It is apparent from the above figures that present production facilities are consuming less than 1% of the cattails shown by the surveys to be available. It is clear that these figures allow for the entry of other firms into the processing of cattails. In the event all available cattails were to be processed each year, approximately 200,000,000 pounds of seed would be acquired. From this seed about 34,000,000 pounds of oil and approximately 166,000,000 pounds of extracted meal could be obtained.[2] The size of the seed may present some difficulties in extraction on a commercial scale.

### Possible Uses

The relatively high linoleic acid content of Typha seed oil suggests that it may find use as a drying oil. Its drying properties could be improved by various treatments well known by the protective coating industries. Also it may be well suited for use in the manufacture of alkyds where the high acid value would not prove a disadvantage.

It was found that Typha seed oil has an unusually high acid number even though the value was determined on freshly extracted oil. The reason for the high acid number of this oil has not been determined. While it may be a normal condition in the oil, it may quite possibly be due to the weathering conditions to which the seeds are usually exposed before being harvested. Most of the cattails now being processed are harvested by hand during the winter when the marshlands are frozen and workmen can gain access to the plants. The seeds are therefore exposed to severe weather conditions, and, being very small, they afford little natural protection to the oils contained therein. A high acid number indicates that relatively high refining losses would occur during alkali refinement of Typha seed oil for edible purposes or other uses requiring a refined oil. It seems likely however, that sufficient uses could be found for this oil to make its production worthwhile.

Typha seeds have been used successfully as a cattle and chicken feed. The crushed and extracted seed meal might well be used for edible purposes. It is fairly rich in proteins and contains ample quantities of carbohydrates. In fact, its high carbohydrate content might make it a valuable source of starch and sugars.

---

[2] Courtesy of Mr. Harold Hamley, Burgess-Manning Company, Chicago, Illinois.

REFERENCES

1. Kimura, Y., Chinese Drug, "Pu-hwang." J. Pharm. Soc. Japan *50*, 843-50 (1930). C. A., *25*, 172 (1931).
2. Sinozaki, Y. and Takumi, S., "Puhwang" Seed Oil. J. Agr. Chem. Soc. Japan *17*, 553-8 (1941). C. A. *36*, 4361 (1942).

# Use of Modified Rosins in Soap

B. S. VAN ZILE * and J. N. BORGLIN
**Hercules Experiment Station**
**Hercules Powder Company, Wilmington 99, Delaware**

WE have been unable to discover when and by whom rosin was first used in soap, but we all know that rosin has been used in the making of soap for a great many years. In the early days of its industrial use it was all gum rosin from the turpentine farms and seems to have been of poor quality. However, it did make possible the production of soap from some fats that would otherwise have been unfit for the making of soap. As time went on, the production of rosin came under better control and it was possible to grade the product according to color. But even then the control of quality was not too exact because of crude methods of production, and it required an expert properly to grade the material.

With the advent of wood rosin into the field, there became available rosins whose characteristics could be quite accurately controlled because of the solvent processes used in refining. However, even these rosins left something to be desired. While the addition of rosin increases the rate of solubility of soap made of high-titer fat and gives a soap that will lather freely, rosin still has some disadvantages when used in certain types of soap where color is important. Chief of these disadvantages is its susceptibility to oxidation with a consequent darkening of the color of the soap. Even a soap made from X grade rosin, while perfectly white when fresh, will darken to a brown color with age.

Knowing the beneficial properties that rosin imparts to soap but also realizing its inherent shortcomings, a number of chemists have been working for several years on the production of modified rosins that would retain the desirable properties and eliminate or mitigate the undesirable ones. We believe this end has been largely achieved in the production of certain modified rosins. It has been found that these modified rosins have properties peculiar to themselves and which can be advantageous when properly used in soap.

IT is the purpose of this paper to point out wherein these modified rosins differ from ordinary rosin and the advantages they offer when used as an ingredient in soap. A great deal of attention has been given to the improvement and stabilization of the color of rosin. To do this color bodies must be removed or destroyed and the rosin rendered less susceptible to oxidation. This can be accomplished by hydrogenation, dehydrogenation, or polymerization.

The tendency for rosin to oxidize with the resulting formation of color bodies is due to the presence of two ethylenic linkages, or double bonds. While these double bonds are quite readily oxidized, they also respond to hydrogenation. And whereas oxidation promotes color formation, hydrogenation destroys color bodies and makes their subsequent formation more difficult.

When the lighter grades of wood rosin are hydrogenated, the product is a clear, very light amber-colored solid that is quite difficult to oxidize. The rate of oxygen absorption will be discussed after dehydrogenated and polymerized rosins have been considered.

---

* Chairman, Committee D-12 on Soap and Other Detergents of the American Society for Testing Materials.

[1] Presented at 19th annual fall meeting of the American Oil Chemists' Society, Chicago, Nov. 7-9, 1945.

When rosin is dehydrogenated, a product is formed which is very resistant to oxidation. At the same time part of the liberated hydrogen reacts with and destroys the color bodies; also, considerable amounts of di- and tetra-hydroabietic acids are formed. The product is light in color (Grade X or better), and its oxygen absorption is very small.

When rosin is polymerized, most of the color bodies are destroyed, and a large proportion of the reactive double bonds are eliminated. The product is WG or WW in color and is not readily oxidized.

The rates of oxygen absorption of three types of modified rosins, i.e., hydrogenated, dehydrogenated, and polymerized, are compared with that of ordinary wood and gum rosin in Figure 1. The plotted data indicate that, under the conditions of the test, hydrogenated rosin (Staybelite[1]) did not absorb a weighable amount of oxygen in 170 hours. Dehydrogenated rosin absorbed about 0.06% and polymerized rosin about 0.8% of their weights in the same length of time. Comparing these figures with the 10.5% absorption of wood rosin and the 11.5% absorption by gum rosin, it is obvious that the modified rosins have been greatly improved in this respect.

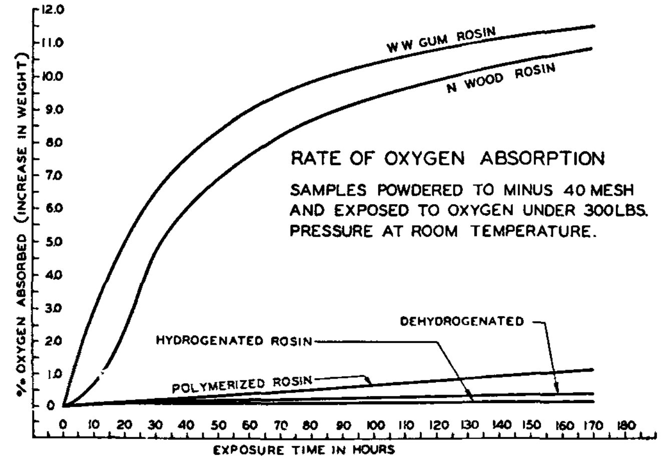

FIG. 1. Rate of oxygen absorption of modified rosins versus wood and gum rosins.

SOAPS prepared using the modified rosins do not darken in color, upon aging, to any greater extent than is normal for soaps made from the same fats without any rosin. This is probably due to the reduction of the number of reactive double bonds. Both hydrogenated and dehydrogenated rosins yield sodium salts with improved solubility characteristics. Either process gives rosins which increase the rate of solution of soaps containing them over that of soaps with equal amounts of ordinary rosins. These modified rosins may be used to replace part or all of the coconut-type oils. The greater solubility of the sodium salt of dehydrogenated rosin should be of especial interest in the preparation of liquid soap products because a 20% solution of it has been found to be stable at room temperature. Polymerized rosin does not lower the titer point of fatty acids to the same degree as do ordinary rosins because polymerization raises the melting point 30°F., or more, above that of the ordinary rosins. Due to this higher melting point soaps containing polymerized rosin are firmer in consistency than those containing the regular low-melting rosins.

Polymerized rosin does not give as light a colored soap as does hydrogenated or dehydrogenated rosin; but where extreme whiteness is not required, it makes a good firm soap that lathers freely and does not darken to any great extent in storage.

Typical analyses of the modified rosins compared to that of a regular wood is given in Table I.

TABLE I.

| | Type of Rosin | | | |
|---|---|---|---|---|
| | Regular WG Wood | Hydrogenated† | Dehydrogenated | Polymerized†† |
| Acid Number | 166 | 162 | 160 | 150 |
| Saponification Number | 172 | 167 | 170 | 160 |
| Unsaponifiable Matter | 6.0% | 9.0% | 8.0% | 7.0% |
| Melting Point (Drop Method) | 181°F. | 168°F. | 177°F. | 214°F. |
| Density | 1.067 | 1.045 | 1.070 | 1.073 |
| Color, U. S. Rosin Standard | WG | X+ | X+ | WG-WW |

†Staybelite grade.[2]
††Poly-pale grade.[2]

The use of modified rosins has been found effective in reducing the dustiness of spray-dried and granulated soap products. This property should be of especial interest to many producers of such products since it eliminates the operation of dust removal which they now find necessary.

As was said earlier in this paper, addition of rosin increases the rate of solubility of soap, especially those made from high-titer fats. This property is usually manifested by the speed with which the soap produces a lather. Naturally, the soap that is most readily soluble will lather the quickest. This rate of solubility is all too often confused with the lathering power of a soap as it is used in a washing machine or laundry wheel. The actual lathering value of a soap should be measured after the soap is in solution. For this determination we used the apparatus described by Ross and Miles (9) in which the conditions for producing a lather as well as the conditions which tend to destroy the lather can be accurately controlled.

The lather tests were made using soaps containing 25% of the several rosins; the data obtained appear in Table II.

TABLE II.

Height of Lather in mm. of Soaps Containing 25% of Rosin or Modified Rosin, 36% Moisture Basis.

| | Soft Water* | | Hard Water* | |
|---|---|---|---|---|
| | Immediate | 15 Min. | Immediate | 15 Min. |
| Tallow Soap, No Rosin (Control) | 220 | 210 | 200 | 185 |
| N Wood Rosin | 225 | 220 | 210 | 200 |
| Hydrogenated Rosin | 235 | 235 | 220 | 215 |
| Dehydrogenated Rosin | 230 | 225 | 225 | 215 |
| Polymerized Rosin | 230 | 220 | 225 | 220 |

*Soft Water 50 p.p.m.—Hard water 300 p.p.m. as $CaCO_3$.

Soap Concentration in Soft Water 0.25% } Calculated on basis of soaps
Soap Concentration in Hard Water 0.50% } containing 36% water

Temperature 120°F.

All values are the average of 10 determinations.

Examination of data in Table II shows that the addition of any one of the rosins to a tallow soap slightly increased both the amount and the stability of the lather. It also shows that the modified rosins were slightly superior to ordinary rosin in this respect.

---

[1] Reg. U. S. Pat. Office by Hercules Powder Company.

[2] Reg. U. S. Pat. Office by Hercules Powder Company.

IT has long been known that soap solutions have a definite germicidal action (1, 2) and that the soaps of the short-chain ($C_8$, $C_{10}$, and $C_{12}$) saturated fatty acids and those of the unsaturated fatty acids have a stronger germicidal action than do those of the longer-chain saturated acids (2). Walker (3, 4, 5) reported that sodium resinates (rosin soaps) had greater germicidal action than soaps of the common fatty acids.

Fleck and Palkin (6) found that pyroabietic acid, which they said consisted of a mixture of dehydroabietic, dihydroabietic, and tetrahydroabietic acids, was much more active than the resinates of ordinary rosins. Stuart and Pohle (7, 8) also found that rosin soaps were more germicidal than fatty acid soaps and that the sodium salts of abietic, dihydroabietic, and tetrahydroabietic acids were more effective than those of normal gum rosins.

The data of Stuart and Pohle are plotted in Figure 2. Their data show that when using a 0.10% solution of the resinates in one-minute exposure, tetrahydroabietic acid killed all the organisms, dihydroabietic acid killed over 99%, abietic acid killed about 62%, while dehydroabietic acid killed about 50%. The control plate showed a count of 3 to 4 thousand of the test organism which was staphlococcus aureus. At a concentration of 0.25% tetrahydroabietic and dihydroabietic acids were reported to have killed all while abietic acid killed about 100% and dehydroabietic acid killed about 80%. Since rosins modified by hydrogenation contain much higher quantities of the tetra- and di-hydroabietic acids than ordinary rosins, their use would seem to be indicated where germicidal properties are desired.

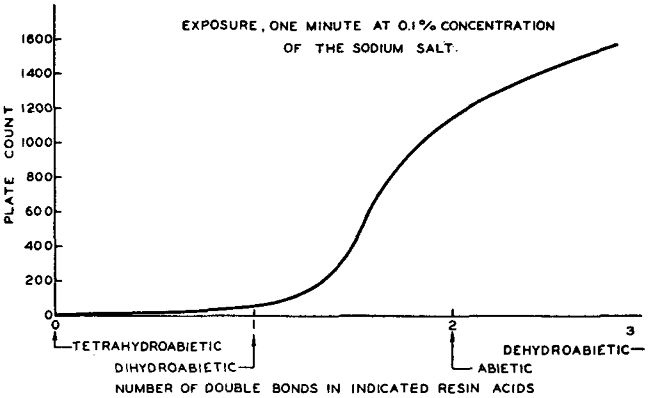

FIG. 2. The effect of unsaturation on the germicidal value of rosin acids test organism: Staphlococcus aureus from the data of Stuart and Pohle (9).

A phenomenon about which we can find no reference in the literature constitutes, we believe, one of the best reasons for the incorporation of rosin in soap. The presence of rosin increases the wetting power of soap. This is illustrated in Figure 3, which shows that a solution of 2.5 grams of tallow soap per liter wets a 5-gram skein of cotton yarn in about 41 seconds. This same weight of a mixture of 90% tallow soap and 10% hydrogenated rosin soap wets the skein in 25 seconds, while 80% tallow soap and 20% hydrogenated rosin soap wets the skein in 16 seconds. The wetting time remains at this minimum until a composition of 30% tallow soap and 70% hydrogenated rosin soap is reached. After this the curve rises sharply until at 100% hydrogenated rosin soap the wetting time is 64 seconds. The fact that the mixtures of tallow soap and hydrogenated rosin soap wet faster than either ingredient alone is quite apparent. The curve in Figure 3 is for hydrogenated rosin, but the curve for dehydrogenated rosin falls practically on the same points. The curve for polymerized rosin shows the same general characteristic, but it does not reach the minimum of 16 seconds until 30% of polymerized rosin soap has been added.

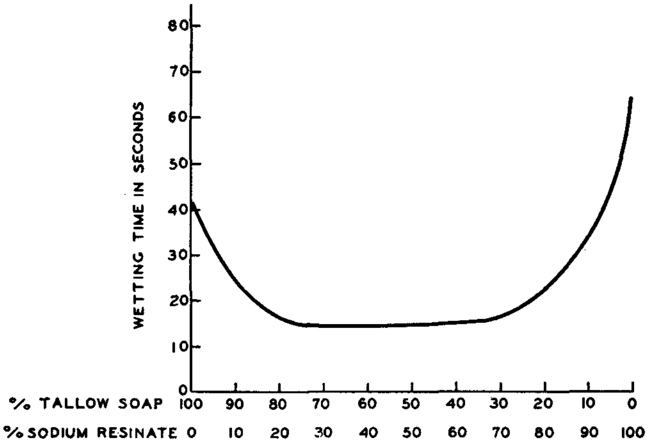

FIG. 3. Wetting-out time for mixture of tallow and hydrogenated rosin soaps.

THE effect of modified rosins on the detergent value of soap products is, in general, about the same as that of the ordinary rosins. While the addition of the modified rosins to fatty acid soap does not enhance the detergent value, at least to any great extent, quite large percentages can be used without lowering the detergent value. Figure 4 shows the detergent value of 42° titer neutral tallow soap at decreasing concentrations. The tallow soap at 0.30% concentration was arbitrarily selected as 100% efficient. By decreasing the concentration in steps of 10%, the lower curve was obtained which theoretically should have been a straight line from the point of 100% efficiency to 0% efficiency at the point of 0% soap. This might have been the case had water of zero hardness been used; but with the water of 50 p.p.m. hardness which was used, it required 0.09% of soap to react with the hardness which moves the zero point into the indicated position. Between these two points (0.30 and 0.09%) the curve is practically a straight line.

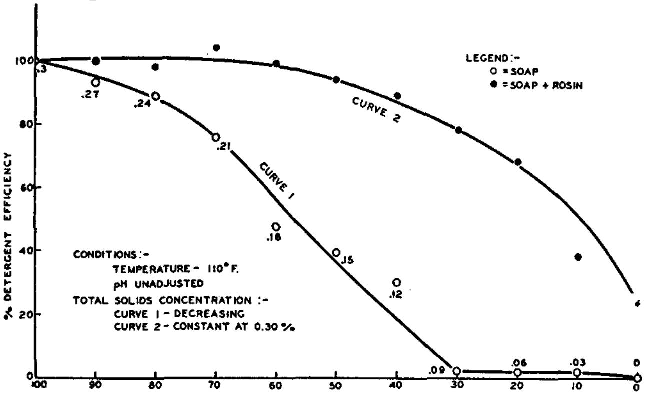

FIG. 4. The effect of hydrogenated rosin on the detergent value of tallow soap.

The upper curve shows the detergent values obtained when the soap concentration was maintained at 0.3% and the tallow soap was removed and replaced with the indicated proportions of sodium resinate of hydrogenated rosin. The distance between the upper and lower curves represents the amount of detergency that the resinate contributed to that of the whole mixture. Only the curve for hydrogenated rosin is shown since it is typical of all those obtained using the several types of modified rosins tested. Since sodium resinate, like sodium laurate, is not a very good detergent at the concentration of 0.3%, we believe that the reason for its maintaining the detergency of the fatty acid soaps, as shown in Figure 4, is due to the increase in the wetting power which was discussed in the preceding paragraphs.

We also have indications that the addition of sodium resinates increases the emulsifying power of soap, but since there is no standard method for the determination of this property, no specific data along this line are presented. This property may, however, contribute something to the detergency of fatty acid soap—resinate mixtures.

In general, the effects of temperature, pH, and the several alkaline builders on soap products containing the modified rosins was found to be the same as for straight fatty acid soaps. These effects are so well known that it is unnecessary to go into more detail in the present paper. The use of modified rosins is not limited to any one type of soap. They have been used in milled toilet soap, floating soap, chip soap, and granulated or spray-dried soaps and have proven entirely satisfactory in every case.

### Summary

We have endeavored to show the advantages that rosins modified by hydrogenation, dehydrogenation, or polymerization have over ordinary rosins when used in soap.

Ordinary rosin darkens in color upon oxidation. The modified rosins are not as susceptible to oxidation, and, therefore, soaps made using them do not darken in color to any greater extent than is normal for a soap made from the same fat stock but without rosin.

The modified rosins when used as a replacement for part of the fat in soap making increase the rate of solubility of soap to a greater extent than do the ordinary rosins. They also show a slight advantage on the amount and stability of the lather.

Hydrogenated rosin should be considered wherever germicidal value is desired since it contains a large proportion of tetra- and di-hydroabietic acids which have been shown by other investigators to have greater germicidal activity than the ordinary rosin acids or the fatty acids.

The addition of modified rosins increase the wetting action of fatty acid soaps.

It is indicated that up to 50% of modified rosin can be added to soap without decreasing detergent action, which, taken together with its other beneficial properties, makes it an ideal extender for fatty soap stocks.

REFERENCES

1. Koch, Mitteilungen a. d. Kaiser. Ges. Amt. *1*, 271 (1881).
2. Klarmann, Soap *9*, No. 12, 23-37 (1933).
3. Walker, J., Infectious Diseases *35*, 557-66 (1924).
4. Walker, J., Infectious Diseases *37*, 181-92 (1925).
5. Walker, J., Infectious Diseases *38*, 127-30 (1926).
6. Fleck and Palkin, J. Am. Chem. Soc., *60*, 921 (1938).
7. Stuart, L. S., and Pohle, W. D., Soap *17*, No. 2, 34-7, 73-4 (Feb. 1941).
8. Pohle, W. D., and Stuart, L. S., Oil and Soap *18*, No. 1, 2-7 (Jan. 1941).
9. Ross, J., and Miles, G. D., Oil and Soap *18*, No. 5, 99-102 (May 1941).

---

# Oxidative Deterioration of Fats in Cereal Products*

**HOWARD O. TRIEBOLD**

**Pennsylvania State College, State College, Pa.**

THE PROBLEM of fat deterioration in cereal products presents more complications than a similar deterioration of commercial fats. The possible effect of each component of the cereal product on fat deterioration must be considered. So also must the various procedures involved in the processing of the product, such as mixing, baking, etc., as well as the packaging. Let us consider briefly each of these factors in their relation to fat deterioration.

*Shortening Agents.* Practically all baked goods as well as prepared mixes contain in their formula one or another of the various commercial fats as shortening agents. It is primarily this added fat which deteriorates and causes the product to spoil. Thus at first glance it would seem logical that the keeping ability of baked products would be related directly to the keeping ability of the shortening used. However, this has not been found to be the case by a number of investigators (Triebold and Bailey [1932-a], Bohn and Olson [1934], and others).

In 1932 Dr. Bailey and myself reported on a study of the keeping ability of 35 commercial cracker samples and the shortenings used in them, secured from as many cracker bakeries scattered over the country. We found that while in general the better keeping crackers were made with shortenings of good keeping qualities, there were several notable exceptions. In certain instances shortenings with poor keeping ability produced crackers with good keeping quality while in other instances the reverse was true.

In an attempt to find an explanation as to why good keeping quality crackers could be produced from a shortening exhibiting poor keeping ability (as indicated by accelerated oxidation studies), lard samples were oxidized to varying degrees of oxygen absorption and used as shortening agents in crackers (Triebold, Webb and Rudy [1933]).

---

*Presented at the Conference on Problems Related to Fat Deterioration in Foods under the auspices of Committee of Food Research, Research and Development Branch, Military Planning division, Office of the Quartermaster General in Washington, D. C., in June, 1945.