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Solubility of Calcium Soaps of Gum Rosin, Rosin Acids and Fatty Acids

W. D. POHLE

Naval Stores Research Division
Bureau of Agricultural Chemistry and Engineering

When soap is used in hard water insoluble soaps (usually calcium and magnesium soaps) are formed. These insoluble soaps precipitate from the solution when there is not sufficient soap to keep them suspended. The hardness of a water is due principally to the soluble calcium and magnesium salts it contains. This study has been limited to the calcium soaps formed when a solution of a soluble calcium salt is mixed with a dilute soap solution.

The amount of insoluble soap formed when soap is used with hard water depends upon the hardness of the water. The ordinary bar, flake or powdered soap is made up of the sodium soaps of numerous fatty acids or fatty acids and rosin. The least soluble calcium or magnesium soaps of the fatty acids or rosin will form and will tend to precipitate as soon as the amount formed exceeds the solubility of the calcium or magnesium soap. This study was undertaken to determine which of the calcium soaps would be likely to precipitate first and to compare the solubility of the calcium soaps of the rosin acids with those of the fatty acids.

Gum rosin is made from the pine oleoresin that exudes from the longleaf and slash pine when the tree is wounded by cutting through the bark into the sap wood. Steam distillation of the pine oleoresin yields a volatile portion (gum turpentine) and a non-volatile portion (gum rosin). The gum rosin is about 90 per cent of rosin acids and about 10 per cent of resenes (neutral compounds and compounds difficult to saponify). The rosin acids are a mixture (5) of d-pimaric acid, l-abietic acid, dihydroabietic acid (4) and unidentified rosin acids. Rosin acids, such as d-pimaric and dihydroabietic acid, are stable toward oxygen at room temperature but rosin also contains rosin acids that are easily oxidized. Oxidation of these unstable acids may affect the properties of products made from rosin.

Experimental

The calcium soaps were precipitated from a hot dilute solution of the sodium soap[1] by the addition of a five per cent aqueous solution of calcium chloride (A.C.S. grade) slightly in excess of the amount needed for complete precipitation of the calcium soap. This solution was filtered through a Buchner funnel and the precipitate washed with distilled water. The moist cake was transferred to a glass-stoppered pyrex flask and distilled water added (100 c.c. to each 2 to 4 gm. of Ca soap). The flasks were then heated on a steam bath for five hours. During this period the flasks were frequently shaken. Immediately after heating the flasks were placed in an oven maintained at 50° C. After the flasks had been in the oven a week, a 20-c.c. sample was removed with a pipette[2] and placed in a weighed porcelain evaporating dish. The water was evaporated by placing the crucible on a steam bath. When the evaporation was apparently complete the crucible was placed in a vacuum oven at 100° C. for an hour. The crucibles were then placed in a vacuum desiccator and allowed to come to room temperature. The crucibles were weighed and the calcium soap in 20 c.c. of solution was determined. The calcium soap in 100 c.c. of solution was then calculated by multiplying by five.

Calcium soaps made from the following products as described above were tested for their solubility in water at 50° C.: Rosin (color grade WW) made from longleaf pine gum; rosin (color grade WW) made from slash pine gum; oxidized rosin[3]; d-pimaric acid ($[\alpha]^{20}_{D}$ + 55°, m.p. 211-213° C.) (6); dehydro-

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[1] Concentration of sodium caprylate solution was 0.7 per cent; all the other sodium soap solutions were less than 0.25 per cent.

[2] The end of the pipette was so covered with a folded filter paper that the solution was filtered before entering the pipette.

[3] The unstable rosin acids in the rosin (color grade WW) were oxidized by powdering the rosin and exposing it in a thin layer to air at room temperature for over two months.

abietic acid ($[\alpha]^{20}_{D}$ + 60°, m.p. 170° C.) (1); l-abietic acid ($[\alpha]^{20}_{D}$ — 87°) (7); dihydroabietic acid[4] ($[\alpha]^{20}_{D}$ — 3°, m.p. 129-130° C.); tetrahydroabietic acid[5] (negative to tetranitromethane test for unsaturation); pyroabietic acid[6]; pure lauric acid; pure myristic acid; pure palmitic acid; pure stearic acid; n-caprylic acid (Eastman Kodak); and a commercial oleic acid (acid No. 199-201, iodine No. 88-89).

The results from these determinations are given in Table 1.

TABLE 1

Solubility of Calcium Soaps in Water at 50° C.

Calcium soap of	Mg. of calcium soap 100 c.c. of solution
Longleaf pine rosin	63
Slash pine rosin	47
Oxidized rosin	100
d-Pimaric acid	19
Dehydroabietic acid	20
Abietic acid	39
Dihydroabietic acid	20
Tetrahydroabietic acid	10
Caprylic acid	310
Lauric acid	13
Myristic acid	9
Palmitic acid	7
Stearic acid	3
Oleic acid	32
Pyroabietic acid prepared at 200° C	36
Pyroabietic acid prepared at 250° C	27
Pyroabietic acid prepared at 275° C	25
Commercial stabilized rosin I	30
Commercial stabilized rosin II	43

Discussion

Because many may wish to know the results obtained with calcium soaps made from gum rosins, the solubility of such soaps was determined. The solubility of calcium soaps made from gum rosins does not answer the question: Will calcium resinate precipitate first when a fatty acid-rosin soap is used in hard water? The amount of calcium soap in solution depends upon the solubility of the various calcium resinates that make up the calcium soap made from gum rosin. The more soluble resinates will go into solution in greater quantities than the less soluble ones, thus the milligrams of calcium resinate per 100 c.c. of solution represent the solubility of the more soluble calcium resinates in the calcium soap made from gum rosin. Because the calcium soaps of oxidized rosin acids are more soluble than the calcium soaps of the unoxidized rosin, it is not surprising that different results were obtained with the two gum rosins. The color of the calcium soaps in the evaporating dish indicated that the soap made from longleaf pine rosin contained more oxidized rosin acids than the sample made from slash pine rosin. Because rosin is made up of numerous rosin acids, it is better to study the solubility of calcium soaps made from individual rosin acids.

Determinations were made of the solubility of calcium soaps prepared from five individual rosin acids; three of these, d-pimaric, dihydroabietic, and l-abietic acids, are known to be present in gum rosin. The calcium soaps of these three rosin acids are more soluble in water than the calcium soaps of lauric, myristic, palmitic, and stearic acids. The data in Table 1 indicate that the calcium soaps of the principal saturated fatty acids in a fatty acid-rosin soap will precipitate before the calcium soaps of d-pimaric, dihydroabietic, l-abietic, and oleic acids.

From the solubility of the calcium soaps of the fatty acids, it is obvious why soaps made entirely of olive oil or coconut oil are less likely to produce a precipitate when used in hard water than those made with palm oil or tallow. The introduction of a double bond in the saturated fatty acid has a marked effect on the solubility of the calcium soap, as shown by the greater solubility of calcium oleate as compared with calcium stearate. A similar change in solubility of the calcium soap with a change in the amount of hydrogen in the molecule is also to be noted for the calcium soaps of l-abietic acid, dihydroabietic acid, and tetrahydroabietic acid.

Pyroabietic acid prepared by the catalytic method is made up of dehydroabietic acid, dihydroabietic acid, and tetrahydroabietic acid. As the temperature of producing pyroabietic acid catalytically is increased from 200° C. to 275° C. the amount of dehydroabietic acid in the product is increased, while the amounts of dihydroabietic acid and tetrahydroabietic acid are decreased (3). The calcium soaps of pyroabietic acid prepared at 200° C. appear to be more soluble than those made from pyroabietic acid prepared at 275° C. The decrease in solubility as the temperature of preparation is increased is due no doubt to the reduction in the amounts of dihydroabietic and tetrahydroabietic acid in the product.

The solubility of calcium soaps prepared from commercially stabilized rosins are included in the table because they may be of interest to some readers.

Summary

The solubility of calcium soaps of rosin acids and fatty acids have been determined and compared.

The solubility of calcium soaps of rosin acids (d-pimaric, dihydroabietic, and l-abietic acids) present in gum rosin was found to be greater than that of the calcium soaps of the following saturated fatty acids: lauric, myristic, palmitic, and stearic acids.

The calcium oleate was much more soluble than the calcium stearate.

As the amount of hydrogen in the rosin acid molecule is increased, l-abietic to dihydroabietic to tetrahydroabietic acid, the solubility of the calcium soap is decreased.

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[4] Prepared by hydrogenation of l-abietic acid with the aid of Pd-C catalyst at room temperature under 2000 lbs. pressure and purified by recrystallization from alcohol.

[5] Prepared by hydrogenation of l-abietic acid with the aid of Raney nickel catalyst at 190° C. and 2000 lbs. pressure.

[6] Samples prepared at 200° C., 250° C., and 275° C., as described by Fleck and Palkin (2).