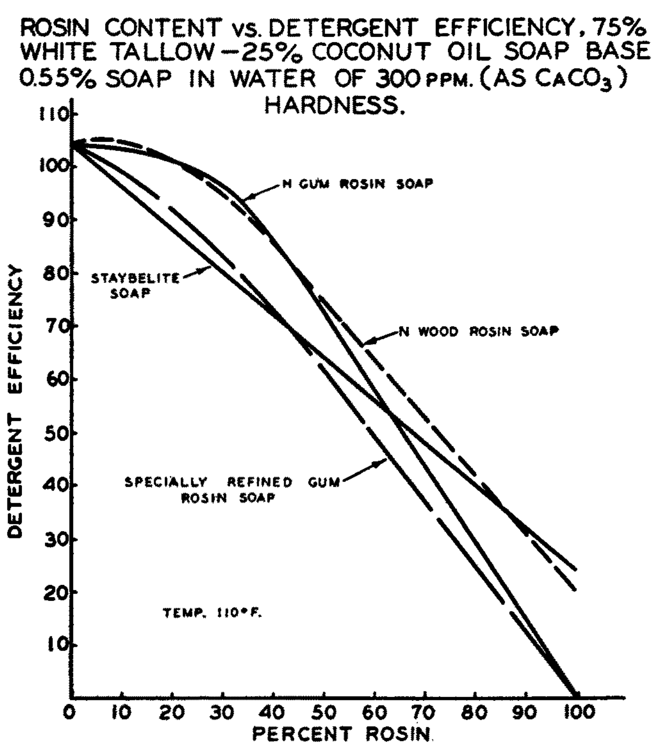


FIG. 17.

TABLE 6

Soap	Detergent Efficiency + 0.30% Soap 50 p.p.m. Hardness 2.94 grains per gal.	0.55% Soap 300 p.p.m. Hardness 17.5 grains per gal.
White tallow (100%)	93	93
White tallow (85%) K wood rosin (15%)	88	89
White tallow (75%) K wood rosin (25%)	92	90

The sudsing power of these soaps decreased somewhat with increase in rosin content. This was more evident in the case of hard water than soft water.

TABLE 7

Sudsing Value

Soap	0.30% Soap in Soft Water		0.55% Soap in Hard Water	
	Immediate	After 5 Minutes	Immediate	After 5 Minutes
White tallow (100%)	245	240	240	220
White tallow (85%) K wood rosin (15%)	240	225	220	190
White tallow (75%) K wood rosin (25%)	230	215	200	150

Staybelite when used in a white high-titre tallow base soap enhanced the detergent action in soft and also hard water. Regular rosin, on the other hand, had no apparent effect on detergent action. The sudsing action was, however, somewhat reduced. Staybelite caused a greater reduction than did regular rosin. Less reduction took place in the case of soft water than hard water.

TABLE 8

Detergent Efficiency

Percent Staybelite in White Tallow Soap	0.30% Soap in Soft Water	0.55% Soap in Hard Water
0	93	93
10	99	104
20	97	103
30	96	91

TABLE 9

Sudsing Value

Percent Staybelite in White Tallow Soap	Soft Water		Hard Water	
	Immediate	After 5 Minutes	Immediate	After 5 Minutes
0	245	240	235	225
10	235	215	225	190
20	220	205	205	180
30	220	140	200	170

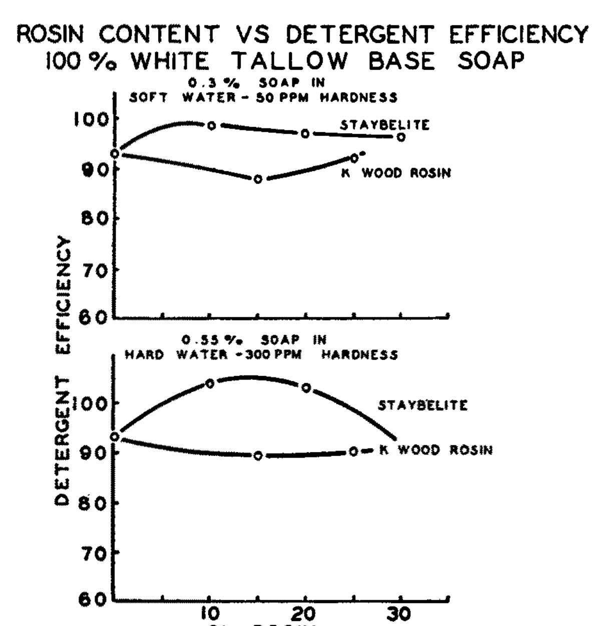


FIG. 18.

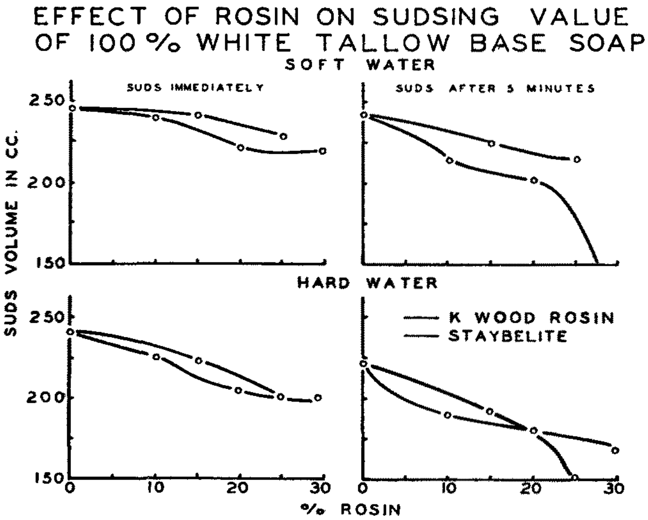


FIG. 19.

Rosin when substituted for part of the brown beef tallow of moderately high-titre value did not detract from the detergent efficiency of the base soap, when the rosin concentration was within the range of that normally used in soap manufacture. The detergent efficiency was somewhat better in the hard water than in the soft water.

The sudsing values for these same soaps were unchanged by the presence of the rosin soaps. This was true for the suds volume and also suds stability in both hard and soft water.

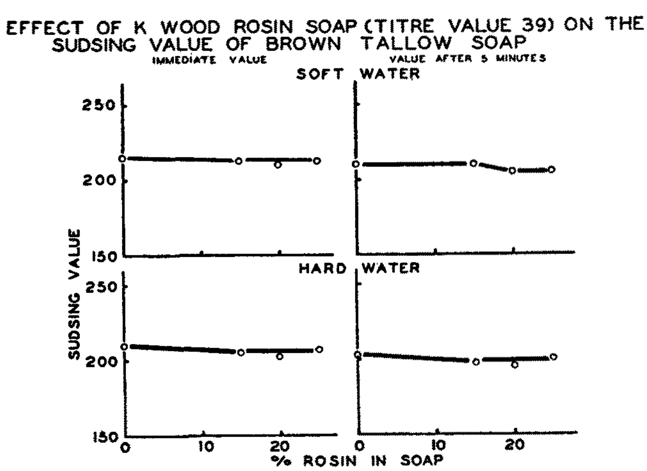


FIG. 20.

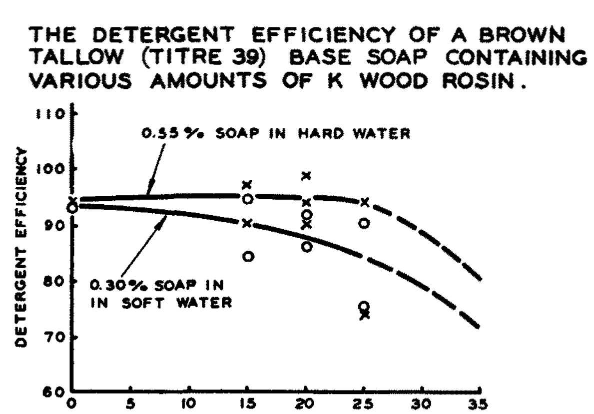


FIG. 21.

It appears from these results that the titre value of the tallow used determines to some extent the detergent action of the rosin-containing tallow soaps but has a more pronounced effect on the sudsing value and suds stability. Tallow of moderately high titre when used with rosin soaps is apparently superior with respect to sudsing properties.

Built Soaps

Built soaps were prepared using a brown tallow (90%)—grease (10%) stock as the base. These soaps were prepared so as to contain three different concentrations of rosin soap. To these finished soaps the builders were incorporated by crutching. The detergent efficiency of these built soaps was high as can be seen from the following test results.

TABLE 10

Soap Composition	(Dry Basis)	pH of Solution	Detergent Efficiency 0.30% Soft Water	0.55% Hard Water
K wood rosin soap	30%	9.4	84	73
Sodium silicate	12			
Sodium carbonate	4			
Base soap	54			
K wood rosin soap	27%	9.95	84	79
Sodium silicate	6			
Sodium carbonate	3.6			
Base soap	63.4			
K wood rosin soap	18%	10	103	83
Sodium silicate	6			
Sodium carbonate	3.7			
Base soap	72.3			

Spray-Dried Soaps Containing Rosin

Spray-dried soaps (white tallow 75%—coconut oil 25% base) which contained various percentages of rosin were prepared and tested.

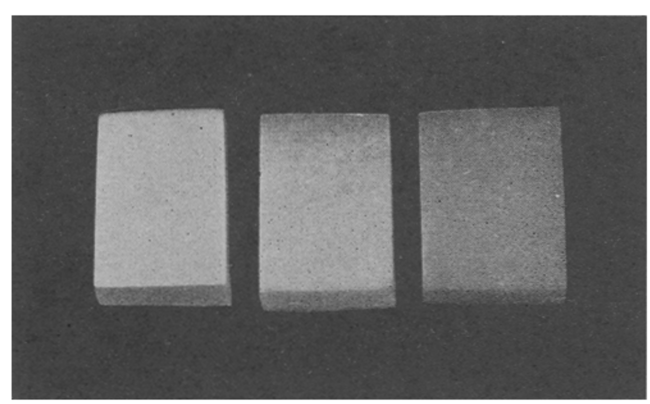


FIG. 22. Effect of rosin and Staybelite on color of bar soaps.
1. White toilet soap. 2. 5% Staybelite. 3. 5% N wood.

The spray-dried soaps were prepared by placing the molten soap in an autoclave at 325°F., which gave a gage pressure of 80 lb. per square inch. The molten soap at this temperature was increased in pressure by means of nitrogen to 250 lb. per square inch and sprayed into a chamber, countercurrent to air at 240°F.

Results showed quite definitely that powdered soaps which contained about 15% or less of the various rosins (dry basis) were not only light in color (substantially snow white) but had no apparent tendency to revert or coalesce when exposed to a temperature

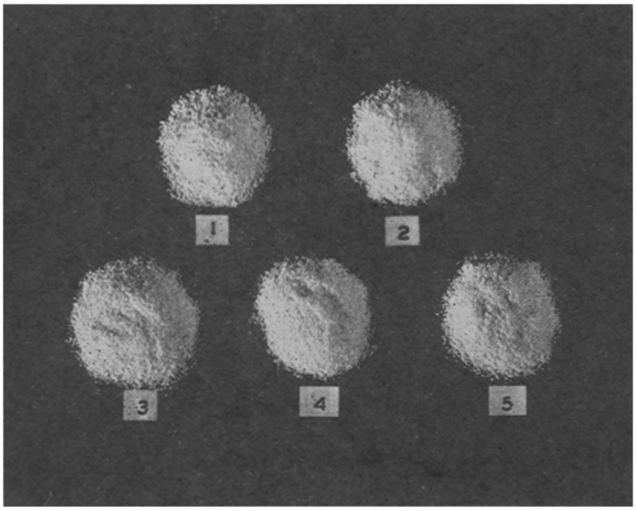


FIG. 23. Effect of rosin and Staybelite on spray-dried soaps.

1. Regular soap powder containing no rosin. 2. As 1 containing 15% of Staybelite. 3. As 1 containing 15% WG wood rosin. 4. As 1 containing 15% N wood rosin. 5. As 1 containing 15% WG gum rosin.

of 80°F. and high humidity (saturated air) for over 300 hours. These aged, spray-dried soaps showed no apparent tendency to discolor. Spray-dried soaps which contained 15% of Staybelite were definitely white in color.

Built soaps (15% rosin) which contained 12% of sodium silicate (dry basis) and 4% sodium carbonate were about equivalent in color and resistance to reversion as the unbuilt soaps.

All of the spray-dried, rosin-containing soaps were effective detergents.

Rate of Solution of Rosin-Containing Soaps

Results indicate that Staybelite is appreciably more efficient than K wood rosin in increasing the solubility of soaps of certain soap bases.

The method used in testing the solubility of soap is one approaching that of actual use, and uses the type water (not distilled water) one would be using and at a temperature normally used. The details of the test are as follows: measure the dissolving rate of the soap in question as 15 lb./min. of 50 p.p.m. hardness tap water at 110°F. (the temperature used in Launder-Ometer and foam tests) falls ten inches upon a 2 x 2 cm. slab of soap supported on a 16 mesh wire screen. The solution rate is equal to the weight of the soap sample, divided by the time in minutes to dissolve the soap.

Since coconut is no longer available in quantity, soaps now made will be composed largely of tallow and whatever other materials may be available. Babassu oil is quite satisfactory as a replacement material for coconut oil; however, it too is imported and consequently the supply is dependent upon oceanic transportation. Rosin and Staybelite (hydrogenated rosin), both of which are produced domestically, deserve serious consideration.

We have prepared and examined white and also brown tallow base soaps which contained varying percentages of rosin and also Staybelite. Evaluation of these soaps indicates that rosin does not improve the solubility of high-titre white tallow base soaps. Staybelite, however, does increase the solubility rate. Both rosin and Staybelite increase solution rate of moderately high-titre brown tallow or tallow-coconut oil base soaps.

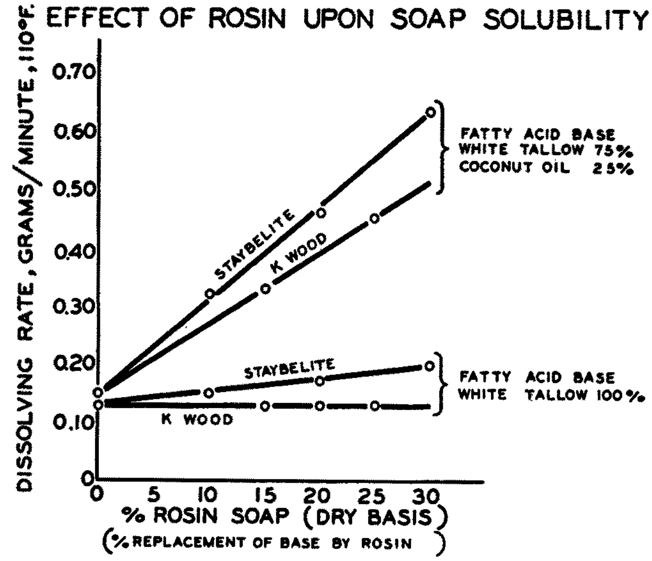


FIG. 24.

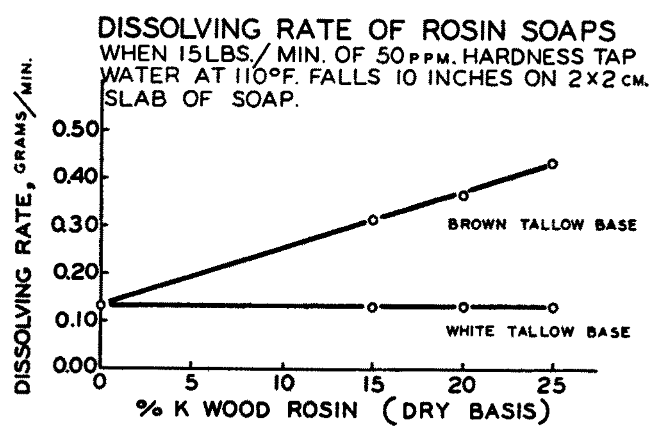


FIG. 25.

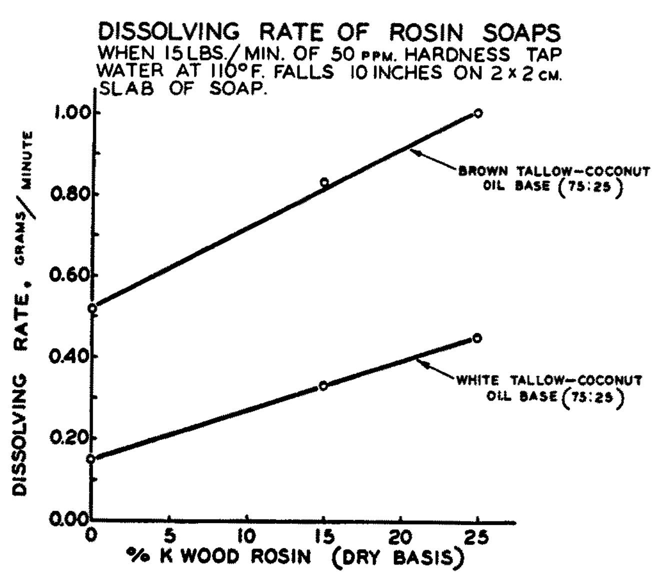


FIG. 26.