

the next higher acid is being distilled at constant temperature in virtually a pure state. Failure to obtain a successful "cutting" is immediately brought to light by the fact that the solidification point of the regenerated acids of the several fractions cannot be made to fall upon a curve for any of the binary systems.

This application of a fundamental principle of phase rule chemistry to the analytical problems of fatty oil and wax investigations has met with much success in demonstrating that the so-called margaric acid (C_{17}) of alfalfa seed oil is in reality a mixture of palmitic and stearic acids (3). It was also used in the identification of the previously unreported myristic acid in alfalfa seed oil (4), and in demonstrating the existence of behenic acid to the extent of 1.3% in peanut oil as well as in establishing the identity of the C_{24} (2.2%) acid therein as *n*-tetracosanic (1). The saturated acids of carnauba wax

from C_{18} to C_{26} , inclusive, have been identified by others (5) in another application of this method.

At present the method is being applied to a study of the saturated fatty acids of various oils with the twofold objective of obtaining revised data on the composition of the former and of demonstrating the probable existence of still unreported individuals therein. Because of the academic interest involved, this study has been made to include also the acids of odd number carbon atom content, alone and in admixture with those of even number. Solidification point diagrams of the acids higher than C_{26} are contemplated that these curves may find application in the examination and identification of the higher fatty acids of the waxes.

BIBLIOGRAPHY

- (1) Vogel, H. A., Ph.D. Thesis, University of Wisconsin, June, 1941.
- (2) Schuette, H. A., and Vogel, H. A., *Oil and Soap* 16, 209 (1939); 17, 155 (1940).
- (3) *Ibid.*, 16, 16 (1939).
- (4) *Ibid.*, 16, 223 (1939).
- (5) Bowers, R. A., *J. Am. Pharm. Assoc.*, 30, 10 (1941).

Foaming Properties of Rosin Soap and Their Comparison With Those of Fatty Acid Soaps

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Questions have frequently been asked about the foaming or sudsing properties of rosin soaps. Tests in the Naval Stores Research Division laboratory gave only qualitative data on the foaming properties of rosin soaps. Therefore, after Ross and Miles (2) described a method for comparing the foaming properties of soaps, it was decided to employ this procedure for evaluating the foaming properties of soaps made from gum rosin, modified rosin, and rosin acids and at the same time compare them with soaps made from individual fatty acids.

Experimental

Preparation of Soaps. The soaps for the foaming tests were prepared as follows:

A five-gm. sample of rosin or fatty acid was dissolved in 100 to 200 c.c. of 95 per cent alcohol. Using phenolphthalein as indicator, the alcoholic solution was almost neutralized with five N. NaOH and the neutralization was completed with 0.5 N. NaOH. The alcohol was evaporated and the sample dried in a vacuum oven at 100° C. The soap was powdered and stored in a vacuum desiccator.

Method. The solutions for the foaming tests were prepared by placing a weighed amount of the anhydrous soap in a 250-c.c. volumetric flask and then dissolving the soap in about 125 c.c. of hot distilled water, after which distilled water was added to make the volume of the solution 250 c.c. at 45° C. The solution was brought to this temperature by placing the flask in a constant temperature bath maintained at 45° C. and leaving it there for 10 to 15 minutes. The

same routine was followed in preparing and testing all of the soap solutions.

The dimensions of the apparatus and conditions of test using the apparatus described by Ross and Miles (2) were: The inside diameter of the tube in which the foam formed was 48 mm. The orifice of the 200-c.c. pipette was 2.8 mm. The height of fall was 92 cm. The tests were conducted at 45° C.

Soaps made by the above procedure from the following products were tested for foaming properties: Rosin (color grade WW) made from longleaf pine gum; rosin (color grade WW) made from slash pine gum; oxidized rosin¹; dehydroabietic acid (m.p. 170° C. $[\alpha]_D^{20} + 60^\circ$); abietic acid ($[\alpha]_D^{20} - 87^\circ$); dihydroabietic (m.p. 129°-130° C. $[\alpha]_D^{20} - 3^\circ$) acid; tetrahydroabietic acid (negative to tetranitromethane test for unsaturation); pyroabietic acid²; hydrogenated rosin³; commercial stabilized rosins; two series of commercial individual fatty acids; and one series of pure individual fatty acids.

Results

The rosin soaps made from slash-pine rosin and longleaf-pine rosin had the same foam producing properties. The curves in Figure 1 show that the oxidation of the unstable rosin acids in rosin tends to make the relation between foam production and

¹ Rosin (color grade WW) powdered and exposed in a thin layer to air at room temperature for over two months.

² Samples prepared at 200° C. and 275° C. as described by Fleck and Palkin (1).

³ Rosin hydrogenated at 170° C. under a hydrogen pressure of 1,900 lbs. per sq. in.

concentration a linear function. The state of oxidation of the rosin used for this test far exceeded that of the commercial rosins used in the manufacture of soap.

The effect of the amount of hydrogen in the rosin acid molecules on the foaming properties of rosin soap is illustrated by the curves in Figure 2. The

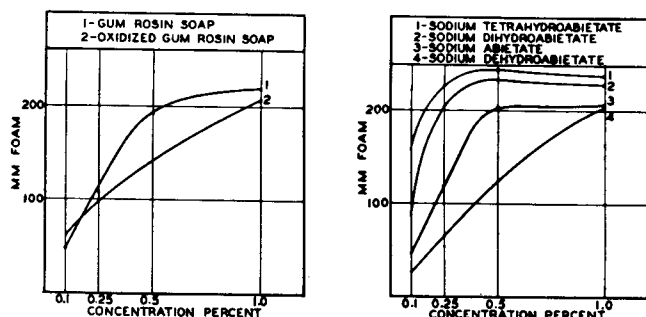


FIG. 1. Effect of Oxidation on the Foaming Properties of Rosin Soap.

FIG. 2. Foaming Properties of Soaps Made from Rosin Acids.

foam producing properties of sodium dehydroabietate is almost a linear function of the concentration. Increasing the amount of hydrogen in the rosin acids increases the foaming property and increases the deviation from a linear relation to concentration. This is also true of soaps made from pyroabietic acid produced at different temperatures. Fleck and Palkin (1) have shown that as the temperature for producing pyroabietic acid catalytically is raised from 200° C. to 275° C., the amount of hydrogen in the product is reduced. The curves in Figure 3 show that as the temperature for producing pyroabietic acid is increased the foaming properties of the pyroabietic acid soap is reduced. This is further evidence that the degree of saturation of the rosin acids has an effect on the foaming properties of rosin soap.

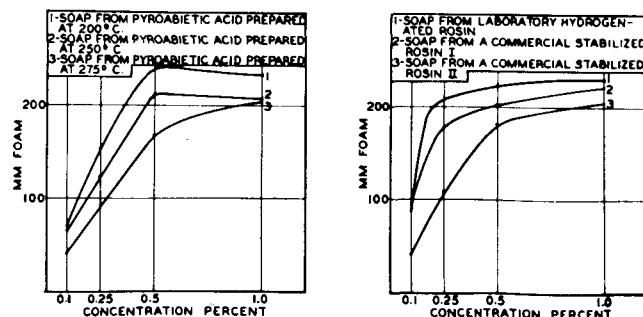


FIG. 3. Foaming Properties of Soaps Made from Pyroabietic Acids Prepared Catalytically at Different Temperatures.

FIG. 4. Foaming Properties of Soaps Made from Stabilized Rosins.

The foaming properties of the soaps made from laboratory-hydrogenated rosin and the commercial stabilized rosins indicate the types of acids in these products differ to some extent (Figure 4). The curve for commercial stabilized rosin II falls between the curves for abietic acid and dehydroabietic acid, while that for the commercial stabilized rosin I falls between the curves for abietic acid and dihydroabietic acid.

To compare the foaming properties of rosin soaps with those of the soaps of individual fatty acids, tests were made using soaps of individual fatty acids prepared commercially. One series of soaps made from commercial acids is given in Figure 5 and another series is given in Figure 6. Because of the marked difference in curves for stearic acid, a series of tests

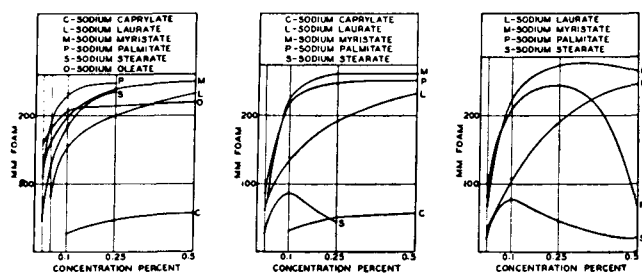


FIG. 5. Foaming Properties of Soaps Made from Fatty Acids Prepared Commercially.

FIG. 6. Foaming Properties of Soaps Made from Fatty Acids Prepared Commercially.

FIG. 7. Foaming Properties of Soaps Made from Pure Fatty Acids.

were run on soaps made from pure lauric, myristic, palmitic, and stearic acids (Figure 7). Jell formation was evident in the 0.25 per cent and 0.5 per cent sodium stearate and the 0.5 per cent sodium palmitate solutions which showed a marked reduction in foaming properties.

Soaps made from rosin, modified rosins, and rosin acids appear to be more like sodium laurate than any of the other individual fatty acid soaps tested.

Summary

The foam production of soaps made from rosin, modified rosins, and rosin acids were evaluated. The foam production of rosin soaps was compared with soaps made from the individual fatty acids.

There was no difference in the foaming properties of soaps made from longleaf and slash pine rosin.

Oxidation of the unstable rosin acids in rosin caused the foaming properties of the rosin soap to become more nearly proportional to the concentration.

The more hydrogen present in the rosin acid molecule the greater were the foaming properties of the rosin soap.

At temperatures between 200° C. and 275° C., the lower the temperature employed for producing pyroabietic acid catalytically, the greater were the foaming properties of the pyroabietic acid soap.

There was a difference in the foaming properties of commercial stabilized rosins.

In foaming properties the soaps made from rosins, modified rosins, and rosin acids were more like sodium laurate than the other individual fatty acid soaps tested.

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BIBLIOGRAPHY

1. Fleck and Palkin, J.A.C.S. 60, 921, 1938.
2. Ross and Miles, Oil and Soap, 18, 99, 1941.