Detergent Action of Rosin Soaps and Fatty Acid - - Rosin Soaps

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The literature on the cleaning action of soaps and the evaluation of detergency, although extensive for fatty acid soaps, contains practically no information for rosin soaps. A study of the detergent action of rosin soap and fatty acid-rosin soap herein presented is part of an investigation under way in the laboratory of the Naval Stores Research Division on the properties of soaps as affected by the use in soaps of resin and rosin acids, rosin and modified rosins.

It is recognized that measurement of only one of the factors related to the detergent action of a product is not sufficient to determine the usefulness of the compound as a detergent. To evaluate the detergent action of soaps more accurately, laboratory washing tests were developed (3, 5, 6). Such tests, while more practicable and reliable than data on factors associated with detergency, are themselves subject to variables that make duplications among different laboratories not a satisfactory as desired. However, results from a washing test differing in some respects from the one employed place the different soaps in the same order with respect to detergent action. Also, if the laboratory washing test simulates some type of practical application, the results should bear some relation to the results the product is likely to give in practice.

The apartment-type washing machine used in the following detergent tests was selected as it dpulicates a practical washing condition. The generally accepted method for preparing a standard soiled cloth was followed. The brightness of the soiled cloths was evaluated before and after washing, by reflectance measurements with a photoelectric photometer.

Method of Measuring Detergent Action

Unsized bleached sheeting with a thread count of 75 was cut into 12-inch squares and soiled by dipping in a carbon tetrachloride solution of lubricating oil, tallow, and lamp black (2,000 ml. CCl_4, 5 gms. lubricating oil, 3 gms. tallow, and 2 to 4 gms. lamp black). The cloth was dipped two or three times into the soiling solution, removed, allowed to drain, and hung up to dry. After drying for 24 to 48 hours at room temperature, the cloths were stored in a box for future use.

The cloths were numbered and their reflectance relative to MgO was measured with a photoelectric photometer[1] using a mercury lamp and filters for isolating blue light of wave length 436 mu. Reflectance measurements were made on each of the four quarters. All reflectance measurements were made on the cloth so folded as to have three layers back of the one on which the reflectance measurement was being made. The average reflectance of the four quarters was taken as the reflectance for the cloth. The cloths used for these detergent tests met the following requirements: (1) The reflectance of the soiled cloths was between 35 and 38 percent and (2) the maximum variation of one quarter from the reflectance for the cloth was less than 2.0 percent and usually about 1.1 percent.

Washing was accomplished in the washing machine by moving the cloth back and forth in the detergent solution (6 liters). The agitator changed direction of motion twice a second. Distilled water was used for preparing all detergent solutions. The cloth was washed for ten minutes in the detergent solution at 40° C., removed, rinsed three times in distilled water at room temperature, dried, ironed, and its reflectance measured. For each rinsing 500 cc. of distilled water was used. Between rinses the cloth was wrung out. The electric iron was used at low heat to prevent scorching.

The reflectance of the cloth after three 10-minute washings, less the reflectance before washing, was taken as an index of the detergent power of the solution. For convenience a gain of 1 percent reflectance will be referred to as a 1 unit of brightness regained. Thus, an increase in reflectance from 35 percent to 65 percent will be called an increase of 30 units of brightness. The average difference for duplicate determinations after three 10-minute washes was less than 1.0 unit of brightness. In the following data, the brightness recovered by washing in distilled water has been subtracted from that recovered by washing in the detergent solution. The units of brightness regained for each of three successive washings in distilled water were 10.2, 0.9, and 1.3, and totaled 12.4. The units of brightness regained by washing in detergent solution, less the units of brightness regained by washing in distilled water, are the units of brightness regained due to the detergent.

The concentrations of the soap solution used in this study are based upon the belief that 0.1 percent soap solution with a builder is typical of commercial laundry practice, while 0.2 to 0.5 percent is used in household practice. In order to cover this range 0.1, 0.25, and 1.0 percent solutions were selected for test.

Materials Studied

Sodium soap made from rosin produced from longleaf pine gum.

Sodium soap made from rosin produced from slash pine gum.

Sodium soap made from rosin produced from scrape.

Sodium soap made from oxidized rosin.[2]

Sodium soap made from abietic acid, $[\alpha]^{20}_{D}$ —84°.

Sodium soap made from pyroabietic acid.

Sodium soap made from hydrogenated rosin.

Sodium soap made from tallow.

Sodium soap made from coconut oil.

In addition, the following compounds were used with rosin soap: Salt ($NaCl$); borax ($Na_2B_4O_7.10H_2O$); sodium hexametaphosphate ($Na_2[Na_4(PO_3)_6]$); sodium carbonate Na_2CO_3); trisodium phosphate ($Na_3PO_4.12H_2O$); sodium metasilicate ($Na_2SiO_3.5H_2O$);

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[1] This instrument was designed by Dr. B. A. Brice (Rev. Sci. Instruments 8, 279, 1937) and loaned to us by R. W. Frey of the Hide, Tanning Materials and Leather Section of Industrial Farm Products Division.

[2] Rosin powdered and exposed to air in a thin layer at room temperature for 2 or 3 months.

and tetrasodium pyrophosphate ($Na_4P_2O_7$) to determine possible effect on detergent action of the soap.

TABLE I

Detergent Action of 0.25% Rosin Soap Solutions

	Units of Brightness regained due to the detergent			
Soap from*	1st Washing	2nd Washing	3rd Washing	Total
Slash pine rosin	13.7	5.4	1.4	20.5
Longleaf pine rosin	12.9	5.7	1.9	20.5
Scrape rosin	12.6	5.7	2.3	20.6
Oxidized rosin	12.1	5.8	2.7	20.6
Pyroabietic acid	11.3	5.1	1.8	18.2
Abietic acid	11.2	5.9	3.2	20.2
Hydrogenated rosin	14.7	6.6	0.9	22.2

*No fatty acid soaps in any of these soap solutions.

Results

The results of the washing tests on a series of 0.25 percent rosin soap solutions are given in Table I. These results indicate there is no appreciable difference in the detergent action of rosin soaps made from rosin produced from gum of the longleaf or slash pine, from scrape or oxidized rosin.

The relative detergent action of soaps of pyroabietic acid, abietic acid, and hydrogenated rosin indicates that the amount of hydrogen present in the rosin acid molecule influences the detergent action of the soap solution. Pyroabietic acid was prepared from abietic acid by the method of Fleck and Palkin (1) at 250° C., and is principally dehydroabietic and dihydroabietic acid (2), while the hydrogenated rosin is chiefly dihydro and tetrahydro rosin acids. In these cases the detergent action of the rosin acid soaps parallels their ability to lower the surface tension of water (4).

The effect of salt and other compounds frequently added to or used with soap, on the detergent action of a rosin soap made from a slash pine rosin was tested. The results are given in Table II.

TABLE II

Comparison of 0.1% Rosin Soap Solution Alone and 0.1% each of Added Material and Rosin Soap

		Units of brightness regained due to the detergent			
pH of Solution	Material added	1st Washing	2nd Washing	3rd Washing	Total
8.7	None	11.2	5.0	1.9	18.1
8.7	Salt	10.8	4.7	2.7	18.2
9.2	Borax	10.6	6.4	2.1	19.1
8.9	Sodium hexametaphosphate	11.6	5.6	1.6	18.8
10.1	Tetrasodium pyrophosphate	15.3	6.0	2.1	23.4
11.1	Sodium carbonate	13.5	5.9	1.6	21.0
11.4	Trisodium phosphate	13.2	6.9	1.3	21.4
11.9	Sodium metasilicate	12.9	6.7	1.4	21.0

Salt, borax, and sodium hexametaphosphate have little or no effect on the detergent action of the rosin soap as measured, while tetrasodium pyrophosphate, trisodium phosphate, sodium carbonate, and sodium metasilicate all increase the detergent action. In the case of the three latter compounds the increase in alkalinity of the detergent solution may be the chief factor responsible for the improved detergent action, while with the tetrasodium pyrophosphate in addition to the smaller increase in alkalinity, the increase in suspending power of the solution may account in part for the improved detergent action. The rosin soap when used alone permitted deposition of soil removed from the cloth on the sides and agitator of the washing machine, but when tetrasodium pyrophosphate was used with the rosin soap, no deposition occurred on the sides or agitators of the washing machine.

Since tallow, one of the principal fats used for soap, is frequently blended with rosin or with coconut oil to produce soap stock, tests on a series of such soaps were included. The results are summarized in Table III. From these tests it appears that blending rosin soap with tallow soap will improve the detergent action of the soap solution having a concentration of 0.25 percent or more. This increased detergent action may be due to decreasing the gelling tendency of tallow soap by the presence of rosin soap.

The effect of temperature on the detergent action of the soap is important, as household soaps are used over a considerable temperature range. To determine the effect of temperature on the detergent action of certain soaps, washing tests were carried out at 40° C. and 70° C., and the difference in detergent action was evaluated by subtracting the units of brightness regained in washing at 70° C. from the units of brightness regained in washing at 40° C. The results in Table IV show that the only soap solutions appreciably affected by increasing the temperature were the 0.1 percent rosin soap solution and the 0.1 percent coconut oil soap solution.

TABLE III

Detergent Action of Two Fatty Acid Soaps, a Rosin Soap, and Fatty Acid-Rosin Soaps

		Units of Brightness Regained due to the Detergent			
Soap	Concentration percent	1st Washing	2nd Washing	3rd Washing	Total
Rosin*	1.0	10.9	7.1	2.0	20.0
Coconut oil	1.0	11.0	4.6	0.1	15.7
Tallow	1.0	11.7	4.7	1.4	17.8
Rosin	0.25	13.3	5.7	1.8	20.8
Coconut oil	0.25	15.5	5.5	1.0	22.0
Tallow	0.25	18.3	4.3	0.2	22.8
Tallow-rosin (Ratio 4-1)	0.25	17.8	5.4	1.5	24.7
Rosin	0.1	11.2	5.0	1.9	18.1
Coconut oil	0.1	13.5	5.7	2.0	21.2
Tallow	0.1	18.2	7.6	1.2	27.0
Tallow-Rosin (Ratio 4-1)	0.1	19.0	6.4	1.7	27.1
Tallow-coconut oil (Ratio 4-1)	1.0	10.4	6.8	0.7	26.9

*Slash pine rosin used in all above tests.

TABLE IV

The Effect of Temperature on the Detergent Action

		Units of Brightness regained washing at 40° C. less the Units of Brightness regained washing at 70° C.			
Soap	Concentration percent	1st Washing	2nd Washing	3rd Washing	Total
Rosin soap	0.1	3.0	—0.4	—0.1	2.5
Rosin soap	0.25	2.0	—0.8	—0.8	0.4
Coconut oil soap	0.1	0.9	0.2	0.5	1.6
Tallow soap	0.1	—1.5	2.1	—0.7	—0.1
Tallow soap	0.25	3.0	—1.6	—1.0	0.4
Tallow soap + $Na_2SiO_3.5H_2O$*	0.1	1.8	—0.5	—1.6	—0.3
Rosin soap + $Na_2SiO_3.5H_2O$*	0.1	—1.1	1.1	—0.6	—0.6

* Solution contained 0.1% soap and 0.1% builder.

Summary

A method for evaluating the detergent action of soaps has been described and applied to a series of soap solutions. The detergent action of rosin soaps, the effect of compounds present in soap or used with soap on the detergent action of a rosin soap, and the effect of rosin soap on the detergent action of tallow soap have been tested. The effect of temperature on the detergent action of some of the detergent solutions has also been determined.

The results of these detergent tests on rosin, fatty acid and fatty acid-rosin soaps indicated the following: (1) Rosin soaps made from different gum rosins, produced from longleaf and slash pine gums, have equal detergent action; (2) The presence of soaps of oxidized rosin acids has no effect on detergent action of the rosin soap; (3) The detergent action of soaps made from pyroabietic acid, abietic acid and hydrogenated rosin parallels their ability to lower the surface tension of water and the amount of hydrogen present in the rosin acids; (4) The addition of builders that increase the alkalinity of the rosin soap solution improves the detergent action of the solution; (5) The blending of rosin soap with tallow soap improves the detergent action of the tallow soap in solutions having a soap concentration of 0.25 percent or more; (6) Temperature affects the detergent action of rosin and coconut oil soaps more than tallow soap.

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Estimation of Saturated Glycerides in Shortenings and Margarines

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INTRODUCTION

Component glyceride data for many fats have been obtained by utilizing oxidation, crystallization and hydrogenation methods. Outstanding in this phase of fat study has been the work of Hilditch and co-workers. Their concept divides fats into two classes.

The first includes seed fats and marine animal fats whose glycerides are characterized by "even distribution" of fat acid radicals within the glyceride molecules.

Further, this concept applies to the hydrogenation of these oils; the saturation of glyceride molecules having unsaturated linkages to fully saturated follows in fairly well defined progressive stages.

The second class of fats, which includes the larger land animal fats, are characterized by glycerides of "uneven distribution" of the fat acid radicals. The amount of fully saturated glycerides present is much greater than in the seed fats with the same ratio of saturated to unsaturated fat acids.

Component fat acid data has not proved to be an enlightening manner by which to demonstrate the quantity and type of saturated glyceride present in a shortening. In this study, an attempt has been made to devise a method which will identify and quantitatively express predominantly saturated glyceride content. The study has included fat mixtures containing vegetable stearin (i.e. hydrogenated soybean oils) of two different degrees of saturation and mixtures containing animal stearin. In brief, the method employs the principle involved in the Bomer Number Test. Gravimetric and iodine number data are obtained for the solid fat fractionated from acetone-fat solution at 30°C.

METHOD

In a graduated centrifuge tube, 20 gms. of melted fat (40-45°C.) is dissolved in a quantity of acetone sufficient to make a total volume of 100 cc. at 30°C.

The fat-acetone mixture is held in a 30° ± 0.2°C. water bath for 18 hours. This period is sufficient to permit the crystallizing of the predominantly saturated glycerides.

The precipitated glycerides are filtered into a tared Gooch crucible. The fat crystals are washed with small portions of acetone, 30°C. until 100 cc. of the solvent has been used in this manner. The tared crucible is held in a vacuum dessicator until a constant weight is obtained.

The iodine number determinations, closed tube and Wiley melting point determinations were made in accordance with the Fat Analysis Committee Methods. The Bomer Numbers were calculated in the usual manner.

RESULTS AND DISCUSSION

The data given in Table No. 1 demonstrated that the predominantly saturated glycerides of cottonseed oil, coconut oil and partially hydrogenated cottonseed oil are not precipitated from acetone solution, 30°C.

The absence of precipitated crystals as indicated above led to investigating the solubility of the three stearins in acetone, 30°C. Table No. 2 shows that predominantly saturated glycerides are soluble in acetone, 30°C.; the extent of solubility is dependent upon the degree of saturation of the glyceride.

From Table No. 3 it is seen that the predominantly saturated glycerides are crystallized from fat-acetone solutions at 30°C. The weight of solid fat recovered for fat mixtures containing 2.19 Iodine number soya stearin is greater than theoretical value for the stearin content of the fat mixture. This is believed to be due to occluding action which may occur during the crystallization period. This, and the low solubility in acetone of the 2.19 Iodine number stearin favor a greater crystallization of predominantly saturated glycerides. Undoubtedly the solubility of the other stearins studied greatly affect the quantity of solid fat which is crystallized from acetone solutions.

Further, the data indicate that oleo stearin has appreciably less percentage of saturated glycerides than either of the two soya stearins.

The closed melting point tube data for fat mixtures with 8% soya stearin Iodine number 20.94 and those with 8% oleo stearin when compared with the data for the corresponding stearins show a preferential solubility of the more unsaturated glycerides in acetone; this separation taking place during the crytasllization period.

SUMMARY

A method has been used which has been successful in estimating the quantity of predominantly saturated glyceride present in a fat mixture such as a shortening or margarine oil base.