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Physical-Chemical Properties of Tall-Oil Soap Solutions[1]

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Summary

Acid-refined tall-oil was separated into resin acid and fatty acids of approximately 94% purity, made into soaps, and compared with those made from oleic acid and rosin. Tall-oil resin-acid soap and rosin soap are roughly comparable in dispersing power and lowering of surface tension and interfacial tension. The tall-oil fatty-acid soap shows some points of inferiority to sodium oleate, as might reasonably be expected because of its greater unsaturation.

METHODS of evaluation of various desirable functions of soaps include physico-chemical properties, launderometer readings, foaming properties, etc. The present paper is confined to the physico-chemical properties of dispersing power, interfacial tension, and surface tension. In a previous paper details of preparation as well as washing and foaming data for these soaps were furnished.

Dispersing Powers

Dispersing power is the property in which poor detergents are most apt to be deficient. The method used for its determination is a modification of the technic of Snell (6), which has recently been described (4). Essentially, it involves dispersing a lightly oiled umber soil in the detergent solution, allowing the dispersion to stand for two hours, removing a sample, and determining the depth at which the turbidity obscures the light. The figures listed in Table I are direct measures of the relative amount of umber suspended according to cm.$^{-1}$ × 100 (4).

Dispersing powers at 60°C. of less than 4 are considered very poor. A value of 8 is fairly good. Most synthetic detergents at moderate concentrations show dispersing powers of 7-12. Fatty soaps yield much higher values. Values at 30°C. are generally higher than at 60°C. Dispersing poorer values are useful in screening detergents, but there can be a gap between ability to disperse this particular soil and actual performance on natural soils attached to fabrics.

At all concentrations tall-oil fatty-acid soap shows a higher dispersing power than tall-oil resin-acid soap. In most cases the dispersing power of the former is about double that of the latter. Rosin soap shows a low dispersing power throughout, roughly matching tall-oil resin-acid soap at 60°C., and a bit higher at 30°C. Oleate soap however gives much higher values than tall-oil fatty-acid soap. Mixtures of 75% rosinate plus 25% oleate soap roughly check corresponding mixtures of tall-oil fraction soaps, but at 50% fatty soap or higher, the rosin-oleate soaps are considerably better.

TABLE I

Dispersing Powers in Distilled Water
Cm.$^{-1}$ × 100

Agent	30°C.			60°C.		
	0.5%	0.2%	0.05%	0.5%	0.2%	0.05%
Sodium Soap of Tall-oil Resin Acids	6.4	6.3	7.2	6.2	5.9	5.1
75% Sodium Soap of Tall-oil Resin Acids 25% Sodium Soap of Tall-oil Fatty Acids	7.2	6.1	7.6	4.8	4.0	5.9
50% Sodium Soap of Tall-oil Resin Acids 50% Sodium Soap of Tall-oil Fatty Acids	9.3	7.5	9.4	5.5	8.1	7.6
25% Sodium Soap of Tall-oil Resin Acids 75% Sodium Soap of Tall-oil Fatty Acids	10.7	10.6	11.3	6.6	12.8	9.1
Sodium Soap of Tall-oil Fatty Acids	11.6	12.0	15.3	7.9	14.3	12.5
Sodium Rosinate	7.9	7.7	4.9	5.9	7.7	5.1
25% Sodium Oleate 75% Sodium Rosinate	7.4	7.5	9.1	1.5	4.2	6.1
50% Sodium Oleate 50% Sodium Rosinate	17.0	26.4	11.9	11.4	18.1	7.6
75% Sodium Oleate 25% Sodium Rosinate	32.2	43.5	16.7	22.2	28.6	13.7
Sodium Oleate	33.2	46.8	25.0	28.6	30.3	23.9
Sodium Soap of Tall-oil	6.8	6.7	8.9	4.6	4.4	5.3
Sodium Soap of Tall-oil with Unsaponifiables Removed	8.9	7.3	9.1	5.4	7.4	7.3

In going from the 100% resin soap to the 75% resin, 25% fatty acid mixture, there is, under some conditions, a slight decrease in dispersing power in both the series. However there is an increase when the 50-50 ratio is reached, this increase being sharp for the rosinate-oleate series, less sharp for the tall-oil fraction series.

Tall-oil soap containing unsaponifiables gives dispersing values which are quite low. These values approximately check those for mixtures of 25% tall-oil fatty-acid and 75% tall-oil resin-acid soap mixtures and are slightly lower than the values for rosin soap. Removal of the unsaponifiable matter improves results moderately, especially at the higher temperature. Thus the dispersing power for the tall-oil soap containing unsaponifiables seems to be used up to a considerable extent in dispersing the unsaponifiables.

Surface and Interfacial Tensions and pH Values

Low surface tension is sometimes taken as a criterion for detergency. Practically the significance is

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that it frequently correlates with foaming power. Surface tension, when considered with the contact angle, does have a definite relation to wetting.

An important factor in detergency is the wetting and displacement of oily films from fibre surfaces by the detergent solution. Tendency to wet oil is measured by the interfacial tension of the solution against benzene containing 0.1% oleic acid (5). The oleic acid is used because natural soils ordinarily contain fatty acid (2). This can introduce complications when alkaline solutions are being evaluated; part of the interfacial tension lowering is due to the formation of oleic acid soap at the interface. However this factor must be included in a correct evaluation. Values were obtained in distilled water at 30°C. with a research type duNouy interfacial tensiometer. Harkins corrections were applied. The results appear in Table II.

Interfacial tensions of 10 dynes are considered fair and values of 5 dynes good. Values of 3 dynes are excellent and cannot be improved upon. Therefore variations within the range of 0-3 dynes mean little. Although on pure substances interfacial tension measurements are accurate within 0.2 dynes, measurements on aqueous solutions of surface active agents may vary several tenths of a dyne.

TABLE II

Surface Tensions, Interfacial Tensions, and pH Values of Soap Solutions at 30°C.

Agent	Surface Tensions dynes/cm. at 30°C.			Interfacial Tensions dynes/cm. at 30°C. against 0.1% Oleic Acid in Benzene			pH of 0.5% Solution at 30°C.
	0.5%	0.2%	0.05%	0.5%	0.2%	0.05%	
Sodium Soap of Tall-oil Resin Acids	36.9	48.0	52.2	3.1	9.4	16.2	9.6
75% Sodium Soap of Tall-oil Resin Acids 25% Sodium Soap of Tall-oil Fatty Acids	31.0	30.6	32.6	2.8	8.8	19.7	9.8
50% Sodium Soap of Tall-oil Resin Acids 50% Sodium Soap of Tall-oil Fatty Acids	30.0	28.2	28.8	2.4	8.3	19.9	10.0
25% Sodium Soap of Tall-oil Resin Acids 75% Sodium Soap of Tall-oil Fatty Acids	28.9	26.9	26.1	2.8	7.3	18.8	10.3
Sodium Soap of Tall-oil Fatty Acids	28.4	26.4	26.1	0.9	6.9	17.6	10.3
Sodium Rosinate	36.3	41.6	46.3	2.3	10.9	19.2	9.5
25% Sodium Oleate 75% Sodium Rosinate	29.0	28.0	32.5	2.4	9.7	20.2	9.6
50% Sodium Oleate 50%Sodium Rosinate	27.0	26.4	26.7	3.0	8.1	18.7	9.0
75% Sodium Oleate 25% Sodium Rosinate	26.8	25.7	26.1	1.8	6.7	18.3	10.1
Sodium Oleate	26.1	24.6	25.1	1.6	5.7	17.2	10.3
Sodium Soap of Tall-oil	32.4	32.2	32.7	4.2	9.1	19.2	10.0
Sodium Soap of Tall-oil with Unsaponifiables Removed	30.2	28.6	30.4	2.5	8.4	19.9	......

At 0.2% concentration, fatty acid soaps give low surface tensions in water, 23-26 dynes per cm. Good anion-active synthetic detergents give higher values, usually 27-32 dynes per cm.

The surface-tension data show that tall-oil resin-acid soap solutions have high surface tensions, varying from 36.9 to 52.2 in the concentration range studied. Rosin soap solutions have values ranging from 36.3 to 46.3, slightly lower than tall-oil resin-acid soap but still higher than good detergents usually show. The tall-oil fatty-acid soap solution values of 26.1-28.4 are lower than those of ordinary synthetic detergents and almost as low as the lowest values achieved by ordinary soaps. Oleate soap is slightly lower, but the differences amount to only 1-2 dynes. In both series of soaps the surface tension drops sharply when the proportion of fatty-acid soap is increased from 0 to 25% and thereafter drops more slowly as the ratio of fatty-acid soap is further increased.

Sodium soap of tall-oil shows values of 32.2-32.7. These are much lower than the values for straight rosin soap. Extraction of the unsaponifiable matter lowers these values further by 2-3 dynes.

In interfacial tension against benzene containing 0.1% oleic acid there is no important difference between the two series of soaps. Rosinate, oleate, and both tall-oil fraction soaps are for all practical purposes equivalent in ability to lower interfacial tension at 0.05% and 0.5% concentration. At the intermediate concentration of 0.2%, the fatty-acid soaps are somewhat better, but tall-oil resin-acid soap is substantially like rosin soap and tall-oil fatty-acid soap like oleate soap.

The pH values of solutions of the soaps are included in Table II. In the absence of excess alkali, resin soaps show lower pH values than fatty acid soaps.

Conclusions

Tall-oil resin-acid soaps, like rosin soaps, are much less effective than fatty soaps in lowering surface tension and in dispersing an artificial soil. These properties correlate respectively with the poor foaming and detergency values of such soaps, as described in the earlier paper. However interfacial tension values for the resin soaps and oleic acid soaps do not differ substantially. Thus resin-acid soaps and rosin soaps would not be ineffective in wetting oily surfaces.

In general, mixtures of resin-type and fatty-type soaps have values for these physico-chemical constants which are in between the values for the separate soaps, but this does not mean that the effects are linearly additive. On the contrary, there are marked deviations from linearity, particularly in surface tension effects, where the more active fatty soaps predominate even when present in rather small proportions.

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