TABLE IV

The Fractionation of Tallow Fatty Acids Obtained Utilizing Flotation for the Physical Separation of Acid Soaps

Strength of soap soln. treated	IV of tallow	IV of solid acids	IV of liquid acids
1%	42.8	15.0	65.9
2%	42.8	14.2	79.1
2%	56.5	5.9	69.0
2%	56.5	9.8	79.9

TABLE V

The Fractionation of Tallow Fatty Acids Obtained Utilizing Centrifugation for the Physical Separation of the Acid Soaps

Strength of soap soln.	Centrifuge tested	No. of g's developed	Residence time	IV of solid acids	IV of liquid acids
ca. 2%	International cup-type centrifuge	ca. 1,000	1 hr	28.2	79.1
ca. 2%	International cup-type centrifuge	ca. 1,000	1 hr	15.9	78.5
ca. 2%	Sharples super centrifuge	ca. 20,000	very slow	10.0	63.6
5.2%	Sharples super centrifuge	6–7,000	1 min	......	66.3
2.4%	Sharples super centrifuge	6–7,000	2 min	......	65.5
2.4%	Sharples super centrifuge	6–7,000	1 min	......	67.4
2.4%	Sharples super centrifuge	6–7,000	2.5 min	......	62.2

mostly genuine flotation of the acid soaps, and not due to an acidulation to the lighter fatty acids, though surface conversion to free fatty acids was probably an important factor in aiding flotation.

It can be seen from table IV that promising results were obtained by flotation; but it was found difficult to float the larger particles which were characteristic of the experiments where better settling occurred.

A slurry which settles well under gravity would be expected to respond well to centrifugation. A typical well crystallized batch from tallow of IV 42.4 was centrifuged under varying conditions (Table V) but the results were generally disappointing, especially those at the highest centrifugal force.

The super-centrifuge failed at all times to give a clear effluent, even at the maximum rpm. Lowering the feed-rate caused the results to be even more disappointing, an effect which is unexplained. Working up the acids from the two phases was simple; the fatty acids were recovered by acidification, warming being necessary for a good phase separation.

Summary

Beef tallow acids of IV 45 yield about 45% of red oil of IV 80–85, and 55% of crude stearic acid of IV 10–20. Tallow acids of IV 60 give equal weight yields of fractions having IV 95 and 25.

REFERENCES

1. U. S. Patent No. 2,293,676—L. D. Myers and V. J. Muckerheide.
2. The Commercial Solvent Separation of Fatty Acids—R. E. Kistler, V. J. Muckerheide, and L. D. Myers, JAOCS, *23*, 146 (1946).
3. U. S. Patent No. 2,107,664—W. P. Gee.
4. U. S. Patent No. 2,443,184—Edwin W. Colt.
5. U. S. Patent No. 2,593,458—Leslie G. Jenness.
6. Kenneth Tomlinson—Private communications.
7. Fatty Acids and Their Derivatives, by Ralston.
8. Levi, Gazz chem. Ital., *62*, 709 (1932).
9. U. S. Patent No. 2,298,501—L. D. Myers *et al.*
10. U. S. Patent No. 2,421,157—L. D. Myers *et al.*

[Received November 27, 1961]

The Separation of Solid Fatty Acids from Liquid Fatty Acids by the Formation of Acid Soaps. II. Pilot Plant Studies

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Abstract

On contemplating pilot plant scale-up of the acid soap process for separating fatty acid mixtures into low and high iodine value fractions, improvements were desirable in acidifying agent used, and the method of separating the solid acid soaps. A further objective was to determine the range of applicability of the process.

Studies indicated that CO_2 can be replaced by mineral acids, or by the fatty acids themselves. A continuous precoat vacuum filter is suitable for the separation of the solid acid soaps. The process is applicable to refinery foots as well as to distilled and undistilled fatty acids.

PART I OF THIS SERIES (1) reported that tallow fatty acids could be separated into high and low iodine value fractions by the crystallization of their acid soaps from water. As in conventional crystallization processes, the more saturated acids concentrate in the crystalline fraction.

It was found that crystallization conditions were critical, optimum conditions involved a soap concentration of 2–5%, pH adjustment between 7.0 and 8.0, initial crystallization temperature not below 25C, and a crystallization period of at least 4 hr, during which time the cooling to a final temperature of 5–15C must be gradual, and agitation gentle.

On contemplating the scaling-up of this process, three areas of development appeared necessary:

1) A more convenient acidifying agent was required, preferably an inorganic acid.
2) A better means of separating the acid soaps.
3) The application of the process to a wider range of fatty acids, including stocks in other forms such as vegetable oil refining foots.

Experimental

Fractionations Using Mineral and Fatty Acids Instead of Carbon Dioxide as Acidifying Agents. In the work reported in Part I, carbon dioxide was used as the source of acidity. The reactions were closely controlled by means of pH, aided by the buffering action of the bicarbonate formed. Since the solution from which acid soaps are crystallized represents an equilibrium between fatty acids and their normal soaps, it should be possible to approach the equilibrium from either side—that is, one should be able to add:

1) half an equivalent of alkali to one equivalent of fatty acid, or
2) half an equivalent of mineral acid to one equivalent of soap, or
3) one equivalent of fatty acids to one equivalent of soap.

The method of reaching the required equilibrium is identified as the "neutralization history" of the solution. Some typical results are contained in Table I.

TABLE I

The Effect of the Route Taken to Reach Equilibrium (Partial *Acidification*) *on the Resultant Fractionation*

Starting material	Neutralization history	IV of liquid acids
Tallow fatty acids IV 63	(a) 1.0 eq. NaOH, then 0.5 eq. HCl	91.4
	(b) 1.0 eq. NaOH, then CO_2 to pH 7.5	98.8
Fish fatty acids IV 196	(a) 1.0 eq. NaOH, then 0.5 eq. HCl	233
	(b) 0.5 eq. NaOH	236
	(c) 1.0 eq. NaOH, then CO_2 to pH 7.5	238
Mixed vegetable Dist. fatty acids IV 83	(a) 1.0 eq. NaOH, then 0.5 eq. HCl	119
	(b) 0.5 eq. NaOH	117
Soybean fatty acids IV 122	(a) 1.0 eq. NaOH, then 0.5 eq. HCl	146
	(b) 0.5 eq. NaOH	143

Obviously the required equilibrium for the formation of acid soaps can be approached by several means without greatly affecting the resultant fractionation, and that the cheaper inorganics can be used instead of CO_2. It was surprising that one equivalent of fatty acids would dissolve in only ½ an equivalent of aqueous alkali.

The Physical Separation of Acid Soaps on a Larger Scale. While with flotation and centrifugation some separation of the solid acid soaps was effected, it was felt that a more positive separation method was required. Consequently, filtration was again studied.

As reported in Part I, filtration without a filter aid was impossible. Even with a filter aid in considerable quantity, the filtration rate was slow and produced unacceptable solids. However the work on settling gave the know-how necessary to grow a superior type of crystal, and it was expected that some degree of success would be attained with filtration. Since washing was essential to produce low IV solids, a continuous precoat vacuum filter was selected for the test work. This was an Oliver 12 x 2 inch Laboratory Precoat Filter. Table II gives the filtration rates obtained.

TABLE II

Pilot Plant Filtrations of Acid Soaps on an Oliver Continuous *Precoat Filter (Drum Speed—15 rph)*

Fatty acid raw material	Soap soln. %	Degree of shave in./rev.	Duration of test hr.	Filtration rate gal/ft²/hr	IV of Solid acids	IV of liquid acids
Fish oil IV 196	6.4	0.010	1½	6.5	88	238
	4.0	0.010	1⅔	9.4	72	236
	5.3	0.005	1½	5.9	41	225
Cottonseed	4.7	0.010	¾	13.5	24	122
Fatty acids IV 96	4.7	0.005	2	6.0	25	122
Soybean fatty acids IV 122	5.6	0.010	2⅚	9.8	70	136

While the filtration rates were only fair, it was found that the use of a precoat continuous filter for the solid acid soaps was practical.

The Application of the Acid Soap Separation to Stocks Other than Tallow. Since this process works for separating the fatty acids present in tallow, it would be expected to perform similarly on cottonseed, fish, and soybean fatty acids. A number of examples of the fractionations of other fatty acids have previously been cited. Table III shows further results on the various raw materials tested.

TABLE III

The Separation of Distilled Fatty Acid Mixtures

Fatty acid raw material		Separation temp. °C.	Solid acids IV	Liquid acids	
Type	IV			IV	% Yield
Cottonseed	96.0	6	24.2	121	74
	96.0	10	24.4	122	73
	98.8	5	41.7	135	61
	98.8	5	25.9[a]	135	67
	98.8	15	35.8	129	68
	98.8	15	20.6[a]	128	73
	98.8	25	32.1	119	77
	98.8	25	16.0[a]	118	81
Fish	196	5	88.4	238	72
Mixed vegetable	82.5	9	13.2	122	64
Soybean	120	10	57.0	140	76
Tallow	43.4	12	17.8	85.2	38
	56.9	5	20.0	101	46
	56.9	15	17.5	96.4	50
	56.9	25	19.4	86.2	56
	56.9	25	14.9[a]	88.0	57
	63.0	11	30.4	98.8	48
	63.0	11	25.7[a]	98.8	51

[a] Indicates that the solid acids were washed to free them of mother liquor.

Since this process entails the formation of a soap solution, it might naturally be expected that it would find its most economic application in the fractionation of the foots produced on refining vegetable and fish oils. Here the alkali necessary for the operation of the process is already present, and acid has to be added in any case. Consequently, it was attempted to fractionate raw soapstocks that had been further treated with alkali to saponify the neutral oil present. See Table IV.

TABLE IV

The Separation of Raw Soapstock

Soapstock raw material		Separation temp. °C	Solid acids IV	Liquid acids	
Type	IV[a]			IV	% Yield
Fish	172	9	33.5	227	72
Cottonseed	103	5	41.6	132	67
	103	15	72.1	127	54
	103	15	42.8[b]	129	69
	103	25	45.9	114	84
	104	8	47.3	136	64
Peanut	90.5	15	16.9	103	86

[a] *IV of the total fatty matter present.*
[b] Indicates solids acids were washed to free them of mother liquor.

It is evident that this separation procedure can be used to advantage on foots as well as distilled and undistilled fatty acids (2).

In handling soap stocks, the electrolyte content of the completely saponified solution prior to fractionation must be watched. Whereas the fractionation will work in the presence of 5 g per l of sodium chloride or sulphate, twice this amount will prevent the process from operating at all.

REFERENCES

1. Munns, W. O., S. Kairys, Dilys A. Manion, and E. M. Meade, JAOCS, 39, ... (1962).
2. U. S. Patent No. 2,895,976—S. Kairys, E. M. Meade, W. O. Munns, and Dilys A. Walder.

[Received November 27, 1961]

Erratum. Vol. 39, page 70, January, 1962, LYON ET AL.: SOLVENT-BLOWN, RIGID URETHANE FOAMS. The passage beginning with the last 1 lines, first column, on page 70 should read:

The average equivalent weight of the polyol mixtures was varied from 70 to 120 and castor oil content from 11 to 58%.

The compressive strengths of foams prepared from these polyol mixtures are shown in Fig. 1. Here the compressive strength of foams calculated to 2 lb./ft.^{3} density is plotted *versus* average polyol equivalent weight. The castor oil content of the polyols used is indicated below the curve. The prepolymer used was the same as that described previously (6) and contained 10.3% pentaerythritol monoricinoleate, 10.3% trimethylolpropane and 79.4% toluenediisocyanate.