Surface Tension of Rosin Soap Solutions

By W. D. POHLE

ASSISTANT CHEMIST, NAVAL STORES RESEARCH DIVISION, BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING, U. S. DEPARTMENT OF AGRICULTURE

THE study of the properties contributed to soap by rosin and resin and rosin acids is included in the efforts of the Naval Stores Research Division to extend the use of naval stores to and in those products where it is best suited. This report covers one phase of the work dealing with the properties associated with the cleaning action of soap.

The removal of dirt or soil by washing with soap and water depends upon several factors. One of the major factors is the surface tension of the detergent solution. All of the factors associated with the cleaning action of soap have been studied with regard to the influence of fatty acids or fatty acid mixtures common in soap, but apparently have not been considered to any appreciable extent with regard to rosin. Since rosin is used in soap and information on the surface tension of rosin and rosin-fatty acid soap is of interest, a series of surface tension measurements was undertaken.

Experimental

The du Nouy tensiometer was used to measure the surface tension of the soap solutions and the results were recorded in dynes per centimeter.

The soap solutions for surface tension measurements were prepared as follows:

To 1 gm of fatty acid, and also to 1 gm of rosin and 25 to 50 ml of water was added just enough 0.5-N NaOH to neutralize the fatty acid or rosin. The alkali needed was determined by previously titrating 1 gm of fatty acid or rosin in alcohol until alkaline to phenolphthalein. The aqueous alkali solution was heated and stirred until clear. The solution was then made up to 100 ml in a volumetric flask, and cooled to room temperature, water was added to bring volume to 100 ml and the solution was thoroughly mixed by shaking.¹

The soap solutions containing 0.1 per cent fatty acid and 0.1 per cent of rosin were prepared by pipetting 10 ml of the above soap solutions into volumetric flasks and adding water until the volume was 100 ml. These solutions, if not alkaline to phenolphthalein, were made so by adding 1, 2 or 3 drops of a NaOH solution. The lower fatty acid soaps and rosin soap in 0.1-per cent solution do not have a pH value of 10, so it was necessary to add alkali since we wished to make all surface tension measurements at approximately the same pH.

The fatty acid-rosin soap solution containing 1 per cent fatty acid and rosin, in a ratio of 3:1, was prepared by mixing 75 ml of the fatty acid soap solution containing 1 per cent fatty acids and 25 ml of the rosin soap solution containing 1 per cent rosin. The fatty acid-rosin soap solution containing 0.1 per cent fatty acid and rosin was prepared by dilution.

All surface tension measurements were made at room temperature, 27° to 29°C.

The rosin products studied were: slash pine rosin; longleaf pine rosin; oxidized rosin²; pyroabietic acid; dehydroabietic acid, m.p. 170° C, $[a] \frac{20}{D} + 61^{\circ}$; abietic acid, $[a] \frac{20}{D} - 87^{\circ}$; dihydroabietic acid, m.p. $129^{\circ}-130^{\circ}$ C, $[a] \frac{20}{D} - 3^{\circ}$; tetrahydroabietic acid, negative to tetranitromethane test for unsaturation.

FATTY ACID PRODUCTS

Caprylic Acid (Tech.) 272-275 36-38 1.5-2.0 Lauric Acid 237-243 42-46 4-13 Myristic Acid Technical grade, distilled under reduced pressure. Stearic Acid 202-203 58-59 Under 1 Oleic Acid 199-200 7-9 88-89 Linseed Oil Acids 198-200 18-20 179-182 Palm Oil Acids 196-203 42-46 40-55 Coconut Oil Acids 260-270 21-25 9-15	1	(laterial	Acid No.	Titre	Iodine Value
Myristic Acid 237-243 42-46 4-13	Çaj	orylic Acid (Tech.)	272 275	36.38	1 5-2 0
Palmitic Acid Technical grade, distilled under reduced pressure. Stearic Acid 202-203 58-59 Under 1 Oleic Acid 199-200 7-9 88-89 Linseed Oil Acids 198-200 18-20 179-182 Palm Oil Acids 196-203 42-46 40-55	Lat	ric Acid	237-243		
reduced pressure. Stearic Acid 202-203 58-59 Under 1 Oleic Acid 199-200 7-9 88-89 Linseed Oil Acids 198-200 18-20 179-182 Palm Oil Acids 196-203 42-46 40-55	Pal	mitic Acid	Technical	grade, distilled	under
Steath Actu 199-200 7-9 88-89 Oleic Acid 198-200 18-20 179-182 Linseed Oil Acids 198-200 18-20 179-182 Palm Oil Acids 196-203 42-46 40-55			reduced	pressure.	
Oleic Acid 199-200 7-9 88-89 Linseed Oil Acids 198-200 18-20 179-182 Palm Oil Acids 196-203 42-46 40-55	Ste	aric Acid	202-203	58-59	
Linseed Oil Acids	Ole	ic Acid	199-200	7-9	
Palm Oil Acids	Tir	seed Oil Acids	198-200	18-20	179-182
Coconut Oil Acids 260-270 21-25 9-15	Pal	m Oil Acids	196-203	42-46	40-55
	Cor	onut Oil Acids	260-270	21-25	9-15

Discussion

The surface tension of the soap solutions made with rosin and rosin acids is given in Table I. There is practically no difference in soap solutions made with rosin from longleaf pine gum, slash pine gum, oxidized rosin or pyroabietic acid. Thus, the origin of the gum used in making the rosin or the state of oxidation does not appreciably affect the surface tension of the rosin soap solution.

However, soap solutions made with purified rosin acids of different composition vary in surface tension. The amount of hydrogen in the molecule of the rosin acid influences the surface tension of the soap solution; the more hydrogen present in the molecule, the lower the surface tension. The difference in surface tension of the rosin soap solution due to the structure of the rosin resulting from the degree of hydrogenation is more marked in the 0.1 percent than in the 1.0 percent solution.

TABLE I.

Surface Tension of Rosin Soap Solution Containing 1 Percent and 0.1 Percent Rosin or Rosin Acids.

	Surface	Surface Tension		
Rosin Soap From:	-Percent Solution dynes per cm.	0.1-Percent Solution dynes per cm.		
Slash rosin (rosin from slash pine g	um) 33.7	42.2		
Longleaf rosin (rosin from long pine gum) Oxidized rosin	33.5 35.0 32.9 37.7 34.2 31.9	42.2 41.4 44.5 49.5 43.2 38.3 31.9		

From a comparison of the surface tension of the rosin soap solutions with those of the fatty acid soap solutions in Table II it is evident that the rosin soaps

¹Rosin (slash) soap solution prepared by neutralizing 1 gm of rosin in alcohol to phenolphthalein end point, drying in vacuum desiccator and dissolving in 100 ml of water had the same surface tension as a similar solution prepared as described. This procedure was not adopted since the soap solutions frequently foamed over when dried in vacuum, and drying on a steam bath increased the chances of oxidation of the unstable rosin acid soaps.

² Longleaf pine rosin powdered and exposed to air in a thin layer for over 6 months.

(longleaf and slash rosin), with respect to surface tension, are more like lauric acid soap than the other fatty

TABLE II.

Surface Tension of Fatty Acid Soap Solutions and Fatty Acid-Rosin Soap Solutions.

	Surface Tension			
	Of Fat	tty Acid	Of Fatty	Acid-Rosin
	Soap So	olutions	Soap So	lutions1
	1.0%	0.1%	1.0%	0.1%
	dynes	dynes	dynes	dynes
Fatty Acid Soap Made from:	per cm.	per cm.	per cm.	per cm.
Caprylic acid	45.6	55.7	33.0	43.6
Lauric acid		46.0	30.2	36.7
Myristic acid	24.3	24.8	26.1	27.7
Palmitic acid	26,52	26.4	25.3	27.4
Stearic acid	25.12	35.8	25.12	34.4
Oleic acid	27.7	27.6	28.2	28.1
Linseed Oil acid	31.1	26.5	30.4	27.5
Palm Oil acid	26.1	27.7	27.5	28.0
Coconut Oil acid		28.1	30.9	28.5

¹ Fatty acid-rosin present in ratio of 3:1 by weight (slash rosin used).

² Surface tension of the soap solution measured at 50°C.

acid soaps tested. Whether this similarity extends to other soap properties has not yet been determined.

Table II gives the surface tension of soap solutions made with the principal fatty acids found in the toilet, household and laundry soaps and of soap solutions made with fatty acids and rosin mixed in the ratio of 3:1 by weight. With the exception of lauric and caprylic acid soap, the presence of rosin soap has little or no effect on the surface tension of the soap solutions. The replacement of a portion of the caprylic acid soap by rosin soap yields a solution with a lower surface tension. The same is true of the 0.1 percent lauric acid soap solution.

Summary

The surface tension of soap solutions made from rosins and rosin acids has been measured and the surface tension of fatty acid soap solutions and fatty acidresin soap solutions have been measured and compared.

Report of the Oil Characteristics Committee - 1939 - 40

THIS committee has been gathering data on various oils, filling in where insufficient with information derived from actual analyses contributed by the members, with the twofold purpose of establishing standards when possible and publishing as complete data on single samples as we can get for the book of methods.

A few years ago, standards for olive oil and for olive oil foots were drafted by another committee of this society. Last year this committee set up a standard for North American Refined Cottonseed Oil. Having embarked on this policy, which is I believe, a novel one for the Society, we are going ahead with increased acceleration. Data on four oils, perilla, soyabean, linseed and tung oils were collated from text authorities, from the A.S.T.M., the U.S.P. and the British Standards Institute and after a tentative draft was submitted the members, the specifications appended herewith were agreed upon by the majority and are offered for approval.

The standards on these oils have been in force by other organizations for quite a number of years. For this reason we selected them and without any timeconsuming labor in duplication of results, have adopted them and changed them somewhat to conform to the peculiar character of our own group of chemists. We cannot presume to delve into the amount of free fatty acids, accidental impurities foots, etc. which are matters regulated by trade rules and are no part of the constants of the oils. Generally speaking, the values we set up, must be broad enuogh to take in pure oils for all purposes, edible or technical, raw or refined, foreign or domestic. Hence for the present, a few basic values have been selected, leaving for future work any additional characteristics of purity.

Work of this nature has begun to attract the attention and interest of the trade. It is hoped that A.O.C.S. Standards on oils may achieve a useful, conspicuous place in its regard, for being concerned only with the genuineness of oils, they neither detract from nor interfere with current standards.

Whenever exceptions occur which give constants not falling within the range of values given, they should be brought to the attention of this committee. It is also suggested that A.O.C.S. Standards be recommended at every opportunity.

W. D. Hutchins G. S. Jamieson W. C. McLeod V. C. MEHLENBACHER R. C. STILLMAN L. M. TOLMAN

J. J. Vollertsen M. F. LAURO. Chairman.

A.O.C.S. STANDARDS

Sp. Gravity @ 25/25 C. Iodine Value (Wijs) Saponification Value Unsap. Matter (F.A.C.) nD @ 25 C.	Tung	Perilla	Soya	Linseed
	0.931-0.937	0.923-0.930	0.917-0.921	0.924-0.931
	160-175	193-208	127*-141	170-204
	189-195	188-197	189-195	188-196
	Max. 1.0%	Max. 1.5%	Max. 1.5%	Max. 1.7%
	1.516-1.520	1.479-1.482	1.470-1.476	1.477-1.483
Heat Test (Worstall)	Max. 8 minutes None			

^{*}The minimum iodine value has been changed to 120, as a result of a communication from the Regional Soybean Industrial Products Laboratory of the U. S. Dept. of Agriculture at Urbana, Ill., in which results were given on 8 commercial varieties grown at stations in five states for four years, showing a range from 104 to 139 with average at 127.5 approxi-

mately the lower limit of our specifications; but since the standard deviation for variation was calculated as 5.2, the minimum was made 120. At this value only five samples were below and these were produced under unusually severe drought conditions.

This committee thanks the senior chemist, Mr. T. H. Hopper for his counsel and help in this matter.