Rosin/Acid Oil-Based Liquid Soap

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ABSTRACT: Soapstock was converted into a liquid soap from its acid oil and formulated with varying amounts of rosin. The characteristics of the acid oil and rosin were experimentally estimated. Liquid soaps were characterized by density, pH, total fatty matter, free caustic alkali, critical micelle concentration, foaming capacity, wetting power, and washing performance. The foaming results indicated that the liquid soap is best used as an ingredient in a washing-machine detergent. The dark aspect of a formulation with 10% rosin precluded higher substitution.

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KEY WORDS: Acid oil, liquid soap, rosin, soapstock.

For centuries, soap was the only cleaning substance available. Historically, it has been claimed that the esteem of a country's civilization is based on its consumption of soap. In the 18th century, because of the shortage of some raw materials, soap was a highly priced luxury, and only wealthy people could afford it. It became handy to other people only after the manufacture of sodium carbonate (soda ash) was developed. The less costly process of Nicolas Leblanc (1791) and later that of Ernest Solvay (1864) for producing soda ash made the manufacture of soap abundant, and consequently cheaper (1,2). Later, builders were introduced into the basic components of a soap to provide household and toilet soaps with a relatively better cleaning performance and for other specific purposes. At the end of the 19th century, the first soap powder for laundry was made using sodium silicate as a builder. Whereas the use of sodium or potassium carbonate leads to a hard or soft soap, respectively, the chemical nature of the lipophilic part (hydrocarbon) of the soap plays by far the largest role in determining the performance of the finished soap. The contributions of the Swedish chemist Carl Sheele (1783) and of the French chemist Eugène Chevreul (1823) in the fatty matter industry and to the field of soap chemistry have been widely acclaimed (2,3).

The global consumption of edible oils has been increasing. In addition, consumers have become increasingly conscious of their diets, resulting in an ever-growing demand for higher-quality oils. To meet this requirement, the oils must be well refined. Some substances such as lecithin and free fatty acids present in the crude oil are responsible for rancidity. The oil-refining process usually results in a nonnegligible amount (more than half a million tons produced annually in the United States) of a by-product called soapstock (4). The latter is also called a "neutralization paste" because it is formed in the alkalinizing operation during the oil-refining process, using either NaOH or a mixture of NaOH and Na₂CO₂. "Acid oil" or "acidulated soapstock" is a crude fatty acid mixture, a product of the acid hydrolysis of soapstock. Like other oil industries in the world, the Algerian oil refinery, Entreprise Nationale des Corps Gras (ENCG, Algiers, Algeria), usually splits this soapstock (RCOONa) into acid oil by a strong acid such 98% sulfuric acid.

Although soapstock was underused and has found limited uses in the past, its applications are now expanding. Most soapstock goes into animal feedstuffs, and the use of acidulated soapstocks in poultry nutrition as an additional fat source and in rabbit rations has been described (5,6). Conversely, a wide market currently exists for their methyl and ethyl esters for such uses as cosmetics, metalworking, and in the textile industry. Recently, conversion of the soybean soapstock into biodiesel, a less expensive diesel fuel substitute, has also been described (7,8).

This paper presents experimental results on the valorization of soapstock, *via* its acid oil, in the manufacture of liquid soap. The liquid soap would be vulnerable to air oxidation, particularly at elevated temperatures, due to the presence of polyunsaturated fatty acids in the acid oil and would result in an objectionable odor. Although adding perfume to the soap would disguise this smell, it was thought that rosin, which consists mostly of resinous acids (mainly abietic acid) would not only provide a pleasant odor but boost cleaning performance.

EXPERIMENTAL PROCEDURES

The chemicals and rosin used in this work were purchased from Prolabo (Paris, France). Acid oil (from the soapstock of a mixture of beef tallow and coconut oil) was provided by ENCG. The equipment used for making, testing, and

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Abbreviations: AV, acid value; CMC, critical micelle concentration; DDBS, sodium dodecylbenzene sulfonate; ENCG, Enterprise Nationale des Corps Gras; IV, iodine value; STPP, sodium tripolyphosphate; SV, saponification value; TFM, total fatty matter; UM, unsaponifiable matter.

characterizing the soap included the following: (i) a pH meter (LpH 230T); (ii) a refractometer, to determine the refractive index and to estimate the degree of whiteness; (iii) a digital densimeter (DM A48), to determine the density or specific gravity; (iv) a tensiometer (TD 2000), to determine the critical micelle concentration (CMC); (v) a tintometer (Lovibond L14), to estimate the aspect of the liquid soap; (vi) an electromagnetic agitator; (vii) an oven (Memmert, 30–120°C); and (viii) a gas chromatograph (Shimadzu; diethylene glycol succinate as the column stationary phase; column 1.5 m in length, 4 mm in diameter; injection port temperature, 240°C; column temperature, 200°C; detector temperature, 280°C; flame ionization detector; N₉ as the carrier gas).

Acid oil analyses. (i) Fatty acid composition of the acid oil. The oil was esterified with methanol in the presence of a catalytic amount of 98% sulfuric acid to determine the composition of the acid oil in the fatty acids. The esterification product was analyzed by gas chromatography to quantify the methyl esters. The results of this analysis were as follows: 1.186% myristic acid (C_{14}), 12.719% palmitic acid (C_{16}), 1.769% palmitoleic acid ($C_{16:1}$), 29.495% oleic acid ($C_{18:1}$), 51.322% linoleic acid ($C_{18:2}$).

(*ii*) Experimental estimation of the acid value (AV). In a 250-mL round-bottomed flask, 30–40 mL of neutralized ethyl alcohol was added to 1 g of acid oil. The alcoholic solution was titrated with 0.326 N ethanolic solution of KOH in the presence of phenolphthalein as an indicator. The acidity, expressed as the percentage of oleic acid, was estimated using Equation 1:

acidity =
$$\frac{V \times N}{1000} \times \frac{M}{w} \times 100$$
 [1]

where V is the volume of KOH consumed in milliliters (11.1 mL); N is the normality of the solution of KOH (0.326 N); M is the molecular weight of oleic acid (282 g/mol); and w is the sample weight in grams (1.057 g).

The AV was determined as described by Norris (9) (Eq. 2) or according to standard DIN 53 402 (Eq. 3):

$$AV = 2 \times acidity$$
 [2]

$$AV = \frac{V \times N \times 56.1}{w}$$
[3]

(iii) Experimental estimation of the saponification value (SV). Into a 250-mL round-bottomed flask equipped with a reflux condenser, 2 g of acid oil and 25 mL of 0.5 N ethanolic solution of KOH were charged. The mixture was stirred under reflux for 1 h. The excess of KOH was back-titrated with 0.5 N aqueous solution of HCl in the presence of 4% solution of phenolphthalein as indicator. The estimation of SV was provided by Equation 4:

$$SV = \frac{(V_0 - V) \times N \times M}{w}$$
[4]

where V_0 is the volume in milliliters of the HCl solution (for the blank test, 25.6 mL); *V* is the volume in milliliters of the HCl solution (for the acid oil, 11 mL); *N* is the normality of the HCl solution (0.5); *M* is the molecular weight of KOH (56.1 g/mol); and *w* is the sample solution in grams (2.0006 g).

(*iv*) Experimental estimation of the iodine value (IV). A Wijs reagent was first prepared by dissolving 12 g of iodine monochloride (ICl) in 1 L of glacial acetic acid in an amber flask.

A 0.2-g amount of acid oil was accurately weighed and charged into a 250-mL flame-dried amber flask. After the addition of 15 mL of carbon tetrachloride, the system was cooled by immersion in an ice bath before adding 25 mL of Wijs reagent. The system was allowed to stand for 3 h at room temperature. A 100 g/L aqueous solution of potassium iodide (25 mL) was then introduced and the mixture was stirred for 2 h. Finally, 50 mL of distilled water was added to the mixture. The titration of this mixture with a 0.1 N solution of sodium thiosulfate $(Na_2S_2O_3)$ in the presence of starch was performed to estimate the excess of iodine. Equation 5 allowed the estimation of IV:

$$IV = \frac{(V_0 - V) \times N \times M}{w}$$
[5]

where V_0 is the volume in milliliters of the Na₂S₂O₃ solution (for the blank test, 23 mL); V is the volume in milliliters of the Na₂S₂O₃ solution (for the acid oil, 4 mL); N is the normality of the Na₂S₂O₃ solution (0.1); M is the molecular weight of oleic acid (282 g/mol); and w is the sample solution in grams (0.1807 g).

(v) Experimental estimation of the unsaponifiable matter (UM). In a 250-mL round-bottomed flask fitted with a reflux condenser, a mixture of 5 g of acid oil and 50 mL of 1 N ethanolic solution of KOH was refluxed for 1 h. After cooling the mixture to room temperature, 50 mL of distilled water was added. The entire mixture was then poured into a separatory funnel and the flask was rinsed with 50 mL of hexane. After vigorously shaking the funnel, the mixture was allowed to stand for a phase separation.

The hexane layer containing the UM was withdrawn. The soapy layer was rinsed twice with 50 mL of hexane, and the hexane extracts were combined and washed twice with 50 mL of ethanol and dried over anhydrous Na_2SO_4 for 24 h. Finally, the hexane was evaporated to dryness and the residue was weighed. The UM was estimated using Equation 6:

$$UM = \frac{w}{w_0} \times 100$$
 [6]

where w_0 is the sample weight (0.50045 g) and w is the residue weight (0.0432 g).

Preparation of liquid soap. Seven liquid soap formulations (F_i) were prepared. A general procedure for their preparation is outlined below and consists of three steps: saponification, boiling, and fitting.

(*i*) Saponification. In an appropriate beaker, a quantity of acid oil is mixed with an amount of aqueous solution of KOH

(25% concentration). The necessary weight of KOH, $\rm W_{KOH}$, was calculated based on Equation 7:

$$W_{\text{KOH}} = (\text{SV}_{\text{AO}} \times W_{\text{AO}} + \text{SV}_{\text{R}} \times W_{\text{R}}) \ (1 + 0.5\%)$$
[7]

where W_{AO} and W_{R} stand for the weights of acid oil and rosin, respectively; 0.5% was the excess of KOH used.

The mixture was stirred under a nitrogen atmosphere while heating at 65°C until a homogenous phase was observed. Saponification was controlled using phenolphthalein as an indicator. The reaction was complete when a red color appeared and lasted for 10 min.

(*ii*) *Boiling*. The soapy paste obtained in the saponification step was vigorously agitated under a nitrogen atmosphere and heated at 65° C for an additional 4 h.

(iii) Fitting. After the boiling process, a volume of water was carefully added to the soapy paste in sequential portions to induce dissolution. A small amount of ethyl alcohol was added to suppress the foam.

Analyses of the liquid soap formulations (F_i). (i) Total fatty matter (*TFM*). The TFM was estimated using Equation 8:

$$\% \text{ TFM} = \frac{(100 - X) \times 100}{113}$$
 [8]

where 100 is the percentage by weight of the liquid soap and *X* is the percentage of water.

(*ii*) Free caustic alkali. In a 250-mL round-bottomed flask equipped with a reflux condenser were charged 10 g of liquid soap and 100 mL of neutralized ethanol (80% vol/vol). The system was heated in a sand bath until a homogeneous phase was observed. The mixture was cooled to room temperature and titrated with a 0.1 N ethanolic solution of H_2SO_4 in the presence of phenolphthalein. The alkali was estimated as the percentage of Na₂O using Equation 9:

$$\% Na_2 O = \frac{0.056 \times V \times N \times 100}{w} \times \frac{31}{56.1}$$
[9]

where 56.1 and 0.056 are the molecular weights of KOH in grams and milligrams, respectively; V is the volume of the solution of H_2SO_4 in milliliters; N is the normality of the H_2SO_4 solution (0.1); *w* is the weight of the sample in grams; and 31 is the equivalent mass of Na₂O.

(*iii*) *Determination of CMC*. The CMC of the liquid soap was taken as the concentration that corresponded to the break-through of the plot $\gamma = f(C)$, where γ is the surface tension in dyn/cm and *C* is the liquid soap concentration in g/L. The measurement of γ was done at a temperature of 27°C with a tensiometer equipped with a Wihelmy plate.

(iv) Foaming capacity. The foaming capacities of the formulations (F_i) were estimated using a device outlined in a previous work (10).

(v) Wetting power. The wetting capacities of the liquid soap formulations (F_i) were estimated by the method depicted in Figure 1. In this figure, a circular piece of cotton fabric (30 mm in diameter) was allowed to sink through the soap solution to the bottom of the beaker. The fabric was released



FIG. 1. Device used for the wetting capacity estimation.

from a point in the solution 2 cm beneath the solution surface, and the time was recorded starting from the release point (t_0) until it reached the bottom (t). The wetting capacity was estimated as the falling time $\Delta t = t - t_0$. The smaller the Δt , the better was the wetting.

(vi) Cleaning performance (10). The cleaning tests for the different formulations using soiled white cotton fabrics (10×10) cm) were carried out in a stainless steel drum (8.70 cm in diameter, 20.20 cm in height); the drum is fitted with an axlearm by which it is rotated during the washing. The soil placed on the fabric was an aqueous solution of tomato paste that was first concentrated in an edible oil. The white fabric was immersed into this solution for a few minutes and dried overnight in a drying oven (temperature 50°C). The fabric specimen was inserted inside the drum containing 50 mL of the liquid soap with 500 mL of distilled water, and the washing cycle consisted of rotating the drum for 15 min. The fabric was then removed, rinsed with cold water, air-dried for 10 min, and finally dried in a drying oven. The whiteness was determined using a digital refractometer with BaSO₄ as a reference. The whiteness of the cleaned fabrics was estimated against that of BaSO₄.

RESULTS AND DISCUSSION

Soapstock, a by-product of edible oil refining, was converted into liquid soap. The treatment of the soapstock with 98-99% sulfuric acid, producing acid oil, was done at ENCG. The fatty acid composition of the acid oil was ascertained by gas chromatography of their corresponding mixed methyl esters. These results indicate that it was composed mainly of palmitic acid, a saturated fatty acid, as well as oleic and linoleic acids, unsaturated fatty acids. The physicochemical characteristics of the acid oil were experimentally determined and are presented in Table 1. The acidity of this acid oil was expressed either as the percentage of oleic acid (96%) or as the AV (AV = 192). Its SV was 208, which is a relatively high value. This fact and its composition (palmitic, oleic, and linoleic acids) suggest that the acid oil is well suited for liquid soapmaking (2). The mean molecular mass of the acid oil calculated from the SV $(56.1/\text{SV} \times 1000)$ was 270, which agrees well with the value obtained from its composition in fatty acids. However, its IV, 134, and its refractive index may place this oil as a semidrying oil,

TABLE 1				
Physicochemical	Properties	of Acid	Oil and	of Rosin ^a

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Property	Acid oil	Rosin ^b
SV (mg/g)	208	169
AV (mg/g)	192	171
EV ^c (mg/g)	16	2
IV (mg/100 g)	134	_
UM (%)	0.86	7.5
H ₂ O ^d (%)	0.6	_
рН (30°С)	5	5.5
d	0.889 (25°C)	1.09 (30°C)
$\eta_D^{24 e}$	1.465	—
.0		

^aResults are the mean of three replicate tests. SV, saponification value; AV, acid value; IV, iodine value; UM, unsaponifiable matter; *d*, density. ^bResinous acids, 90–95%.

^cEV is the ester value, calculated as SV – AV.</sup>

^dMoisture was estimated as a weight loss of a sample at $105 \pm 2^{\circ}$ C (AFNOR 1968).

^eThe refractive index was estimated according to AFNOR T60 214.

commonly used in making alkyd resins for lacquers. The absence of linolenic acid in the composition also reflects this semidrying property. Although it is true that the IV would also indicate a plausible oxidative degradation of the liquid soap, this phenomenon can be avoided by storing the soap in closed containers.

As expected, the AV and SV of the rosin were very close to each other, ~170, a value that places the rosin in the range for soapmaking.

Liquid soap formulations (F_i) were made by saponification of a mixture of acid oil and a varying amount of rosin with potassium hydroxide, as given in Table 2. Potassium hydroxide was used instead of sodium hydroxide to produce a soft liquid soap. Distilled water was also used instead of tap water to avoid the adverse effects of the ions Ca²⁺ and Mg²⁺ and to produce a clear liquid soap. Additives such as sodium silicate were deliberately not used in the formulations. The different analyses performed on the formulations are presented in Table 3. Density and pH both increased slightly with an increase in rosin. However, the pH values suggest an alkalinity of the formulations that would enhance the washing performance, as noted in Table 4.

The TFM was found in the range of 22–34%, which is within the value limit recommended by British Standard Specifications for liquid soaps for domestic and industrial purposes (11).

The CMC of F_i were lower than that of the renowned anionic detergent DDBS (sodium dodecylbenzenesulfonate, ~0.65 g/L). It is worth noting that an increase in rosin induced a decrease in the CMC, providing better foaming. The foaming results shown in Table 4 are in accordance with the CMC values and also with the IV of the starting acid oils. These results indicate that the liquid soaps (F_i) foamed less than an anionic detergent powder (10). This low foaming suggests that liquid soaps may be used in washing-machine laundry applications, as laundry washing requires low foaming.

It is well known that wetting power is a property that determines the efficacy of a surfactant solution in soil removal. Easier soil removal is partially a result of a good wetting of the

		1		
F _i	Acid oil (g)	Rosin (g)	(Na ₂ O equivalent, g)	KOH (g) Water (mL)
F_0	100	0	20.904 (11.560)	600
F_1	98.5	1.5	20.829 (11.184)	600
F_2	97.5	2.5	20.810 (11.510)	400
F3	97	3	20.792 (11.498)	600
F ₄	95	5	20.718 (11.457)	600
F_5	93	7	20.643 (11.416)	650
F ₆	90	10	19.989 (11.054)	650
0				

TABLE 2 Formulations of Liquid Soap (*F*_i)

ABLE 3	
esults of Analyses of the Liquid Soap Formulations $(F_i)^3$	

			Water		Alkali		
	Density	рН	content	TFM	Na ₂ O		CMC
Fi	(30°C)	(30°C)	(%)	(%)	(%)	Appearance ^b	(g/L)
F_0	0.9973	9.80	62.60	31.32	0.010	15Y/3R	0.49
F_1	1.0001	9.97	59.7	33.89	0.024	35Y/6R	0.48
F_2	1.0013	9.91	63.2	48.50	0.022	75Y/7R	0.47
F3	1.0030	9.91	62.5	31.41	0.028	85Y/7.5R	0.46
F ₄	1.0032	10.57	67.8	26.72	0.024	86Y/11R	0.44
F_5	1.003	10.50	73	22.12	0.022	39Y/27.9R/0.3B	0.42
F ₆	1.0034	10.60	72	23.00	0.028	7.9Y/27.9R/6B	0.34

^aWith the exception of density, pH, and critical micelle concentration (CMC), the results were the mean of three replicate test results. TFM, total fatty matter.

^bThe letters Y, R, and B stand for the colors yellow, red, and blue, color respectively.

TABLE 4	ŧ			
Results	of the	Foaming	of	Fi

	Volume of foam produced (mL)						Anionic detergent	
Time	F ₀	F ₁	F_2	F ₃	F_4	F_5	F ₆	powder ^b
0 s	260) 260	260	260	260	270	280	_
30 s	250) 240	245	250	240	260	276	360
180 s	220) 220	225	230	230	240	250	310
300 s	19() 190	195	200	210	220	230	265

^aResults were are the mean of three replicate test results. The mean values were are rounded off. ^bSodium dodecylbenzene sulfonate (DDBS)-based detergent formulation (Ref. 10) in weight %: DDBS (15), sodium tripolyphosphate (STPP) (20), Na₂SO₄ (47), sodium silicate (10), water (6.5), and other builders (1.45).

TABLE 5 Results of the Wetting Powers of F_i^a

Concentration			Δt (s)		
(g/L)	F ₀	F ₂	F_4	F_5	F ₆
5	10	10	9.5	8	6
4.5	11.5	11.5	10	9	7
3.5	13	12.5	12	11	9
3	13.5	13	12.5	12	11

^aBased on single test results. For abbreviation see Table 2.

 TABLE 6

 Results of Cleaning Performance of Experimental Formulations^a

	F ₀	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	Anionic detergent powder ^b
Whiteness of the soiled fabric (%)	35.60	32.60	33.40	30.10	34.22	31.50	31.70	30.22
Whiteness of the washed fabric (%)	46.20	44.30	45.61	43.20	46.70	46.60	47.20	57.62
Washing performance (%)	10.60	11.70	12.21	13.10	12.48	15.10	15.50	27.40

^aExpressed relative to the whiteness of BaSO₄. Results were are based on single test results.

^bDDBS-based detergent formulation (Ref. 10) in weight %: DDBS (15), STPP (20), Na₂SO₄ (47), sodium silicate (10), water (6.5), and other builders (1.45). For abbreviations see Table 4.

substrate by the surfactant solution. The wetting capacities of the rosin-based liquid soap formulations (F_i) were generally higher than that of the standard one (F_0) , as shown in Table 5. In addition, it is not surprising to note that the higher the concentration of the formulation, the better is the wetting power.

With respect to appearance, the results in Table 3 reveal that the liquid soap formulations darkened with increasing rosin content. A substitution of 10% rosin gave a dark liquid soap, and for this reason, no higher substitution was considered.

The different formulations (F_i) were subjected to a washing test; the results are given in Table 6 and are expressed as the degree of whiteness of the soiled cotton fabric. The washing performance of liquid soaps, including the standard one,

was less than moderate, and they were lower than that of a DDBS-based detergent formulation (10).

The results of the present investigation have shown the possibility of converting the soapstock into liquid soap. The unpleasant odor of the latter can be reduced by partially substituting the acid oil by rosin. Based on the foaming results, this liquid soap is recommended as an ingredient for washing-machine laundry.

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