

than cottonseed oil. This average lower price is due to soybean oil being a substitute oil for cottonseed, peanut, and corn oil in the edible field, requiring additional processing to make it usable. Similarly in the drying oil field soybean oil is classed as a "semi-drying" oil and therefore sells at a discount to linseed oil.

This "substitute" character will continue until research work eliminates the flavor stability problem in the edible field or until the separation of the oil into "fractions" makes them more valuable for edible and drying oil uses.

Postwar Soybean Oil Usage

What is the outlook for increased soybean oil usage in the United States in the post-war period? In the drying oil field some recent observations have been quite optimistic and others have indicated that an abundance of various drying oils will be available (14, 15, 16).

Reference to Figure No. 2 and Table No. 5 shows that soybean oil has not been a vital factor in the drying industry in the past. In 1941 its steady slow growth reached a usage just short of 50,000,000 lbs. a year (about 5% of the total oil usage in the "drying oil" industry). During the past three years due to restrictions this annual usage has dropped to somewhat less than half this quantity. It should be possible to recapture this lost ground and perhaps extend it, but the competition will be severe, particularly from such new products of research as dehydrated castor oil which will challenge the recognized advantage of soybean oil alkyds as a non-yellowing interior finish.

In the edible field the post-war competition of other oils will also be intense, but the picture for domestic soybean oil appears fairly bright for the following reasons: it is unlikely that the cotton crop will be increased hence the available cottonseed oil will remain near its present level. Similarly, the supply of peanut oil from domestic sources is not likely to

expand under less controlled post-war conditions. It follows then that large supplies of other oils will be needed to furnish the oil for a 2.2 to 2.6 billion pound vegetable edible oils market. We know that soybean oil has had public acceptance in all types of edible products of good quality in these war years.

There are no other domestic oils available in large volume, and competition will come mostly from coconut and similar oils for usage in margarine and salad-cooking oils. For margarine there is considerable "legislative" advantage in using oils from domestic farms to compete with butter fat from the same and other domestic farms. All of these factors favor continued usage of soybean oil in the edible field.

The war has given soybean oil an enviable opportunity in the edible fats and oils industry. It is up to the soybean industry to continue actively an enlightened program to improve the quality of crude soybean oil by all methods—agronomic improvement of varieties, improved growing, harvesting, cleaning and storing of beans, improved oil processing with rewards for superior quality, continued research to improve its flavor stability, and continued development of "fractionated" soybean oil.

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Solidification Points of Binary Mixtures of Caprylic and Capric Acids¹

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ON several occasions in the past progress reports (3) have been made from this laboratory on studies centering around the solidification points of binary mixtures of adjacent pairs of the saturated fatty acids of even number carbon atom content. Extension of these studies beyond the C_{32} - C_{34} pair has been temporarily halted because the probable present limit appears to have been reached in the practical application of the solidification-point diagrams of straight-chain acids to problems in fatty oil and wax analysis. Still unreported are pertinent data for the C_8 - C_{10} pair, acids lying in the zone between those members of this homologous series whose solidification points are determinable by the procedure already

described (3a) and those whose physical state requires modification of procedure for the determination of this constant. To complete the record (Table 2) on those even acids whose behavior has been to date studied is the object of this communication.

TABLE I
Properties of Saturated Fatty Acids

Acid	Molecular Weight		Melting Point °C.		Solidification Point °C.	
	Found	Theory	Found	Reported	Found	Reported
Caprylic	144.8	144.2	16.4	15-16	16.05
Capric	172.0	172.3	31.6	30.8-31.5	31.60

Because of their availability as distilled, natural products it was not deemed necessary to synthesize

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TABLE II
Solidification Points of Binary Mixtures of Caprylic and Capric Acids

C ₈ -acid	Composition		Solidification Point
	mol-percent		
	C ₁₀ -acid		°C. (corr.)
0.00	100.00		31.60
4.59	95.41		29.85
9.25	90.75		27.95
14.35	85.65		25.70
20.44	79.56		23.00
25.31	74.69		20.80
30.01	69.99		18.65
33.98	66.02		16.60
39.94	60.06		13.40
45.44	54.56		10.45
46.50	53.50		9.80
47.20	52.80		9.40
48.59	51.41		8.50
49.41	50.59		8.00
49.95	50.05		7.00
51.07	48.93		7.00
51.99	48.01		7.00
53.17	46.83		7.05
54.25	45.75		7.00
55.25	44.75		6.90
57.52	42.48		6.60
58.73	41.27		6.45
61.52	38.48		6.15
64.01	35.99		5.80
66.54	33.46		5.20
67.07	32.93		5.05
68.82	31.18		4.60
71.02	28.98		3.80
72.80	27.20		2.75
73.37	26.63		2.55
74.35	25.65		2.60
75.89	24.11		2.85
76.94	23.06		3.00
79.10	20.10		3.65
81.82	18.18		4.60
86.10	13.90		6.95
91.91	8.09		10.35
96.01	3.99		13.05
100.00	0.00		16.05

the acids which were used in this study. They were recovered from technically pure acids (Armour and Company) containing about 90% of the major constituent, some 3 to 5% of the next lower and about 5 to 7% of the next higher homolog, plus a small quantity of unsaturated acids. That this raw material is a satisfactory one for the recovery of a chemically pure product, when the procedure hereinafter described is followed, becomes evident by reference to Table 1 in which are given several fundamental properties of the acids in question. Esterification, bromination (2) before fractional distillation, purification of the regenerated acid as its barium salt, and replicated crystallizations of the liberated acid from acetone mark the major steps in this operation.

Preparation of Acids

ESTERIFICATION (1) of the raw material with methanol—three times the weight of fatty acids taken was used because the alcohol serves both as reactant and as solvent—was effected in the presence of concentrated sulfuric acid as catalyst, 3% by weight of the fatty acids being used. The methyl esters were extracted from the reaction mixture with petroleum ether after which, without removal of the solvent, they were washed first with dilute potassium carbonate solution for recovery of unconverted fatty acids and then with water which, in turn, was removed by treatment with anhydrous sodium sulfate. Recovery of the solvent revealed 95 to 98% yields of methyl esters.

Bromination was carried out in chloroform solution, the solvent-to-ester ratio being at least four to one, a dilution insuring a clear solution at the reaction temperature, 0° C. Liquid bromine was slowly added in slight excess, the end-point being determined either quantitatively by means of the iodine number or qualitatively with potassium iodide-starch

paper. The excess bromine was removed, after a half-hour reaction period, with sodium thiosulfate solution. Washing with water, dehydration with anhydrous sodium sulfate, and recovery of solvent left the methyl esters in condition for fractional distillation.

The brominated methyl ester mixture was fractionally distilled at 1 mm. Hg. pressure through a Widmer column. A fore-run of about 10% was discarded; a distillation residue of about 15% containing the brominated esters was left unfractionated. The main fraction—its boiling range was narrow—was twice fractionated in a similar manner. That portion of the last fractionation which, distilling at constant temperature, had a saponification equivalent in close agreement with that of the desired methyl ester, was reserved for recovery of its acid by conventional procedures.

It was found, however, that regeneration of the fatty acid from its pure ester by saponification with alcoholic potassium hydroxide solution followed by treatment with hydrochloric acid presented some difficulties. Without fail the solidification point of the regenerated acid indicated contamination with about 1% of ester, a condition apparently traceable to a reaction which had been catalyzed by the presence of the mineral acid. Complete removal of the alcohol from the soap proved to be impossible even by drying

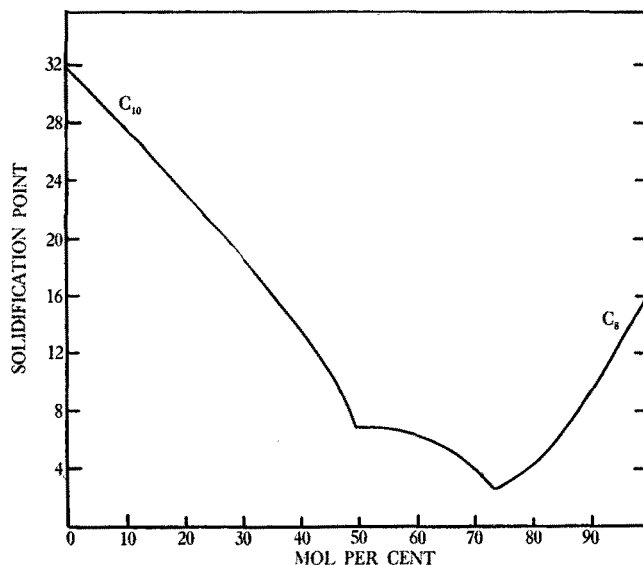


FIG. 1. Solidification point diagram of binary mixtures of caprylic and capric acids.

at low pressures. The soaps had entrained small, though significant, amounts of alcohol which were being tenaciously held back by the solid soap gel. This situation was eventually corrected by adding barium hydroxide to the products of saponification for the purpose of forming the insoluble barium soaps—they have a granular structure and hence no tendency to produce the type of gelation that sodium or potassium soaps do—and then thoroughly washing them, after filtration, with petroleum ether. Successive crystallizations of the regenerated acid were made from acetone until a constant solidification point was reached. In the case of caprylic acid, crystallizations were made from acetone-water solution at 0° C.

Summary

Clearly defined inflections characterize the solidification point diagram of binary mixtures of caprylic

and capric acids. These diagrams have been presented together with pertinent data and a description of a tested procedure for preparing these acids from readily available raw material.

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Referee Board Report

The Referee Board has only routine activity to report for the year 1944-5. Twenty-seven Referee Certificates were issued, as already published in *Oil & Soap*. The usual 10 check samples of cottonseed were distributed. The number of check oil samples was reduced to a single series consisting of three sam-

ples each of crude cottonseed and of crude soybean oil.

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Abstracts

Oils and Fats

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THE FUTURE OF SOYBEAN OIL. O. H. Alderks. *Chem. Eng. News*, **23**, 1168-70 (1945). During 2 world wars the use of soybean oil has jumped tremendously. After World War I it declined just as rapidly, but after reaching a low point in 1928, consumption began to expand again, gradually at first, then rapidly to where it now challenges cottonseed oil for leadership in production and use. Agronomic improvement and better technology in refining and processing have improved the competitive outlook for soybean oil in postwar years.

DETECTION OF OLIVE OIL IN EDIBLE OIL MIXTURES. J. Fitelson. *J. Assoc. Off. Agr. Chem.* **28**, 283-4 (1945). The method depends on the determination of squalene. Olive oil contains considerably more squalene than the other common edible oils. The squalene content of edible vegetable oils were: olive 136-708 mg. % (average 383), cottonseed 3-15 (8), peanut 8-49 (27), corn 16-42 (28), soybean 5-22 (12), sunflower 8-19 (12), teaseed 8-16 (12), sesame 3-9 (5) and rape 24-28 (26).

INVESTIGATION OF THE SEED OILS OF SOME SUDAN MIMOSACEAE. D. N. Grindley. *J. Soc. Chem. Ind.* **64**, 152 (1945). The seeds of this family have a very low content of fixed oils, which are rather dark in color and contain a high proportion of unsaponifiable matter. The fatty acids consist in most cases of 20-30% of saturated acids, including about 3% of higher acids (arachidic, behenic and lignoceric), the balance being a mixture of oleic and linoleic acids in proportions varying from about 2:1 to 3:4 according to the species.

OBSERVATIONS ON TESTS FOR SUPPOSED α -DICARBONYL COMPOUNDS IN AUTOXIDIZED FATTY SYSTEMS. H. Jasperson, R. Jones and J. W. Lord. *J. Soc. Chem. Ind.* **64**, 143-5 (1945). The colorimetric tests for α -dicarbonyl compounds proposed by Prill and by O'Daniel and Parsons have been applied to the specific dicarbonyls, diacetyl and diketostearic acid, and to autoxidized ground-nut oil and Me linoleate. Spectroscopic examination of the colors has shown that in autoxidizing fatty systems the substances responsible for the colors are not necessarily dicarbonyls.

THE EFFECT OF THERMAL TREATMENT AND HYDROGENATION ON THE ABSORPTION OF A FEW VEGETABLE OILS. A. Roy. *Ann. Biochem. Exptl. Med.* **4**, 17-22 (1944). The oils examined were fed to normal adult rats previously maintained on a fat free diet, a portion of this diet being replaced by an equivalent amount of the oil. The fats were fed in the normal state or after heating at 200, 250 or 275° for one hour or 300° for 45 minutes. Groundnut and coconut oils were also fed after hydrogenation to different degrees. Except in the case of groundnut oil all the oils showed a decrease in absorption after submission to thermal treatment but no effect after hydrogenation. Determination of the I value of the fats showed that this decrease in absorption was not related to the degree of unsaturation but appeared to be related to the rate of hydrolysis of the fats by lipase. (*Nutr. Abs. & Revs.* **14**, 690).

SOUTH AFRICAN FISH PRODUCTS. XVI. THE COMPONENT ACIDS OF THE HEAD, BODY, LIVER AND INTESTINAL OILS OF THE JACOPEVER (SEBASTICHTHYS CAPENSIS, GMEL.). N. J. Van Rensburg, W. S. Rapson and H. M. Schwartz. *J. Soc. Chem. Ind.* **64**, 139-40 (1945). The jacopecover has already been characterized as a fish with a diffuse system of fat storage. The liver oil is distinguished by its tendency to a lower degree of unsaturation than the corresponding head, body and intestinal oils, and by an inverse relationship between the content of oil in the liver and its I value. As a first step in the precise location of these effects, the component acids have been determined in the head, body, liver and "intestinal" oils from the jacopecover in moderately fat condition. It has been found that these jacopecover oils conformed in type to those from other fish with diffuse systems of fat storage. In relation to the head, body and intestinal oils, the liver oil was distinguished by an enhanced content of C₁₆ and C₁₈ unsaturated acids and a decreased content of the more highly unsaturated C₂₀ and C₂₂ acids.

SOUTH AFRICAN FISH PRODUCTS. XVII. THE COMPONENT ACIDS OF THE LIVER OIL OF THE STOCKFISH (MERLUCCIVUS CAPENSIS, CAST.). N. J. Van Rensburg, W. S. Rapson and H. M. Schwartz. *J. Soc. Chem.*