Segregation of Fatty Acids by Preferential Neutralization*

RICHARD NICHOLSEN and MARVIN W. FORMO, Archer-Daniels-Midland Company,
Minneapolis, Minn.

MUCH work has been done on a variety of different methods for separating mixtures of saturated and unsaturated fatty acids, both as the free acids and as the naturally occurring mixed glycerides. Most of the methods described in the literature have been based on either fractional crystallization or on selective solution in certain organic solvents. The common commercial practice of "winterizing" certain oils, particularly fish oil, is an example of a rather crude application of the first process. The directed rearrangement process recently described by Eckey involving a combination of interesterification of the oil and fractional precipitation of solid glycerides is a highly refined example of the crystallization of oils (1). Recently the Emersol Process of fractionally crystallizing fatty acids from an organic solvent has been commercialized (2). Numerous workers have published laboratory data about similar crystallization processes (3, 4, 5, 6, 7, 8, 9, 10). The best known examples of selective extraction technique are the furfural extraction patented by Freeman (11) and commercialized by the Pittsburgh Plate Glass Company and the propane extraction patented by Hixson and Miller (12) and commercialized by the M. W. Kellogg Company under the name Solexol Process. In addition to these practical methods of accomplishing the separation of mixed fatty acids several other procedures such as chromatographic adsorption and molecular distillation are known to have received some attention in recent years.

This paper is concerned with a method for separating mixtures of saturated and unsaturated fatty acids which has been only briefly described in the technical literature but is capable of achieving very good separations. It depends on the fact that when such mixed fatty acids are neutralized by certain mixed alkalies, one alkali has a greater preference for the saturated acids and another alkali has greater preference for the unsaturated acids. It has been found that in general alkalies forming soluble soaps tend to neutralize the unsaturated acids and alkalies forming insoluble soaps tend to prefer the saturated acids. Separation is thus accomplished by simply filtering the insoluble soaps from a solution of the soluble soaps.

The analytical method for separation of saturated acids from unsaturated acids by differences in solubility of lead soaps was developed years ago (13, 14), but that technique is quite different from that being considered here. There have been a few suggestions in the literature that partial hydrolysis of glycerides showed a slight preferential effect (15, 16, 17, 18). The only references to a process showing true preferential neutralization are the patents of Ernst Schlenker (19, 20, 21) and some unpublished work of Walter Hoback at Lehigh University. Schlenker's patents disclose very little specific information in the form of examples with exact data, but Hoback showed that soybean fatty acids could be separated into fractions by preferential neutralization to give a liquid fraction having an iodine value of 146. He also showed that linseed fatty acids could be separated similarly to produce a fraction having an iodine value of 203.

The first experimental study in our laboratory was made with water-white distilled soybean acids of 139.2 iodine value. A series of neutralizations was carried out using mixtures of sodium hydroxide and barium hydroxide such that the total amount of alkali was just sufficient for complete neutralization but varying the proportions of the two alkalies in the mixture. In each case 50 g. of the acids was dissolved in 50 g. of hot denatured alcohol, and a mixture of the alkalies in 100 g. of hot distilled water was then added to the alcohol solution of the acids with stirring. The mixtures were filtered by gravity through Whatman No. 4 paper, and the solid soaps were washed with 50 ml. of hot distilled water. The soluble soaps were split by boiling their solutions with sulfuric acid, and the separated fatty acids were washed with water until neutral to litmus and dried by filtering through anhydrous sodium sulfate. This technique was not expected to give accurate yield data, but reproducible comparative results were obtained. Results for the unsaturated acid fractions from this series are shown in Table I.

TABLE I

Preferential Neutralization of 50 g. Samples of Soybean Fatty Acids (Iodine Value = 139.2)

Equiv. % of NaOH	Equiv. % of $BA(OH)_2$	% Yield of acids from sol. soaps	I.V. of Sol. Acids	Calcd. I.V. of insoluble acids
20	80	2	....	....
30	70	11	156.8	137
40	60	19	159.5	134.8
50	50	28	158.6	132
60	40	33	157.0	130.1
70	30	36	156.4	129.5
80	20	55	154.7	120.3

These preliminary data indicated that the most complete separation was obtained when the ratio of sodium hydroxide to barium hydroxide was about 40:60. Since barium soaps are appreciably soluble in alcohol, this solvent was eliminated from the reaction mixture for the next work. The mixed alkalies were dissolved in hot water as before and poured into the heated fatty acids with stirring. There was no difficulty in achieving complete neutralization, but the solid soaps did not settle from the solutions as readily on standing. Filtration, however, was not difficult, especially when a Buchner filter was used. With these changes in technique a 35% yield of unsaturated fatty acids of 164.8 iodine number was obtained from the same starting acids.

Using the 40:60 ratio which gave the highest iodine value in the experiments outlined in Table I, several neutralizations were carried out to check on the effect of order of addition. Each alkali was separately dissolved in half of the normal amount of water. In one experiment the sodium hydroxide was added first, followed after several minutes by the barium hydroxide solution and in the other case the barium hy-

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droxide was added first followed by the sodium hydroxide. These additions gave liquid fractions having I.V.s of 159.0 and 157.8 compared with 159.5 for the run in which the alkalies were added as a mixed solution. Yields were nearly the same in all cases. Apparently the order of alkali addition has little effect on either the yields or iodine values of the two fractions.

The use of potassium hydroxide in place of sodium hydroxide was considered to check whether more soluble soaps might result in a sharper separation. A series of neutralizations of soybean acids was carried out using varying ratios of potassium and barium hydroxides and omitting the use of alcohol as a solvent. The results are given in Table II.

TABLE II

Potassium-Barium Preferential Neutralization

Equiv. % of KOH	Equiv. % of $Ba(OH)_2$	% Yield of F.A. from Sol. Soaps	I.V. of Sol. Acids	Calcd. I.V. of Insol. Acids
30	70	28	159.2	131.3
40	60	42	162.6	122
50	50	43	162.8	121.3
60	40	36	160.4	127
70	30	58	155.7	116

These data show very little difference between the K:Ba ratios of 40:60 and 50:50. The unsaturated fraction is of somewhat lower iodine value than that obtained using sodium hydroxide, but the yield is somewhat better.

There are a number of other alkalies besides barium hydroxide which form insoluble soaps with fatty acids. Three of these were tested in conjunction with sodium hydroxide using the same 139.2 I.V. soybean fatty acid sample used previously. All of these neutralizations were carried out in the absence of alcohol. Data for calcium, strontium, and lithium hydroxides are given in Tables III, IV, and V.

TABLE III

Sodium-Calcium Preferential Neutralization

Equiv. % of NaOH	Equiv. % of $Ca(OH)_2$	% Yield of Acids from Sol. Soaps	I.V. of Sol. Acids	Calcd I. V. of Insol. Acids
30	70	8	143.9	138.5
40	60	14	137.3	139.6
50	50	24	150.0	120
60	40	51	158.4	119
70	30	48	155.8	124

TABLE IV

Sodium-Strontium Preferential Neutralization

Equiv. % of NaOH	Equiv. % of $Sr(OH)_2$	% Yield of Acids from Sol. Soaps	I.V. of Sol. Acids	Calcd I. V. of Insol. Acids
30	70	28	161.9	130.2
40	60	36	160.7	127.0
50	50	50	158.0	120.1
60	40	62	155.3	112.4
70	30	60	156.4	113.4

TABLE V

Sodium-Lithium Preferential Neutralization

Equiv. % of NaOH	Equiv. % of LiOH	% Yield of Acids from Sol. Soaps	I.V. of Sol. Acids	Calcd. I.V. of Insol. Acids
30	70	22	162.5	132.8
40	60	55	157.7	117
50	50	51	155.1	122.5
60	40	70	154.0	104.0
70	30	56	152.2	122.5

It is clear from these results that these substitutions offer no advantage over the original sodium-barium mixtures, iodine values of the soluble acids being lower in all cases. Furthermore these soap mixtures were more difficult to filter, the calcium soap particularly tending to form slimy, gummy filter cakes.

A study was made of the effect of such variables as temperature of reaction, rate of alkali addition, concentration of alkali, rate of cooling, effect of tempering, and temperature of filtration on the sharpness of separation, the yield of unsaturated acids, and the filterability of the soaps. It was found that cooling the soaps to 40°F. before filtering resulted in unsaturated fractions of appreciably higher iodine value, but the yields were considerably lower. Carrying out the neutralization at room temperature resulted in soaps which were very difficult to filter. Prolonged tempering of the soap mixtures at 150° to 180°F. did not improve the filterability. Slow addition of the mixed alkalies led to some improvement in filterability and yields, but the difference was slight. Use of more dilute alkali solutions gave some improvement in yield with little change in iodine value.

From a production standpoint the usage of the glyceride would be a definite economic advantage over fatty acids as a starting material. An equivalent amount of 40:60 sodium hydroxide-barium hydroxide mixture in 100 ml. of water gave only incomplete saponification after 48 hours of heating with soybean oil at steam-bath temperature. A similar mixture in an autoclave at 125 pounds pressure for 6 hours gave complete saponification, and the filtration of the mixed soaps gave a soluble fraction which gave 17% of fatty acids of 161 I.V. on acidifying with dilute sulfuric acid. The reaction products were difficult to remove from the autoclave, and as a result the recovery was rather poor. It undoubtedly could have been improved by using a properly designed autoclave.

A number of metals which form insoluble soaps cannot be used in the preferential neutralization reaction because of the insolubility of their hydroxides. A solution of the neutral sodium soaps was treated with soluble salts of lead, ferric and ferrous iron, calcium, aluminum, barium, magnesium, manganese, lithium, mercuric mercury, nickel, tin, and zinc. Preferential precipitation was observed in all cases excepting aluminum in which the soluble fraction liberated no fatty acids on treating with dilute acid and iron which was not checked because of the extreme difficulty in filtration.

The value of the unsaturated acid fraction from the sodium-barium precipitation was demonstrated by esterifying some liberated acids with glycerol. The fraction chosen for the work had an iodine value of 161.8 and an acid value of 192. Esterification was carried out by heating the acids with a 5% excess of glycerol at temperatures varying from 160 to 440°F. over a period of 7 hours. The reaction was unusually fast and the resultant acid value was low, undoubtedly accounted for by the presence of small amounts of barium soap which had escaped splitting. The synthetic drying oil had an acid value of 2.57, an iodine value of 153.9, and a saponification value of 191.8. The set-up time as determined by the Sanderson method, using 0.11% of lead and 0.003% of cobalt added as naphthenates, was 7 hours. An alkali refined soybean oil of 129.2 iodine value required more than 24 hours to set up using the same drier combination. The synthetic oil had only a slight tack after 24 hours whereas the soybean oil film had a marked tack one week after application.

The preferential neutralization process was also applied to mixed fish oil fatty acids. The fish oil fatty acids were obtained from Varnish Grade Fish Oil by saponifying with an excess of alcoholic potassium hydroxide and splitting the soaps with hydrochloric acid. The acids were not distilled, but they were dried by filtering through anhydrous sodium sulfate. They had an acid number of 186 and an iodine number of 206.2.

A series of neutralizations of these acids with mixed sodium and barium hydroxide was carried out similar to those described with soybean acids. No alcohol was used. Neutralization was carried out at about 200°F.; filtration was at room temperature. The data for the unsaturated acid fractions are shown in Table VI.

TABLE VI

Preferential Neutralization of Fish Oil Fatty Acids (Iodine Number of Original Acids 206.2)

Equiv. % of NaOH	Equiv. % of Ba $(OH)_2$	% Yield of Acids from Sol. Soaps	I.V. of Sol. Acids	Calcd. I.V. of Insol. Acids
20	80	4	292.8	202.2
30	70	18	291.2	188
40	60	28	283.7	176
50	50	39	284.3	156
60	40	50	283.1	129.4
70	30	59	247.2	147
80	20	88	240.5 (?)	

The extremely high iodine number of 292.8 was very interesting, but the yield was so low that the product of 283.1 iodine number, obtained in a yield of 50% by neutralizing with 60% sodium hydroxide and 40% barium hydroxide was considered more important. Some of thees acids were esterified with glycerol to a synthetic drying oil of 2.19 acid number, 258.3 iodine number, and 182.8 saponification number. With .5% lead and .05% cobalt this oil dried in 1½ hours as measured by the Sanderson method. The film was completely tack-free overnight whereas fish oil films normally remain rather sticky for several days.

Summary

It has been shown that soybean fatty acids neutralized with a mixture of 40% of sodium hydroxide and 60% of barium hydroxide (on equivalent basis) form about 35% soluble soaps, which after separating from the insoluble soaps and splitting with sulfuric acid, form fatty acids of about 165 iodine number. From these acids a synthetic drying oil was prepared by esterification with glycerol which formed films almost as good as those of linseed oil.

It was also shown that the same process applied to fish oil fatty acids, but using in this case 60% of sodium hydroxide and 40% of barium hydroxide, resulted in a yield of about 50% of fatty acids of about 283 iodine number, which when esterified with glycerol gave a very fast drying synthetic drying oil forming tack-free films.

Acknowledgment

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Correction

An error in the April issue of the Journal, page 161, Vol. 26, which appeared in Table II, should be corrected by reference to the following table, as supplied by the author, Harold Wittcoff, for his paper "Drying Oils From 2,2,6,6-Tetramethylolcyclohexanol and Linseed Fatty Acids":

TABLE II

Drying Times for the Linseed Acid Esters of Polyhydric Alcohols

	Drier	Time (hours)			
		Initial Set	Set to Touch	Lint-free	Dried Hard
Linseed Acid Ester of:					
Glycerol	.03% cobalt + .25% lead	1.2	3.5	5.0	7.0
Pentaerythritol	.03% cobalt + .25% lead	.80	1.9	2.3	4.0
TMC	.03% cobalt + .25% lead	.66	1.3	2.0	4.0
Glycerol	.03% cobalt + .03% manganese	4.0	6.0	9.0	11.0
Pentaerythritol	.03% cobalt + .03% manganese	3.0	4.5	6.0	8.0
TMC	.03% cobalt + .03% manganese	3.0	4.0	4.5	8.0
Glycerol	.03% cobalt + .25% calcium	1.2	2.8	3.8	7.0
Pentaerythritol	.03% cobalt + .25% calcium	.90	1.8	2.3	5.0
TMC	.03% cobalt + .25% calcium	.80	1.5	2.0	5.0