oils. The literature on this subject was reviewed by Otto (*Bol. divulgacão inst. oleos 1945, No. 3, 91*). Martinot-Laqarde (*J. Soc. ing. automobile 14,* 237) fostered the use of castor and peanut oils as fuels for Diesel engines. Amrute (*Australasian Engr. Mar. 1947,* 60) described as a successful adaptation of peanut oil for Diesel engines during the war. However, its use was abandoned when mineral oil again became available.

Gaseous fuels were experimentally prepared from peanut, castor, cottonseed, and coconut oils by thermal cracking and the conditions for optimum yields were determined (Mandlekar *et al.—J. Sci. & Ind. Res. (India) 5B,* 45). The fuel recovery was about 50% at the most.

A miscellaneous group of unrelated fat products was difficult to classify in the preceding paragraphs. A protective coating to protect the skin against flash burns contained fats, solvents, metallic soap, borax, and pigment (Fauley & Ivy—*U. S. 2,425,311*). In a reclaiming process for synthetic rubbers, saturated fatty acids and a solvent were used to swell the rubber (le Beau—*U. S. 2,423,033*). A sealing composition for food container joints contained ethyl cellulose, vegetable oil, resin, and inert fillers (Millelot—*U. S. 2,419,224*). A pressure sensitive adhesive tape was coated with a base consisting of polyvinyl butyl ether and factice (Nelson & Morris—*U. S. 2,415,901*). A cleaning composition for removing sludge from internal combustion engines was a mixture of organic solvents and a fatty acid amine (Skinner—*U. S. 2,418,908-9*). A dielectric structure comprised adsorbent cellulosic material impregnated with castor oil (Coggins & Ahearn—*U. S. 2,418,820*). Various soaps, fatty acids, and fatty amines were added to bituminous paving compositions (Allen—*U. S. 2,416,134;* Johnson—*U. S. 2,426,220*). Stearin pitch was added to bituminous adhesives (Moore & Greenfield—*U. S. 2,418,135*). Stearic acid was recommended for combating foam formation in the analytical Kjeldahl nitrogen determination (Hadorn—*Mitt. Gebiete Lebensm. Hyg. 38,* 46). Foaming and priming in steam generators were reduced with the following combinations of compounds: oleic acid and diethylenetriamine, stearamide and trioxy-methylene, castor oil and triethyltetramine, and others (Imperial Chemical Industries, Ltd.—*Brit. 568,510*). Fatty acid derivatives of piperazine were effective antifoaming compounds for steam boilers (Jacoby—*U. S. 2,428,801*). A review of fats in the pharmaceutical industry by Gauthier (*Inds. corps gras 3,* 68) included within its scope oil solutions for injections, suppository fats, fats for ointments, medicinal fatty derivatives, and soaps.

The Hydrolysis of Soap Solutions. IV. The Composition of Acid Potassium Laurates and Acid Sodium Oleates as Determined by Conductivity Measurements

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ACID soaps, the characteristic product of the hydrolysis of soaps, were first described by Chevreul in 1823. He found that they were acid salts of the same nature as sodium acid acetate, NaAc·HAc. In 1927 McBain and Stewart (1) prepared potassium hydrogen dioleate and showed that it was a definite compound containing one equivalent of acid to one equivalent of soap. Its composition over a wide range was found to be independent of the proportions of oleate and acid used in the solvent. The acid soap could be recrystallized unaltered from alcohol or from oleic acid. The existence of several other acid soaps was established by later phase rule studies by McBain.

Acid soaps have been prepared, among other ways, from neutral soap and acid in alcoholic solution, and in aqueous solution by the addition of excess acid. They are also formed by hydrolysis. Most investigators have found acid soaps of the types 2 soap · 1 acid, 1 soap · 1 acid, and possibly 1 soap · 2 acid, though other types are not excluded as was shown by Ryer's preparation of 2NaSt·3HSt (2).

Ekwall (3, 4) considered that he prepared the acid laurates, 2NaL·HL, NaL·HL, and NaL·2HL, from alcoholic solution. By studies involving the use of excess acid, he identified NaL·HL as a product of hydrolysis in aqueous solutions above 0.006 *N* and 2NaL·HL above around 0.02 *N*; NaL·2HL could not be identified. Conductivity measurements and analysis of filtrates of soap solutions containing excess acid lead him to the view that NaMy·HMy is formed in dilute solutions of sodium myristate, and 2NaMy·HMy in solutions of somewhat higher concentrations. 2NaP·HP and NaP·HP have been shown to exist by phase studies of McBain; (5) and Ekwall (6) found NaP·2HP, but without critical tests. McBain, Taylor and Laing (7) observed that the equivalent conductivity of sodium palmitate fell to a very low value when one equivalent of acid was present to two equivalents of palmitate, corresponding with the formation of an insoluble undissociated acid soap, 2NaP·HP. NaP·HP was identified as a product of hydrolysis in dilute aqueous solutions by Ekwall (8), and also NaSt·HSt. In phase studies McBain (9) showed evidence for the existence of 2NaSt·HSt and NaSt·2HSt.

Acid potassium myristate, palmitate, and stearate containing one equivalent of acid to one of soap were prepared by Levi (10) from alcoholic solution.

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Experimental

The composition of potassium acid laurates and of sodium acid oleates was determined by the method of McBain, Taylor, and Laing (7), that is by observing the change in conductivity when excess acid is added to the aqueous soap solution. The soap systems containing 0, 25, 50, 100, and in two cases 150 moles per cent excess acid were prepared by adding carbon dioxide-free alkali to a weighed amount of Kahlbaum's acids. These were heated on a water bath from 15 to 30 minutes, cooled, and diluted to volume with conductivity water (specific conductivity = 0.7 x 10^{-6} at 25°C.). The 0.04 and 0.02 *N* potassium laurate solutions were made by diluting 0.1 *N* solutions, but all the others were prepared directly. These systems containing excess acid are heterogeneous mixtures at 25°C., containing precipitated acid soap alone or together with excess acid. The acid soap settles out quite readily in the laurates containing 25 moles per cent excess, but those with greater excess remain as pasty mixtures. The acid oleates are milky suspensions with a slightly yellowish tinge. Those with 50 moles per cent excess remained quite uniform on long standing; in those with 25 and 100 moles per cent excess acid some solid aggregated and rose to the top of the mixture. Mixed acid soaps were prepared by adding oleic acid to 0.1 *N* potassium laurate and excess lauric acid to 0.1 *N* sodium oleate. The precipitated soaps resembled the oleates in appearance.

Measurements were made using the Grinnell Jones-Dyke type of bridge, and an oil thermostat at 25° C. ± 0.01. The point of balance was obtained by use of a cathode ray oscillograph. Tables I and II give the specific and equivalent conductivities (in general, the mean of two measurements), and the pH of these potassium laurate and sodium oleate systems. Figures 1 and 2 show the change of specific conductivity of these systems with addition of excess acid.

The conductivities for the laurates cannot be expected to be highly accurate because the systems with acid soap are heterogeneous, and the amount of settling or enclosure of air can influence the individual data. However, the main results are unmistakable. Examination of Figure 1 for potassium laurate shows that conductivity decreases almost linearly on the addition of excess acid up to 50 moles per cent, then after a slight break falls until 100 moles per cent excess have been added; addition of 150 moles per cent (in 0.04 and 0.02 *N*) produced no further change. This indicates the formation first of $2KL \cdot HL$, then $KL \cdot Hl$. This interpretation is supported by an examination of the pH curve, Figure 3.

In the sodium oleate system, Figure 2, the specific conductivity falls linearly until 50 moles per cent excess oleic acid have been added, then after a sharp break, decreases but slightly with further addition of acid. This indicates the formation of the acid soap, $2NaOl \cdot HOl$. This is in agreement with Ekwall's deductions from the same type of measurement made on more dilute solutions (3). He concluded that in solutions above 0.004 *N*, $2NaOl \cdot HOl$ is formed, while in those 0.004-0.008 *N*, $NaOl \cdot HOl$ is formed. McBain and Stewart (11) in the study of 0.2-0.02 *N* potassium oleate solutions concluded that the composition of the acid soap was likewise $2KOl \cdot HOl$.

TABLE I

The Specific and Equivalent Conductivities, and the pH of Solutions of Potassium Laurate With and Without Excess Acid, at 25°C.

N_v	Moles % Excess Acid	Specific Conductivity x 10^3 mhos	Equivalent Conductivity	pH
	Lauric			
0.2	0	9.72	48.6	9.80
	25	6.758	33.79	9.48
	50	4.718	23.59	9.53
	100	0.526	2.63	7.15
0.1	0	5.460	54.60	9.70
	25	3,925	39.25	9.60
	50	2.125	21.25	9.62
	100	0.4840	4.84	7.30
0.04	0	2.999	75.00	9.48
	25	2.497	62.42	9.17
	50	1.593	39.82	8.82
	100	0.6036	15.09	7.52
	150	0.5728	14.32	7.38
0.02	0	1.797	89.85	8.90
	25	1.324	66.20	8.30
	50	0.8931	44.65	7.78
	100	0.6239	31.20	7.57
	150	0.6201	31.00	7.42
	Oleic			
0.1	25	3.498	34.98	9.14
	50	1.096	10.96	9.03
	100	0.7443	7.443	8.18

TABLE II

The Specific and Equivalent Conductivities, and the pH of Solutions of Sodium Oleate with and Without Excess Acid, at 25°C.

N_v NaOl	Moles % Excess Acid	Specific Conductivity x 10^3 mhos	Equivalent Conductivity	pH
	Oleic			
0.1	0	2.500	25.00	......
	25	1.537	15.37	9.35
	50	0.7581	7.581	9.05
	100	0.4867	4.867	8.2
0.05	0	1.213	24.26	10.18
	25	0.8181	16.36	9.83
	50	0.5335	10.77	9.53
	100	0.4656	9.312	8.42
0.01	0	0.3450	34.50	10.1
	25	0.2816	28.16	9.70
	50	0.2000	20.00	9.58
	100	0.1384	13.84	8.65
	Lauric			
0.1	50	1.665	16.65	8.45
	100	1.495	14.95	7.85

When oleic acid is added to 0.1 *N* potassium laurate, the specific conductance falls linearly up to 50 moles per cent excess, then changes very slightly up to 100 moles per cent excess, indicating an acid such as $2KL \cdot HOl$. With addition of lauric acid to sodium oleate there is a similar change in conductance indicating the formation of $2NaOl \cdot HL$. Its specific conductance is almost twice as great as that of $2NaOl \cdot HOl$.

Figure 3 shows the change of pH of these mixtures with the addition of excess acid. In 0.1 and 0.2 *N* laurate, there is but a slight decrease in pH with the addition of 25 and 50 moles per cent excess, followed by a large drop when 100 moles per cent excess have been added. The change in pH of the 0.02 *N* laurate solution corresponds with that observed in the specific conductance of the system. The pH of sodium oleate solutions decreases almost linearly with the addition of acid up to 100 moles per cent. The decrease in pH is proportionally greater than the decrease in conductance on the addition of 50 to 100 moles per cent excess acid. The pH of 0.1 *N* sodium oleate containing excess oleic acid is higher than that with excess lauric acid, while that of 0.1 *N* potassium laurate with excess lauric is higher than that with excess oleic acid up to 65 moles per cent excess; then the reverse is true.

It is noteworthy that all of these solutions are alkaline: those containing 50 moles per cent excess fatty acid are quite alkaline, those with 100 and 150 moles per cent excess acid are still very slightly alkaline.

Summary

The effect of excess lauric and oleic acids on the conductivity and on the pH of 0.2-0.02 *N* potassium laurate and 0.1-0.01 *N* sodium oleate systems was observed. The decrease in the specific conductivity corresponded with the formation of the acid soaps, 2KL·HL, KL·HL, 2NaOl·HOl, NaOl·HOl, and the mixed soaps 2KL·HOl and 2NaOl·HL. The mixed soaps resemble the oleates in appearance. All of these systems, even with 100 or 150 moles per cent excess acid, were slightly alkaline.

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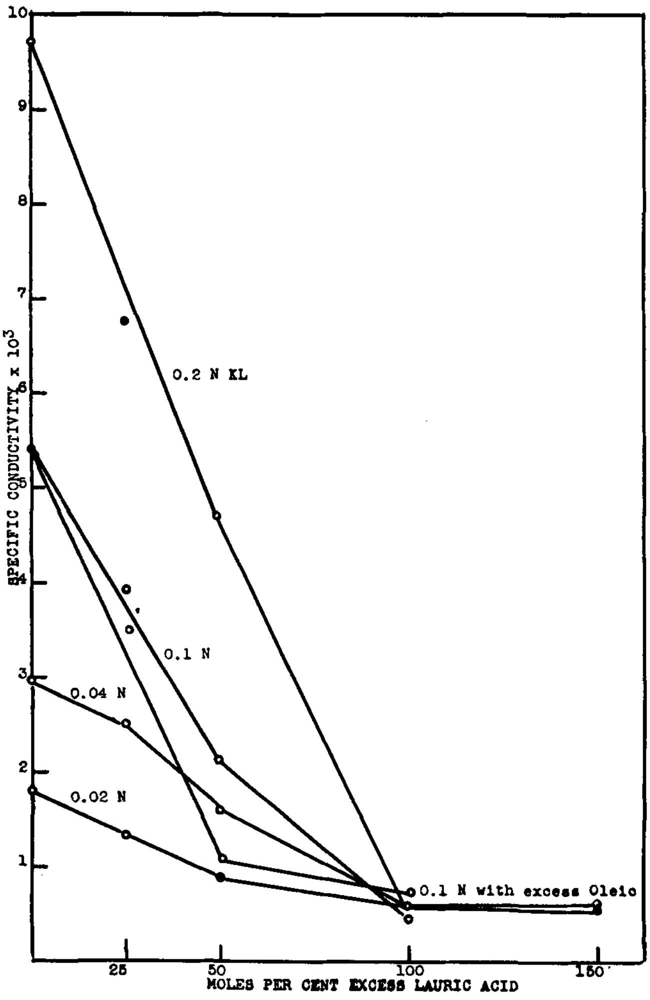

FIG. 1. The effect of excess acid on the specific conductivity of potassium laurate at 25°.

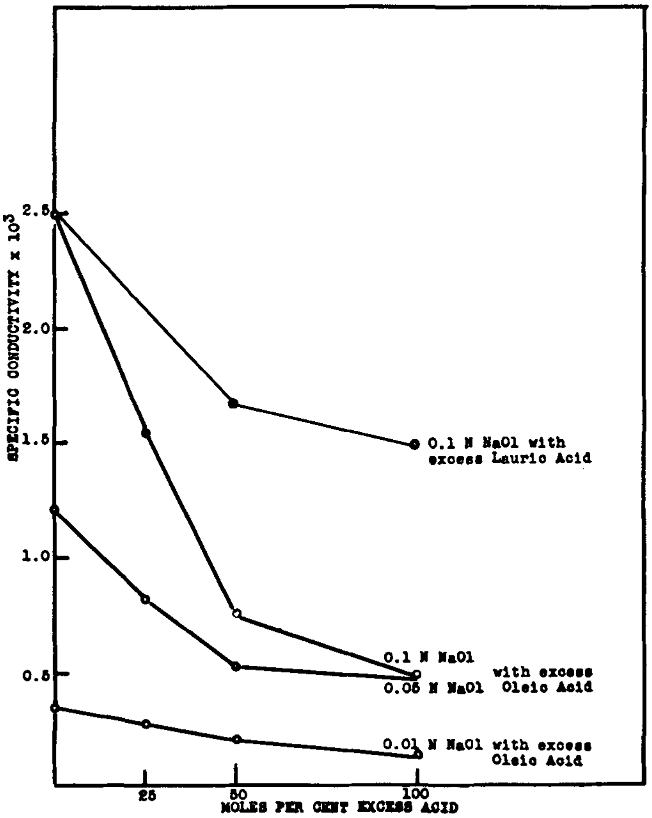

FIG. 2. The effect of excess acid on the specific conductivity of sodium oleate at 25°.

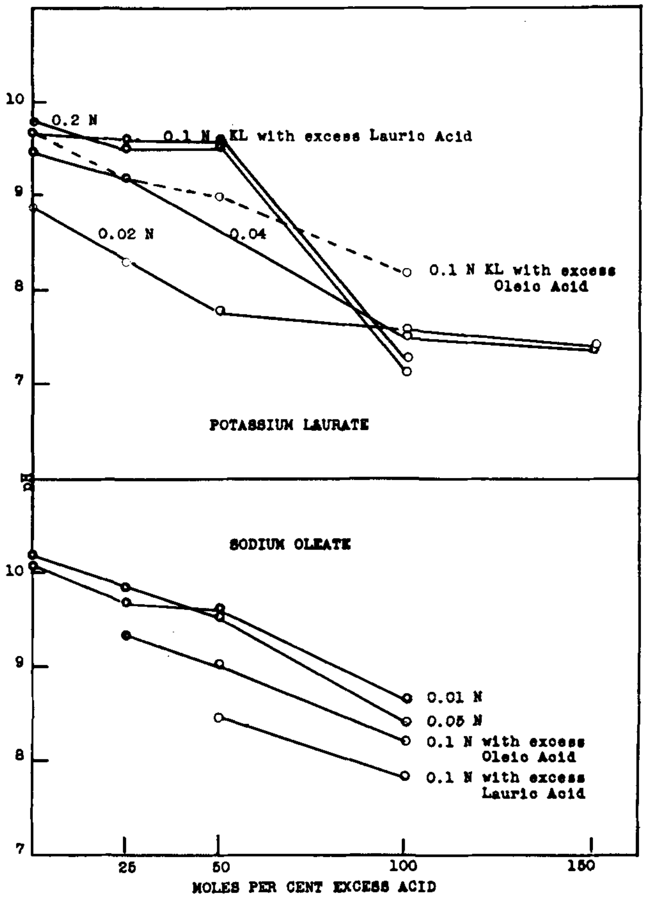

FIG. 3. The effect of excess acid on the pH of KL and NaOl solutions at 25°.