If the goods is to be sanforized it must again be treated with an oil having hygroscopic properties and then sent through a steam jet to shrink the goods and draw the weave together.

WEAVING

Previous to the weaving of textiles it is usually necessary to apply warp sizing to the warp threads. Sulphated oils are mixed in with the gum and starch size to eliminate harshness, and impart flexibility after the size has dried on the threads. If the sizing is wiry, injury may result during weaving.

MISCELLANEOUS TEXTILE OPERATIONS

Because of the general nature of this article, the processing of all textile products cannot be thoroughly described. The purpose is to give a picture of the manner and extent to which fats and their derivatives find application in the textile industry.

The outlines given above carry the most common textile materials through processing preparatory to dyeing and finishing. Table (1) lists the many textile operations and the fat derivatives used in each case. When the properties of the various fat derivatives are kept in mind it is easy to reason the purpose of their use in each case. It is important to remember that wherever wetting, penetrating, emulsifying, scouring, softening or lubricating is demanded, one or several of the fat derivatives will serve; and wherever water is used in processing one of the fat derivatives will in some way facilitate the operation.

REFERENCES

Hart, R. J., Am. Dyestuff Reptr. 26, 522-553 (1937).
Adkins & Folkers, Jour. Amer. Chem. Soc. 53, 1095 (1931).
M. R. Fenske, 436-437, Unit Processes in Organic Synthesis.
H. C. Borgetty, Amer. Dyestuff Reptr. 26, 177 (1937).
P. L. Mann, Amer. Dyestuff Reptr. 26, 177 (1937).
H. H. Mosher, 26, 186 (1937).
Jacob Katz, 28, 671 (1937).
Rayon Handbook, 3rd Edition.
Wool Handbook.

Solidification Point Curves of Binary Acid Mixtures II. Palmitic, Stearic, Arachidic, Behenic, Lignoceric*

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THE saturated, straight-chain fatty acids offer one of the most complete series of compounds for the study of behavior as influenced by homology. In this instance, of theoretical interest is not only the effect of increasing length of the alkyl group upon the tendency towards compound formation between adjacent members of even-number carbon atom content, but also the changes in the pertinent solidification point curves which are deemed to reveal this property. Of practical interest is the fact that solidification point curves of binary systems of fatty acids are an analytical aid in the determination of the composition of two-component fatty acid mixtures (1).

Preparation of Fatty Acids

Palmitic and stearic acids were recovered from commercial products of *ca* 90 per cent purity by methods already described (2). Arachidic acid was isolated by fractional distillation of its methyl ester from a mixture of hydrogenated fish oil fatty acids. Behenic acid was prepared by hydrogenating its unsaturated homolog, erucic, which had been previously isolated from rape seed oil. Lignoceric (n-tetracosanic) acid was prepared from behenic acid by malonic ester synthesis. The quality of these acids is on a par with the high purity products prepared by Francis & Piper (3). Their properties are summarized in Table I.

TABLE 1.
Properties of Saturated Fatty Acids.

	Molecular Weight		Melting Point °C.		Solidifying Point °C.	
Acid	theory	found	reported	found	reported	found
Palmitic	256.4	256.7	60.95-62.90	62.90	62.30-62.60	62.22
Stearic	284.5	284.6	69.60-70.10	69.95	69.39	68.85
Arachidic	312.5	312.9	75.15-75.35	75.30	74.20	74.35
Behenic	340.6	341.0	79.60-80.00	79.80	79.20-79.70	79.35
Lignoceric	368.6	369.0	84.00-84.15	84.10	83.10-83.90	83.40

Determination of Solidification Points

Solidification temperatures were determined for palmitic-stearic, stearic-arachidic, arachidic-behenic, and behenic-lignoceric acid mixtures. Their percentage compositions ranged in approximately five per cent increments from zero to 100 mol per cent of each constituent. Because past experience (2) had shown that critical points in the solidification point curves of adjacent pairs of members in this homologous series may be expected at approximately fifty and seventy molper cent of the lower acid involved, the increment of change in composition was reduced in order the better to define the curve in these zones. Approximately forty points were established for each pair. All of them fell upon a smooth curve.

No essential change was made in the procedure previously described (2) for the determination of solidification points. Because of the higher melting points of the acids in question, the water jacket of the original apparatus was replaced by an oil bath electrically heated with an internal coil connected in series with a variable resistance.

As before, a sample weighing about 0.7 g. was melted in a three-inch test tube suspended in a loose-fitting glass collar. The bulb of a calibrated thermometer graduated in intervals of 0.2° was then completely immersed in the liquid, after which the heat input of the bath was so regulated that the rate of temperature fall of the system, using only the surrounding atmosphere as cooling medium, became approximately 0.8°C. per minute. This arrangement proved to be very satisfactory for the determination of the solidification point temperatures noted in the 44° to 80°-range characteristic of the fatty acid mixtures of this series (Table 2).

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*Assistance in the preparation of these materials was furnished by the personnel of Works Projects Administration Official Project No. 65-1-53-2349.

While the contents of the test tube were gradually cooling, the tube itself was slowly rotated by means of a belt passing around its upper portion and attached to a motorized stirrer. Rotation of the tube, by providing some measure of stirring, served a two-fold purpose, viz.: it kept the contents homogenous and controlled, but did not eliminate the supercooling effect which in this instance is desirable. Supercooling is desirable in the sense that it marks the approach of solidification because on its release the temperature quickly rises to a maximum which becomes constant until total solidification has taken place. If the supercooling effect had been entirely eliminated by stirring the mixture rapidly, then the temperature would have slowly dropped and at no time would it have been constant. In systems involving solid solutions, as obtains here, it is a fact that the temperature can change during the process of slow solidification but that when solidification is made to proceed rapidly, as is the case here because of controlled supercooling, the change in temperature is so small as to be imperceptible on a thermometer.

Discussion

The systems in question are systems of continuous solid solutions. In as much as their solidification points are in every instance points of constant temperature while the whole mixture is solidifying, the behavior of each mixture is very much like that of a chemical entity.

From this interpretation of the behavior of these binary systems comes the concept that here we have a solidification point diagram in which the *liquidus* and the *solidus* curves are very nearly superimposed upon each other. The usual wide transition areas between *liquidus* and *solidus* curves which are found in most binary systems here become narrow line-areas.

The general characteristics of all the curves studied are two breaks, one of which is near the 48 mol-per cent and other near the 73 mol-per cent line of the acid of lower molecular weight. These breaks may be variously interpreted but the most likely one appears to be that *one equi-molecular compound* is formed in the system and that the curve can be split into halves at the 50 mol-per cent line. Each half, then, is a system of type III of Roozeboom's classification (4) of solid solution systems in which there is a continuous series of solid solutions with one minimum solidification point mixture. The two minimum points at approximately 48 and 73 mol-per cent, respectively, are not eutectic points as has been intimated previously (1a). They simulate very closely the behavior of a pure compound or a true eutectic, yet they are neither. This is shown by the fact that there is no sensible evolution of heat upon cooling a mixture of any other composition through the temperature of the minimum solidification point mixture for that curve. If these breaks occurred at points representing actual compounds or if they represented true eutectic points, solidification of any mixture should not be completed until that minimum temperature is reached. This is obviously not the case since total solidification took place at constant temperature. The conclusion that two compounds are formed, one consisting of three molecules of the lower acid to one of the higher, the other equimolecular with respect to both of them, is untenable. Additional evidence in contradiction of the view that the breaks of the curve represent compound-formation in the system may be found in the fact that they vary from one to three per cent from the points of alleged composition; and this variation is too large to be explained away on the grounds of experimental error for the mixtures were made up with a precision of less than 0.1 per cent and temperature readings are accurate to .05°C.

The general tendency of the curve (Figure 1) to become continuous with increasing molecular weight of the member pairs of these binary systems provides an interesting pictorial demonstration of the effect of homology. The sharpness of the break and the sharp slope of its descent as it falls back into the curve as a whole are indications of the stability of the equi-molecular compound formed. Compound-formation is definitely indicated in the lower curves. With ascent in the series, however, a state is approached where compound-formation, as shown by the break, becomes very weak and unstable so that in the behenic-lignoceric acids system there is only a small deviation in the continuity of the curve. It follows, therefore, that compound-formation is there limited and that dissociation of the compound is almost complete.

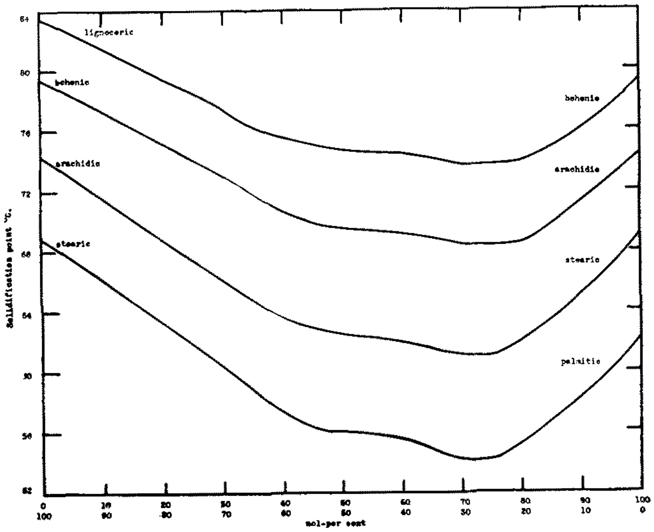

Figure 1. Solidification Point Curves of Binary Acid Mixtures

TABLE 2.

Solidification Points of Binary Acid Mixtures.

Palmitic-Stearic Mixture			Stearic-Arachidic Mixture		
C_{16} *mol. pct.*	C_{18} *mol. pct.*	Sol. Pt. °C. *(corr.)*	C_{18} *mol. pct.*	C_{20} *mol. pct.*	Sol. Pt. °C. *(corr.)*
0.00	100.00	68.85	0.00	100.00	74.35
2.81	97.19	68.15	2.80	97.20	73.65
6.05	93.95	67.20	5.85	94.15	72.80
9.77	90.23	66.20	7.65	92.35	72.30
14.00	86.00	65.00	13.03	86.97	70.80
18.64	81.36	63.80	14.09	85.91	70.55
18.85	81.15	63.72	16.71	83.29	69.80
24.33	75.67	62.20	21.49	78.51	68.30
31.29	68.71	60.10	23.46	76.54	68.00
34.16	65.84	59.20	26.76	73.24	67.00
38.85	61.15	57.70	28.90	71.10	66.50
39.82	60.18	57.28	30.74	69.26	65.95
42.33	57.67	56.70	35.03	64.97	64.80
44.19	55.81	56.52	38.24	61.76	63.90
45.65	54.35	56.25	39.16	60.84	63.75
47.73	52.27	56.00	42.03	57.97	63.25
49.54	50.46	56.02	43.38	56.62	63.15
50.26	49.74	56.00	46.69	53.31	62.75
52.87	47.13	56.00	46.72	53.28	62.70
56.11	43.89	55.85	48.69	51.31	62.50
58.65	41.35	55.70	50.46	49.54	62.30
62.24	37.76	55.45	52.00	48.00	62.20
65.00	35.00	54.90	54.05	45.95	62.15
65.36	34.64	54.85	55.82	44.18	62.15
68.06	31.94	54.45	58.30	41.70	62.05
68.30	31.70	54.42	60.60	39.40	61.85
68.98	31.02	54.39	62.78	37.22	61.72
70.80	29.20	54.21	63.99	36.01	61.50
71.72	28.28	54.20	66.60	33.40	61.25
73.32	26.68	54.20	69.76	30.24	61.10
73.40	26.60	54.20	72.19	27.81	61.00
74.34	25.66	54.20	74.59	25.41	60.90
76.48	23.52	54.35	76.20	23.80	60.98
77.65	22.35	54.60	76.47	23.53	61.00
80.26	19.74	55.15	79.09	20.91	61.60
85.16	14.84	56.60	85.40	14.60	63.35
90.01	9.99	58.20	88.68	11.32	64.18
94.30	5.70	59.70	88.79	11.21	64.23
97.19	2.81	60.85	93.50	6.50	66.10
100.00	0.0	62.22	97.49	2.51	67.75
			100.00	0.00	68.85

Arachidic-Behenic Mixture

C_{20} *mol. pct.*	C_{22} *mol. pct.*	Sol. Pt. °C. *(corr.)*
0.00	100.00	79.35
3.79	96.21	78.55
6.97	93.03	77.90
11.65	88.35	76.90
16.17	83.83	76.00
19.03	80.97	75.40
25.36	74.64	74.05
29.87	70.13	72.95
32.56	67.44	72.35
34.76	65.24	71.75
35.04	64.96	71.70
37.51	62.49	71.05
39.74	60.26	70.50
42.51	57.49	70.05
44.69	55.31	69.80
47.45	52.55	69.50
50.15	49.85	69.30
52.42	47.58	69.24
55.64	44.36	69.20
59.27	40.73	69.05
62.63	37.37	68.85
64.55	35.45	68.65
67.29	32.71	68.44
70.18	29.82	68.25
71.96	28.04	68.20
73.70	26.30	68.20
75.04	24.96	68.20
77.10	22.90	68.23
78.85	21.15	68.30
80.57	19.43	68.40
81.96	18.04	68.65
84.47	15.53	69.40
87.30	12.70	70.20
89.01	10.99	70.65
91.79	8.21	71.65
93.74	6.26	72.25
96.01	3.99	73.00
96.94	3.06	73.25
100.00	0.00	74.35

Behenic-Lignoceric Mixture

C_{22} *mol. pct.*	C_{24} *mol. pct.*	Sol. Pt. °C. *(corr.)*
0.00	100.00	83.40
4.97	95.03	82.55
10.01	89.99	81.55
15.17	84.83	80.50
20.05	79.95	79.47
22.62	77.38	78.95
25.07	74.93	78.45
27.30	72.70	78.00
29.71	70.29	77.45
32.35	67.65	76.82
34.94	65.06	76.20
37.46	62.54	75.75
39.94	60.06	75.45
42.52	57.48	75.20
45.05	54.95	74.95
47.41	52.59	74.78
49.94	50.06	74.60
52.47	47.53	74.55
54.72	45.28	74.50
57.33	42.67	74.48
59.89	40.11	74.45
62.33	37.67	74.35
64.97	35.03	74.10
67.28	32.72	73.93
69.70	30.30	73.75
72.55	27.45	73.75
74.69	25.31	73.75
76.97	23.03	73.75
79.94	20.06	73.87
82.48	17.52	74.25
84.91	15.09	74.70
87.56	12.44	75.35
91.73	8.27	76.42
95.93	4.07	77.80
100.00	0.00	79.35

Summary

Earlier studies on solidification point curves for binary systems of the saturated fatty acids of even-number carbon atom content have been extended to include the C_{16} to C_{24} group. The effect of homology is here beginning to become more obvious than it is in the lower brackets of this series of compounds in that the three-segment curve which is there a characteristic feature is gradually approaching in form that of the smooth, continuous type. This phenomenon has been interpreted in the light of a decreasing tendency toward compound-formation. It has been postulated that one equi-molecular compound is formed between adjacent pairs of fatty acids of even-number carbon atom content.

This study is being continued in the hope of bringing into the picture acids of higher carbon content than those already studied. Systems containing the odd-number carbon atom members of this homologous series will also be investigated.

Acknowledgments

This investigation was supported by a grant from the Wisconsin Alumni Research Foundation Fund. Armour and Company supplied the "Neo-Fats," from which the palmitic and stearic acids were recovered, and the hydrogenated sample of their "Neo-Fat 19" which served as our source of arachidic acid. To Prof. C. H. Sorum of the University of Wisconsin we are indebted for his assistance in the interpretation of the curves.

Literature Cited

(1) Schuette, H. A., and Vogel, H. A. This Journal, **16**, 17; 223 (1939).
(2) Schuette, H. A., and Vogel, H. A., ibid., 209.
(3) Francis, F., and Piper, S. H., J. Am. Chem. Soc., **61**, 577 (1939).
(4) Roozeboom, H. W. B., Z. physik. Chem., **30**, 396 (1899).

Abstracts

Oils and Fats

Edited by
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Dry germ removing of feed corn, a process to improve our fat supply. Felix Grandel. *Fette u. Seifen 47,* 185-8 (1940).

Present state of phosphatide research. W. Halden. *Fette u. Seifen 47,* 52-4 (1940). Review of recent work.

Development and present state of the I. G. hydrogenation processes. W. Boesler. *Chem. Ztg. 64,* 81-5 (1940).

Laboratory-type molecular or short-path still for vegetable and animal fats and oils. S. B. Detwiler and K. S. Markley. *Ind. & Eng. Chem. Anal. ed. 12,* 348-50 (1940).

The melting point of fat mixtures. Thor Lexow. *Fette u. Seifen 47,* 204-13 (1940). The flow pt. of Pohl, the Ger. standard, the Pohl and Finkener drop pts., the raised m.p., the flow-m.p., clear m.p., m. interval were investigated and discussed from the pt. of view of their value for margarine manuf.

What the user wants in edible oils. G. W. McBride. *Food Ind. 12,* 56-8 (1940). It tells briefly how to select an oil of desired flavor or blandness, and how to retain that flavor in the finished product.

Determining the refining grade of a fat. I. Surface tension and the "ring test." H. P. Kaufmann and P. Kirsch. *Fette u. Seifen 47,* 191-6 (1940). The difference between the surface tension of refined and crude oils is not great enough to serve as test to detect refining. II. The foaming capacity of fats. *Ibid.* 198-201. Crude vegetable oils foam when finely divided air bubbles are passed through them. Highly refined oils and triglycerides do not form under these conditions. The foaming qualities plus the stability of the foam is with most fat a measure of the refining grade of the fat. The results from coconut and palm kernel fats were not consistent. Lecithins, slimes, and saponins are the cause of foaming; which is also favored by free fat acids and unsaponifiables. Heat increases the foam volume but decreases foam stability.

Staling vs. rancidity in roasted coffee. antioxygens produced by roasting. Lucius W. Elder, Jr. *Ind. & Engr. Chem. 32,* 798-801 (1940). Comparison of the oxidation induction period of oil extracted from coffee before and after roasting shows that the roasting process increases the stability of the oil fraction toward the development of rancidity by a factor of approx. 3. The oil from green coffee when subjected to the roasting treatment by itself does not acquire increased stability. A practical test involving the storage of ground roasted coffee which had been treated with a small amount of pyrrole shows that the oil fraction is definitely stabilized, but resistance to staling is unaffected by such treatment.

Mechanism of the pyrolysis of castor oil. S. Isikawa, et al. *Science Repts. Tokyo Bunrika Daigaku A3,* 273-85 (1939). Castor oil was conducted through a combustion tube filled with clean sand or silica and heated to about 500°. The product obtained was a free-flowing mass which was sepd. by fractional distn. into 24% crude enanthaldehye, b_{18} 40-87°, 27.5% un-