mixed acetin fats yield wide plastic range products of a keeping quality heretofore unknown. Utility in many other edible fat products will no doubt become apparent as the fats are investigated further.

The unique properties of mixed acetin fats also suggest many potential applications to inedible uses. Some of the more promising ones include plasticizers for various polymers, a replacement for palm oil in tinning, and as hydraulic oils.

Summary

The most striking effect of the introduction of the acetyl group into the glyceride molecule is the reduction in melting point. This effect permits the preparation of low melting fats and oils, or acetin fats, of a high degree of saturation and of a significantly increased oxidative keeping quality.

Mixed acetin fats containing monoacetyl (monoacetins), diacetyl (diacetins), and normal triglycerides were made by random interesterification of normal fats or oils with triacetin, followed by removal of the residual triacetin.

In general, mixed acetin fats may replace normal triglycerides in any edible fat use. Edible fat products including shortenings, margarines, or spreads, salad oils, and frying oils were made from acetin fats and oils.

Suggested inedible use applications of the acetin fats and oils include plasticizers, tinning oils, and hydraulic oils.

REFERENCES

1. Feuge, R. O., Vicknair, E. J., and Lovegren, N. V., J. Am. Oil Chem. Soc., *29*, 11 (1952).
2. Baur, F. J., and Lange, W. (to the Procter and Gamble Company), U. S. Pat. 2,614,937 (1952).
3. Jackson, F. L. (to the Procter and Gamble Company), U. S. Pat. 2,615,159 (1952).
4. Baur, F. J. (to the Procter and Gamble Company), U. S. Pat. 2,615,160 (1952).
5. Feuge, R. O., Vicknair, E. J., and Lovegren, N. V., J. Am. Oil Chem. Soc., *30*, 283 (1953).
6. Feuge, R. O., Gros, A. T., and Vicknair, E. J., J. Am. Oil Chem. Soc., *30*, 320 (1953).
7. Eckey, E. W., Ind. Eng. Chem., *40*, 1183 (1948).

[Received October 26, 1953]

Reactions of Fatty Acid Chlorides. I. Preparation of Fatty Acid Anhydrides

N. O. V. SONNTAG, J. R. TROWBRIDGE, and I. J. KREMS, Research and Development Department, Colgate-Palmolive Company Inc., Jersey City, New Jersey

During the course of a program of research on chemical utilization of fatty acid chlorides it became evident that although there have been reported a variety of synthetic methods, there does not exist a systematic survey of the preparation of the anhydrides of the higher fatty acids. This communication deals with an investigation of various syntheses including a newer one employing fatty acid chlorides and the application of the optimum to the preparation of the anhydrides of the fatty acids from decanoic to stearic including oleic. Furthermore there are presented revised and new physical data determined by modern techniques on materials of unambiguous purity.

Aliphatic acid anhydrides have been prepared almost exclusively from either the alkali or silver salts of acids and the corresponding acid chlorides, (B), (23, 37, 41, 44); from certain acids and acetic anhydride, (C), (18, 19, 26, 28, 43); from the acid chloride, corresponding acid and pyridine, (D), (4) or from the acid chloride-pyridine adduct and water, (E), (2):

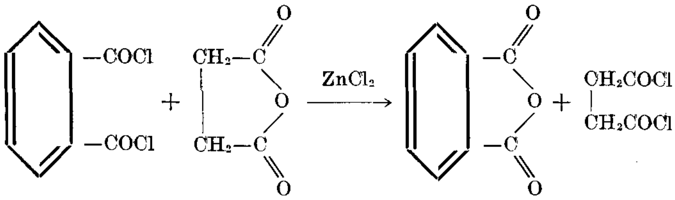
$$\text{(B)}\ \mathrm{RCOCl + RCOOM \longrightarrow (RCO)_2O + MCl}$$

$$\text{(C)}\ \mathrm{2RCOOH + (CH_3CO)_2O \longrightarrow (RCO)_2O + 2CH_3COOH}$$

$$\text{(D)}\ \mathrm{RCOCl + RCOOH + C_5H_5N \longrightarrow (RCO)_2O + C_5H_5NHCl}$$

$$\text{(E)}\ \mathrm{2RCOC_5H_5NCl + H_2O \longrightarrow (RCO)_2O + 2C_5H_5NHCl}$$

The suggestion of Zetzsche (45) that anhydrides could be easily prepared from the acid chloride and acetic anhydride, based upon his observation that benzoic anhydride could be obtained from benzoyl chloride and acetic anhydride, has apparently never been applied to aliphatic acid anhydrides. In the aromatic series the conversion of phthaloyl chloride to phthalic anhydride with maleic or succinic anhydrides at 140-200° in the presence of zinc chloride has been reported by Kyrides (24):



Acetyl chloride has been used to convert efficiently dicarboxylic acids such as glutaric, adipic, and sebacic acids to anhydrides (12, 27, 42). Yields of 55-75% of acid anhydrides have also been claimed by heating the acid to 120-125°, adding excess acetyl chloride dropwise, heating to 180°, and fractionating the products under vacuum (13). These reactions may be postulated as proceeding in three ways based upon known experimental evidence.

$$\begin{array}{ll}
\text{(I)} & \mathrm{2RCOOH \rightleftharpoons (RCO)_2O + H_2O} \\
 & \mathrm{R'COCl + H_2O \rightleftharpoons R'COOH + HCl} \\
\hline
 & \mathrm{2RCOOH + R'COCl \rightleftharpoons (RCO)_2O + R'COOH + HCl}
\end{array}$$

$$\begin{array}{ll}
\text{(II)} & \mathrm{2RCOOH \rightleftharpoons (RCO)_2O + H_2O} \\
 & \mathrm{2R'COCl + H_2O \rightleftharpoons (R'CO)_2O + 2HCl} \\
\hline
 & \mathrm{2RCOOH + 2R'COCl \rightleftharpoons (RCO)_2O + (R'CO)_2O + 2HCl}
\end{array}$$

$$\begin{array}{ll}
\text{(III)} & \mathrm{2RCOOH + 2R'COCl \rightleftharpoons 2RCOOCOR' + 2HCl} \\
 & \mathrm{2RCOOCOR' \rightleftharpoons (RCO)_2O + (R'CO)_2O} \\
\hline
 & \mathrm{2RCOOH + 2R'COCl \rightleftharpoons (RCO)_2O + (R'CO)_2O + 2HCl}
\end{array}$$

The intermediate formation of water appears more probable in the case of the dicarboxylic acids where the anhydride formed consists of 5, 6, or perhaps 7 membered rings [equations (I), (II)]. The series of (II) is modeled on the reaction in the presence of pyridine (4). The disproportionation reaction sequence (III) appears more probable for monocarboxylic acids where the elimination of water is not facilitated by ring formation.

Our work has indicated that elegant conversions of fatty acid chlorides to anhydrides may be achieved through the use of acetic anhydride.

$$\text{(A)}\quad 2RCOCl + \underline{(CH_3CO)_2O} \longrightarrow (RCO)_2O + 2CH_3COCl$$

This synthetic route to fatty acid anhydrides offers an alternate path to these derivatives, which has advantages over other methods of preparation.

Experimental

Decanoic, lauric, myristic, palmitic, stearic, and oleic anhydrides were prepared in better than 90% yields from purified acid chlorides with acetic anhydride. The acid chlorides of decanoic, lauric, myristic, palmitic, and stearic acids were obtained from commercial 90-97% fatty acids with excess phosphorus trichloride. The excess of reagent was removed completely before vacuum distillation of the crudes. Oleoyl chloride was obtained from high-purity methyl oleate by saponification to oleic acid followed by treatment with oxalyl chloride (phosphorus trichloride and thionyl chloride afforded impurer products). The once-distilled acid chlorides of decanoic, lauric, myristic, and palmitic acids were then fractionally distilled through all-glass Raschig-ring packed columns to obtain homolog-free acid chlorides which contained less than 0.1% free fatty acid by the Bauer analysis (6). The crude oleoyl chlorides prepared from both oxalyl chloride and phosphorus trichloride were purified by a falling-film distillation in a laboratory model of the Gold still (17). The physical properties of the acid chlorides are given in Table I.

TABLE I

Physical Properties of Fatty Acid Chlorides

Acid chloride	B.P./m.m.	d_4^{25}	n_D^{25}	M_D[1]	M_D[2]	M_D[3]
Decanoyl	82°/4	0.9293	1.4380	53.26	53.87	0.61
Lauroyl	106°/1	0.9169	1.4427	62.50	63.22	0.73
Myristoyl	135°/1	0.9078	1.4460	71.73	72.50	0.77
Palmitoyl	154°/1	0.9016	1.4482	80.97	81.65	0.68
Stearoyl	173-175°/1	0.8969	1.4510	90.20	90.94	0.74
Oleoyl, $(COCl)_2$	195°/2[a]	0.9099	1.4610	89.74	90.74	1.00
Oleoyl, $SOCl_2$	170-175°/2	0.9032	1.4584	89.74	90.97	1.24
Oleoyl, PCl_3	195-200°/2[a]	0.9108	1.4616	89.74	90.75	1.01

[1] Molar refraction obtained as sum of atomic refractions (Eisenlohr).

[2] Molar refraction calculated from d_4^{25} and n_D^{25} with Lorentz-Lorenz formula.

[3] Positive exaltation of M_D[2] over M_D[1]. A brief discussion of this phenomenon is given in Sonntag, N. O. V., Chem. Rev., 52, 253 (1953).

[a] B.P. is wall temperature in Gold falling-film distillation column.

1. ANHYDRIDES FROM ACID CHLORIDES AND ACETIC ANHYDRIDE

To prepare the fatty acid anhydride the acid chloride was heated together with from 100-300% excess of acetic anhydride in a round bottom flask and the vapors fractionated through a 9-12 in. Vigreux column until the theoretical quantity of acetyl chloride had been fractionated off. After removal of the acetyl chloride the excess acetic anhydride was distilled off under vacuum and the residue in the flask was recrystallized from ethyl ether or suitable hydrocarbons such as Skellysolve F. The preparation of palmitic anhydride is typical.

Palmitic Anhydride. Ten milliliters (9.02 g., 32.8 mmoles) of palmitoyl chloride, $n_D^{25} = 1.4482$, and 6.69 g. (6.16 ml., 65.5 mmoles, 300% excess) of acetic anhydride (Carbide and Carbon Chemical Company, technical grade, redistilled, b.p. 140-145°) were heated in a 50-ml. round bottom flask arranged for fractionation through a 9-in. Vigreux column connected to a water-cooled condenser. Two and three-tenths milliliters of acetyl chloride (2.4 g., 32.3 mmoles, 98.5%) were slowly collected during 30-60 minutes as the boiling point of the fractionated liquid rose to 60° (flask temperature 130-150°). At this point about 100 mm. vacuum were applied cautiously to remove excess acetic anhydride, heating being continued until the flask temperature was 160° and the pressure reduced to 10 mm. for 15 minutes. Total distillables were 4.3 ml. (4.68 g., 45.8 mmoles, 93.2% of excess acetic anhydride). The contents of the flask solidified on cooling to an almost white solid, which, after being taken up in Skellysolve F and being decolorized with charcoal, gave on crystallization at 0°, 7.45 g. (15.1 mmoles, 91.6%) of palmitic anhydride, pearly white plates, m.p. 63.8-64° [reported m.p. 65-66° (3), 62-63° (5), 63° (44), 63-64° (18), 64° (20, 41)]. Saponification equivalent—theoretical 247.4; found 247.

Oleic Anhydride. One hundred grams (337 mmoles) of high-purity methyl oleate prepared from olive oil essentially by the method of Swern and Parker (39), [I.V. = 86.1; analysis: 99.6% methyl oleate, 0% saturated methyl esters, 0.4% polyunsaturated methyl esters (9, 28), and less than 0.1% methyl elaidate (38)] were saponified with 40% excess aqueous potassium hydroxide under a nitrogen atmosphere to yield, after acidification, washing with water and drying, 89.0 g. (315 mmoles, 93.6%) clear, colorless oleic acid [I.V. = 89.9, $n_D^{25} = 1.4582$, $d_4^{25} = 0.8869$, M_D calc. = 86.39, M_D found = 86.93, I.R. absorption spectrum (Fig. II) indicated qualitative absence of elaidic acid].

Conversion to oleoyl chloride was tried in three ways. One portion (17.3 g., 61.3 mmoles) was treated with 9.4 g. (5.7 ml., 79.2 mmoles, 30% excess) of freshly distilled thionyl chloride (Eastman, b.p. 75-76°) at room temperature for 22 hours. The excess reagent was removed under vacuum and the residue vacuum distilled to give 13.05 g. (43.4 mmoles, 70.6%) crude oleoyl chloride, almost water-white, b.p. 170-175° at 2 mm., $n_D^{25} = 1.4584$. A second portion (17.3 g., 61.3 mmoles) was treated with 3.69 g. (2.36 ml., 26.9 mmoles, 30% excess) phosphorus trichloride (Oldbury) at 50° for 22 hours, the lower phosphorous acid layer removed, the upper layer stripped of excess reagent under reduced pressure, and falling-film distilled to give 7.73 g. (24.9 mmoles, 42%) oleoyl chloride, almost water-white, b.p. 195-200° (wall temperature) at 2 mm., $n_D^{25} = 1.4616$. A third portion (16.1 g., 57.0 mmoles) was refluxed with 23.6 g. (187.4 mmoles) of oxalyl chloride, b.p. 62-63°, for 2 hours and gave, after removal of excess reagent, 12.4 g. (41.2 mmoles, 72.4%) of water-white high-purity oleoyl chloride, b.p. on falling-film distillation 195° (wall temperature) at 2 mm., $n_D^{25} = 1.4610$, $d_4^{25} = 0.9099$, M_D calc. = 89.74, M_D found = 90.74.

TABLE II

Properties of Fatty Acid Anhydrides Prepared from Acid Chlorides

Anhydride	% Yield	Melting point		Saponification equiv.		d_4^t	n_D^t
		Reported[a]	Observed	Calc.	Found		
Decanoic	93.4	23.9°(18)	23.2°[b]	163.3	164	0.8865^{25}	1.4400^{25}
Lauric	94.8	41°(23); 41.8°(18); 44°(26)	41.2-41.5°[c]	191.3	192	0.8559^{70}	1.4299^{70}
Myristic	95.0	51°(23); 53.4°(18)	53.2-54.0°[c]	219.0	220	0.8511^{70}	1.4334^{70}
Palmitic	91.6	55-66°(3); 62-63°(5); 63°(44); 63-64°(18); 63.5-64°(32)	63.8-64.0°[c]	247.4	247	0.8482^{70}	1.4360^{70}
Stearic	92.0	64°(20, 41); 70-71°(5); 70.5°(44); 72°(20)	70.0-70.4°[c]	275.4	273	0.8445^{70}	1.4384^{70}
Oleic (PCl_3)	90.0	22-22.2°(18)	22.0°[b]	273.4	......	....	....
Oleoyl, ($SOCl_2$)	91.0	....	....	273.4	......	....	....
Oleoyl, $(COCl)_2$	93.5	....	22.1°[b]	273.4	274	0.8849^{25}	1.4630^{25}

[a] Reported m.p. for anhydrides prepared by other methods.
[b] Corrected m.p. in capillary.
[c] Corrected m.p. on Kofler stage.

All oleoyl chloride samples were converted to anhydrides in the following manner. Ten milliliter portions (30.0 to 30.3 mmoles) and 6.18 g. (5.71 ml., 60.6 mmoles, 300% excess) of acetic anhydride were heated under a dry nitrogen atmosphere and fractionated through a 9-in. Vigreux column until nearly theoretical amounts of acetyl chloride had been removed (flask temperature 140°). Excess acetic anhydride and the traces of the remaining acetyl chloride were then slowly distilled under vacuum, finishing at 5 mm. for 15 minutes at a flask temperature of 140°. After cooling, the residues in the flasks were recrystallized from Skellysolve F at —35°, using cold Buchner funnels to collect the solid anhydrides. Properties of the products are given in Table II.

2. Anhydrides Through Other Preparative Methods

Lauric Anhydride from Lauroyl Chloride, Lauric Acid, and Pyridine. Five grams (25.0 mmoles) of lauric acid, m.p. 43.5-44.0°, was added dropwise in the molten state to a preformed mixture of 5.44 g. (5.94 ml., 25.0 mmoles) of lauroyl chloride, 3.94 g. (4.01 ml., 50.0 mmoles) of dry pyridine and 25 ml. of dry benzene with stirring. The mixture was stirred at room temperature for 30 minutes, then the precipitate removed by filtration on a cold Buchner funnel, washed with two 25-ml. portions of dry benzene, and filtrate and washings combined. Excess pyridine and benzene were then removed from the solution by distillation under vacuum. The residual oil was taken up in 100-ml. Skellysolve F, filtered, the filtrate concentrated to 35 ml., and cooled to 0°. Crystallization gave a white solid which, after filtration through a cooled Buchner funnel and drying at reduced pressure over phosphorus pentoxide, amounted to 4.0 g. of crude lauric anhydride, m.p. 40.3-40.8° [analysis by method of Smith and Bryant (35): 85.0% lauric anhydride]. From the mother liquor on concentration and further cooling to 0° there was obtained an additional 0.6 g. of crude anhydride, m.p. 38.5-39.5° (analysis: 62.7% lauric anhydride). Total crude anhydride was 4.6 g. corresponding to 3.8 g. lauric anhydride (9.94 mmoles, 39.8%).

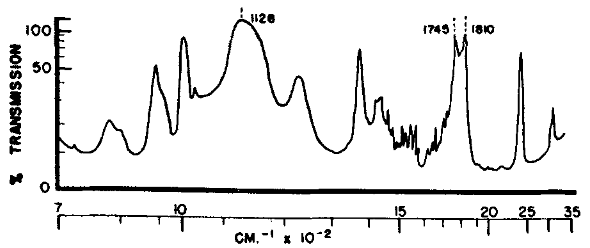
Lauric Anhydride from Lauroyl Chloride, Pyridine, and Water. Lauroyl chloride (5.44 g., 5.94 ml., 25.0 mmoles) was slowly added with stirring to 3.94 g. (4.01 ml., 50.0 mmoles) of dry pyridine in 25 ml. of dry benzene at 5-10°. After 20 minutes 0.22 ml. of distilled water was added microdropwise, and the mixture was stirred for 40 minutes at 5-10°. The precipitate of pyridinium chloride was removed after two filtrations and was washed with two 25-ml. portions of dry benzene, the washings and filtrate being combined. Evaporation at reduced pressure then removed the excess pyridine and benzene. The residual oil was taken up in 100 ml. of Skellysolve F, filtered, concentrated to 30 ml., and cooled to 0°. Crystallization afforded 0.7 g. of crude lauric anhydride, m.p. with sintering 38.0-40.00 (analysis: 67.3% lauric anhydride). The mother liquor, concentrated and cooled to 0° a second time, gave an additional 1.0 g. of anhydride, m.p. 31.5-37.0° (analysis: 52.0% lauric anhydride). Total yield crude anhydride was 1.7 g., corresponding to 0.99 g. lauric anhydride (2.59 mmoles, 20.8%).

Oleic Anhydride from Oleic Acid and Acetic Anhydride. Four grams (14.17 mmoles) of the oleic acid prepared from olive oil was converted to oleic anhydride with 2.89 g. acetic anhydride by heating and fractionally distilling acetic acid from the mixture with a flask temperature towards the end of 200°. The excess acetic anhydride was removed by vacuum distillation to yield the product, a clear pale colored oil (3.45 g., 6.3 mmoles, 89%), n_D^{25}=1.4630, [I.R. absorption spectrum (Fig. 1H) showed presence of oleic acid (maxima at 1710 cm^{-1}) but no evidence of elaidic acid or anhydride].

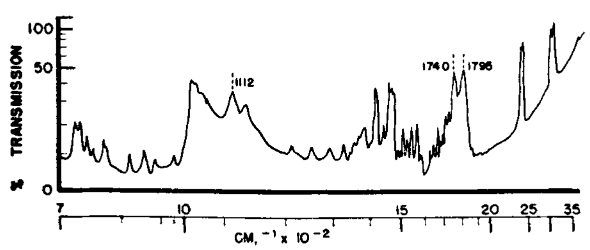
Another 4-g. sample of the same acid was heated for three hours at a temperature of 230° under a dry nitrogen atmosphere. After cooling, recrystallization gave a return of 3.8 g. (13.4 mmoles, 95%) of almost colorless oleic acid, n_D^{25}=1.4588 [I.R. absorption spectrum (Fig. 1J) showed no evidence for elaidic acid or for oleic or elaidic anhydrides].

3. Properties of the Fatty Acid Anhydrides

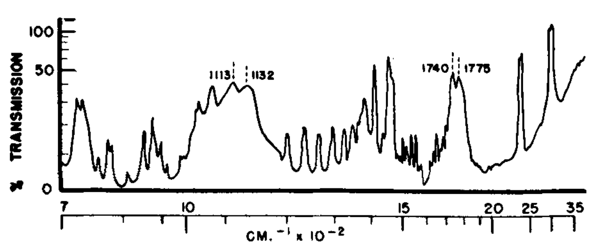
The fatty acid anhydrides obtained from purified acid chlorides with acetic anhydride were all pearly plate-like crystalline solids except for decanoic and oleic anhydrides, which were colorless oils at room temperature. The compounds melted sharply in the general temperature range of the fatty acids from which they were initially derived. Some properties are summarized in Table II. Previous reports have emphasized physical properties other than melting point only briefly, except for certain lower homologs (25). Infrared absorption spectra for the series as



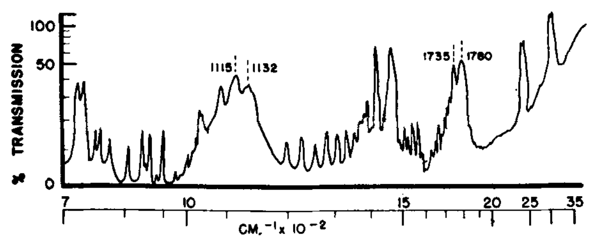
1A - ACETIC ANHYDRIDE



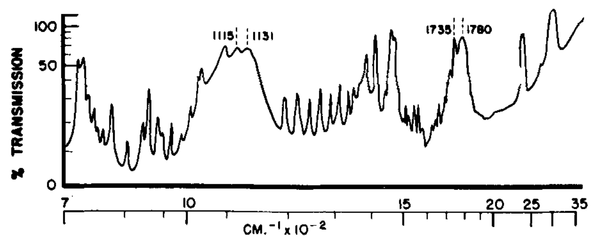
1B - DECANOIC ANHYDRIDE



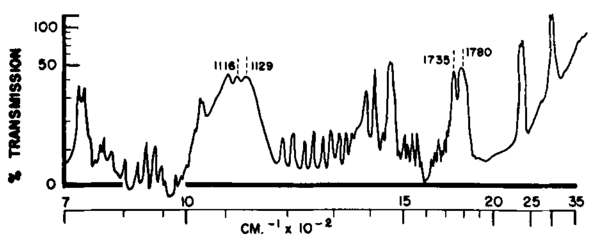
1C - LAURIC ANHYDRIDE



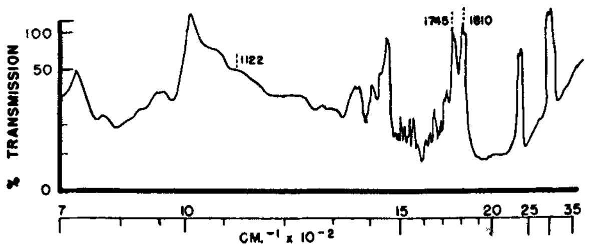
1D - MYRISTIC ANHYDRIDE



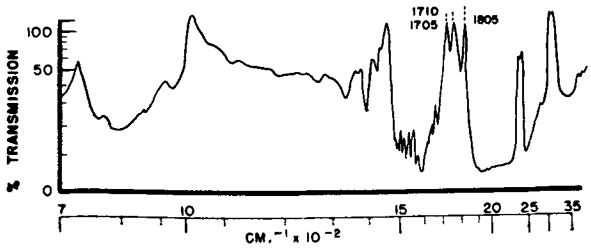
1E - PALMITIC ANHYDRIDE



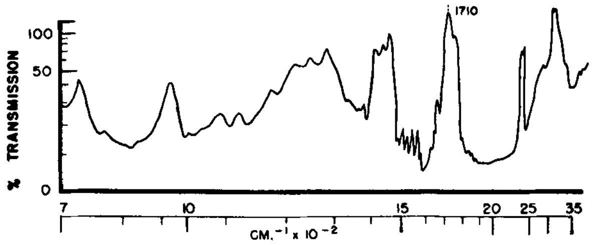
1F - STEARIC ANHYDRIDE



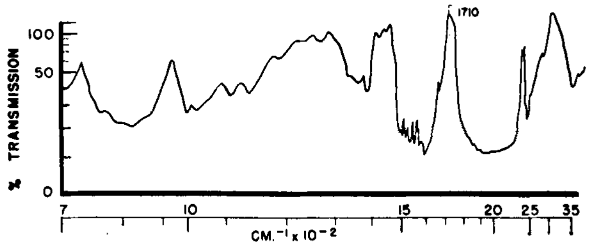
1G - OLEIC (FROM $(COCl)_2$) ANHYDRIDE



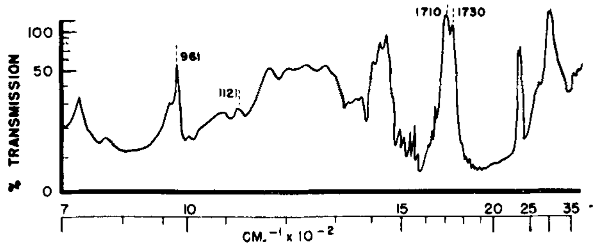
1H — OLEIC ANHYDRIDE FROM OLEIC ACID & ACETIC ANHYDRIDE



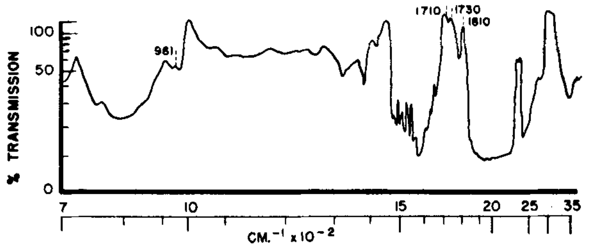
1I - OLEIC ACID



1J - OLEIC ACID AFTER HEATING AT 230°



1K - ANHYDRIDE (?) (FROM $SOCl_2$)



1L - ANHYDRIDE (FROM PCl_3)

FIG. 1. Infrared absorption spectra for fatty acid anhydrides.

indicated in Figure 1 and Table III, were taken with a Perkin-Elmer Model 12C single beam infrared absorption spectrophotometer and indicate the qualitative absence of free fatty acid in each case for saturated anhydrides. The spectrum of acetic anhydride (b.p. 141°, Bakers analyzed) has been inserted for comparison. A trace of oleic acid appears to be indicated in the oleic anhydride from oleoyl chloride prepared in turn from oxalyl chloride (Fig. 1G, maxima at 1710 cm^{-1}).

TABLE III

Infrared Absorption Bands for Fatty Acid Anhydrides in CM^{-1}

Anhydride	I C=O	II C=O	–O–C–
Acetic[a]	1745	1810	1128
Decanoic	1740	1795	1112
Lauric	1740	1775	1113, 1132
Myristic	1735	1780	1115, 1132
Palmitic	1735	1780	1115. 1131
Stearic	1735	1780	1116, 1129
Oleic [from $(COCl)_2$]	1745	1810	1122

[a] Acetic anhydride was Baker c.p., redistilled, b.p. 141°.

Discussion

The synthetic route to anhydrides involved in this method provides an example of the acyl interchange reaction generally believed to proceed through reversible equilibria.

$$RCOCl + (R'CO)_2O \rightleftharpoons R'COCl\uparrow + RCOOCOR'$$
$$2RCOOCOR' \rightleftharpoons (RCO)_2O + (R'CO)_2O$$

The mixed anhydride may disproportionate, as above, or indeed may react with another mole of acid chloride.

$$RCOOCOR' + RCOCl \rightleftharpoons (RCO)_2O + R'COCl\uparrow$$

The overall equation in either case is then

$$2RCOCl + (R'CO)_2O \rightleftharpoons 2R'COCl\uparrow + (RCO)_2O$$

To achieve the interchange it is only necessary to remove the lower boiling component from the mixture by fractional distillation. Thus the equilibrium can be shifted in the right direction if R'COCl has a lower boiling point than either RCOCl, $(RCO)_2O$, $(R'CO)_2O$, or RCOOCOR' and is removed. This condition is easily achieved with $R' = CH_3$, and a fatty acid chloride, RCOCl, containing from 10 to 18 carbon atoms, the acetyl chloride, b.p. 52°, being easily distilled from the mixture and the over-all transformation occurring at relatively low temperatures (slowly up to 80°, moderately fast near 100°, extremely rapid at 150-160°). A similar reaction is involved in the preparation of a fatty acid anhydride from fatty acid and acetic anhydride.

$$RCOOH + (R'CO)_2O \rightleftharpoons R'COOH\uparrow + RCOOCOR'$$
$$2RCOOCOR' \rightleftharpoons (RCO)_2O + (R'CO)_2O$$

or

$$RCOOCOR' + RCOOH \rightleftharpoons (RCO)_2O + R'COOH\uparrow$$

overall:

$$2RCOOH + (R'CO)_2O \rightleftharpoons (RCO)_2O + 2R'COOH\uparrow$$

However, in the usual case with $R' = CH_3$ and RCOOH, any fatty acid containing from 10 to 18 carbon atoms, the reaction is slower and requires that the mixtures be exposed to considerably higher temperatures in order to fractionate off the acetic acid, b.p. 116° (slow at 100-130°, moderately fast at 150-170°, rapidly at 200-230°). For the synthesis of saturated fatty acid anhydrides either synthetic route is satisfactory as these materials are sufficiently stable at the temperatures required, and the products may be decolorized with charcoal before recrystallization. Although lauric, palmitic, and stearic anhydrides have been reported prepared directly from the acids with acetic anhydride in only 68% (18), 50% (5), and 50% (5) yields, respectively, the method is capable of better conversions as indicated by the reported 91.5% yields obtained in the preparation of both decanoic and myristic anhydrides (18).

Yields of high purity acid anhydrides from good grades of acid chlorides are always greater than 90% of theoretical including a recrystallization step. Since most crude fatty acid chlorides, especially those prepared with phosphorus trichloride, contain from 3-5% free fatty acid and since high-purity acid chlorides slowly generate fatty acid through hydrolysis

TABLE IV

Comparison of Various Preparative Methods for Fatty Acid Anhydrides[b] with Acid Chloride Method

Method	Reference	Yield[c]	Solvent	Comments
(A) $RCOCl + (CH_3CO)_2O$	....	Excellent[b]	None	High quality obtained without necessity of crystallization. Color and purity depend only on original acid. Best method for unsaturated acid anhydrides.
(B) $RCOCl + RCOOM$[a]	(44)	Good–Excellent	Suspension type solvent or none	Crude product contains salt and requires solution, filtration, and recrystallization. A dry solvent must be used.
(C) $RCOOH + (CH_3CO)_2O$	(43)	Good–Excellent	None	Good, inexpensive method for saturated and unsaturated anhydrides. Requires higher temperature, is somewhat slower, color of crude product may be inferior.
(D) $RCOCl + RCOOH + C_5H_5N$	(4)	Good	Benzene	D and E not well applied to higher homologs, product contains considerable free acid. Pyridinium chloride is hygroscopic, difficult to filter. Strictly anhydrous reactions require dry benzene and pyridine which may be regenerated but requires a mol of alkali.
(E) $RCOCl + C_5H_5N + H_2O$	(2)	Fair–Good	Benzene	
(F) (a) $RCOOH + CH_3COCl$ (b) Disproportionation	(13)	Fair–Good	None	Addition of CH_3COCl to the acid at 120-125° is not convenient.
(G) $RCOOH + P_2O_5$	(14)	Poor	Benzene or None	Poor yields and difficulty of separating anhydride from syrupy by-products make this method unsatisfactory.
(H) (a) $RCOOH + CH_2 = C = O$ (b) Disproportionation	(22)	Good	None	Method not suited for laboratory use but could be important industrially. Acetic anhydride prepared this way.
(I) $RCOOM$[a] $+ (COCl)_2$	(1)	Good	None	Effective but expensive method.
(J) $RCOOH + (COCl)_2$	(1)	Good–Excellent	None	Expensive. Product may contain acid chloride.
(K) $RCOOH + C_5H_5N + SOCl_2$	(15)	Excellent	Ethyl Ether	More suitable than D and E with reactions occurring rapidly at —78°C. for lower homologs. Trichloroacetic acid gives acid chloride rather than anhydride. May cause isomerization in the case of unsaturated products.
(L) $RCOOH + C_5H_5N + SOBr_2$	(16)	Excellent	Ethyl Ether	No particular advantage over K.
(M) $RCOOH + C_5H_5N + C_4H_9OSOCl$	(16)	Excellent	Ethyl Ether	Not practical, starting material relatively inaccessible.

[a] Lower aliphatic acid anhydrides.
[b] Fatty acid anhydrides from acids containing 8 to 18 carbon atoms.
[c] Because of large reported variations in yields these are expressed as excellent (90%), good (75-90%), fair (50-75%), poor (<50%).

on storage, it would be desirable to conduct the interchange reaction with an acid chloride at a temperature toward the end of the reaction at which acetic acid will be fractionated off in order to assure that fatty acid contaminant is converted to anhydride by means of the excess acetic anhydride present.

On the other hand, while there is only little advantage in the preparation of saturated fatty acid anhydrides through the acid chloride, the preparation of high-purity unsaturated fatty acid anhydrides like linoleic or linolenic anhydrides would appear to be more advantageously carried out through the acid chloride. To prevent thermal migration of double bonds, conjugation of separated double bonds or interconversion of cis to trans isomers by heat, anhydride formation is preferably carried out at as low a temperature as is possible.

The choice of reagent in acid chloride preparation also determines the quality of the unsaturated anhydride ultimately produced. Thionyl chloride apparently caused a partial elaidinization of oleic acid for the acid chloride yielded an anhydride which contained an appreciable quantity of elaidic anhydride as indicated by infrared absorption (Fig. 1K, maxima at 961 cm^{-1}). Elaidinization may be assumed to result, probably through the action of the other products of acid chloride formation, namely, sulfur dioxide and hydrogen chloride, both of which are capable of causing this cis to trans interconversion (33, 34).

$$RCOOH + SOCl_2 \longrightarrow RCOCl + HCl + SO_2$$

That the effect of the heat required to convert oleoyl chloride (from thionyl chloride) to oleic anhydride was probably not responsible for the cis to trans interconversion was indicated by the fact that a sample of the elaidic acid-free oleic acid was converted to anhydride with acetic anhydride at a higher temperature than that used in the acid chloride reaction without noticeable elaidic anhydride formation (Fig. 1H). In addition, heating oleic acid for three hours at 230° under nitrogen afforded no detectable cis-trans interconversion or anhydride formation. Although it has been shown that a commercial grade of myristic acid could be dehydrated to anhydride in 4 to 30% yields by heating from 3 to 12 minutes at temperatures near 350° (11), this dehydration apparently does not occur significantly with oleic acid at 230° [see also (21)]. If hydrogen chloride were responsible for the cis to trans interconversion during the preparation of an unsaturated acid chloride with thionyl chloride, it would then be expected that the same phenomenon would be observed with acid chlorides prepared with phosphorus trichloride. With this reagent hydrogen chloride is always evolved during the reaction. The anhydride from oleoyl chloride prepared with phosphorus trichloride, indeed, was shown to contain a smaller but significant quantity of elaidic anhydride (Fig. 1L, small maxima at 961 cm^{-1}). Phosphorus pentachloride as an acid chloride reagent is subject to the same objection, as maleic acid has been reported converted to fumaryl chloride through its use (29). In addition, the possibility of double bond addition during attempts to prepare acid chlorides with either thionyl chloride or phosphorus trichloride is a further factor limiting the use of these reagents for the preparation of high-purity unsaturated acid chlorides. Presumably double-bond addition can be minimized by operating at the ice water temperature during acid chloride formation (40). The various effects of different acid chloride reagents upon unsaturated acids require further elucidation to establish the extent of these unusual reactions. We have further indicated that a high-purity oleic anhydride (Fig. 1G) could only be prepared through the use of an oleoyl chloride in turn prepared from oxalyl chloride. This result reflects the experience of other investigators (6, 12), who have recommended the use of oxalyl chloride for the preparation of unsaturated acid chlorides.

Some advantages and disadvantages of the acid chloride-acetic anhydride preparation of fatty acid anhydrides have been compared with those of other synthetic methods and are summarized in Table IV. Our experience with several synthetic methods involving pyridine (Methods D and E) has indicated that these are not advantageously applied to higher fatty acid anhydrides. Lauric anhydride could only be prepared in 39.8% yield through Method D according to the general directions of Allen *et al.* (4), and in only 20.8% yield by Method E according to Adkins and Thompson (2). A recent synthesis of anhydrides from the acid, thionyl chloride and pyridine (15, 16), has been reported to give almost quantitative yields.

Acknowledgment

The authors are grateful to J. T. Pizzo, Exploratory Organic Division, who aided in the synthetic work, and to K. O. Kellenbach, J. P. Kelly, and G. N. Fraunfelker, all of the Analytical Division, who took the infrared absorption spectra and performed the required analyses. R. B. Wearn and A. I. Gebhart of the Research and Development Department, who provided helpful discussions and criticisms, have been closely connected with the conception and pursuit of the program.

Summary

The anhydrides of decanoic, lauric, myristic, palmitic, stearic, and oleic acids have been prepared in better than 90% yields through the corresponding acid chlorides with acetic anhydride. Oleic anhydride could only be prepared satisfactorily when oleoyl chloride was prepared, in turn, with oxalyl chloride. A comparison has been made of the various synthetic methods.

REFERENCES

1. Adams, R., and Ulich, L. H., J. Am. Chem. Soc., *42*, 599 (1920).
2. Adkins, H., and Thompson, Q. E., J. Am. Chem. Soc., *71*, 2242 (1949).
3. Albitsky, A., J. Russ. Phys. Chem. Soc., *31*, 103 (1899); Chem. Centr. *70*, 1070 (1899).
4. Allen, C. F. H., Kibler, C. J., McLachlin, D. M., and Wilson, C. V., Org. Synthesis, *26*, 1 (1946).
5. Autenrieth, W., and Thomae, G., Ber. *57B*, 430 (1924).
6. Bauer, S. T., Oil and Soap, *23*, 1 (1946).
7. Behal, A., Ann. Chim. et phys., (7) *19*, 281 (1900).
8. Bleyberg, W., and Ulrich, H., Ber. *64B*, 2504 (1931).
9. Brice, B. A., Swain, M. L., Herb, S. F., Nichols, P. L., and Riemenschneider, R. W., J. Am. Oil Chem. Soc., *29*, 279 (1952).
10. Cason, J., Sumrell, G., and Mitchell, R. S., J. Org. Chem. *15*, 850 (1950).
11. Davidson, D., and Newman, P., J. Am. Chem. Soc., *74*, 1515 (1952).
12. Daubert, B. F., Fricke, H. H., and Longenecker, H. E., J. Am. Chem. Soc., *65*, 2124 (1943).
13. Fournier, H., Bull. soc. chim. France, (4) *5*, 925 (1909).
14. Gal, H., and Etard, A., Compt. rend., *82*, 457 (1876).
15. Gerrard, W., and Thrush, A. M., J. Chem. Soc., *1952*, 741.
16. Gerrard, W., and Thrush, A. M., J. Chem. Soc., *1953*, 2117.
17. Gold, M. H., Anal. Chem., *21*, 636 (1949).
18. Holde, D., and Gentner, R., Ber., *58B*, 1418 (1925).
19. Holde, D., and Rietz, K., Ber., *57B*, 100 (1924).
20. Holde, D., Ripper, J., and Zadek, K., Ber., *57*, 103 (1924).
21. Hurd, C. D., The Pyrolysis of Carbon Compounds, Chemical Catalog Company Inc. (Reinhold Publishing Company), New York, N. Y., 1929, p. 333.
22. Hurd, C. D., and Dull, M. F., J. Am. Chem. Soc., *54*, 3427 (1932).

23. Krafft, F., and Rosiny, W., Ber., *33*, 3577 (1900).
24. Kyrides, L. P., J. Am. Chem. Soc., *59*, 207 (1937).
25. Lewis, D., J. Chem. Soc., *1940*, 32.
26. Mannich, C., and Nadelmann, A. H., Ber. *63B*, 797 (1930).
27. Mol, D., Rec. trav. chim., *26*, 381 (1907).
28. Official and Tentative Methods of the American Oil Chemists' Society, Tentative Method cd 7-48 (Rev. May 1951), 2nd Ed. (1946).
29. Perkin, W. H., Ber., *14*, 2548 (1881).
30. Prat, J., and Etienne, A., Bull. Soc. chim., (5) *11*, 30 (1944).
31. Presting, W., Chem. Tech., *4*, 152-6 (1952).
32. Rankov, G., Ann. univ. Sofia II, Faculte phys.-math. Livre 2, *33*, 221 (1937); Chem. Abstracts *32*, 3335 (1938).
33. Skraup, S., Monatsh., *12*, 108 (1891).
34. Skraup, S., Monatsh., *12*, 118 (1891).
35. Smith, D. M., and Bryant, W. M. D., J. Am. Chem. Soc., *58*, 2452 (1936).
36. Sonntag, N. O. V., Chem. Rev., *52*, 237 (1953).
37. Staudinger, H., and Schwalenstocker, H., Ber. *68B*, 728 (1935).
38. Swern, Daniel, Knight H. B., Shreve, O. D., and Heether, M. R., J. Am. Oil Chemists' Soc., *27*, 17 (1950).
39. Swern, Daniel, and Parker, W. E., J. Am. Oil Chemists' Soc. *29*, 614 (1952).
40. Taufel, K., and Kunkele, F., Fettchem. Umschau, *42*, 27 (1935).
41. Villier, A., Ber., *9*, 1932 (1876).
42. Voerman, G. L., Rec. trav. chim., *23*, 269 (1904).
43. Wallace, J. M., and Copenhaver, J E., J. Am. Chem. Soc., *63*, 699 (1941).
44. Whitby, G. S., J. Chem. Soc., *1926*, 1462.
45. Zetzsche, F., Enderlin, F., Flutsch, C., and Menzi, E., Helv. Chim. Acta, *9*, 181 (1926).

[Received November 16, 1953]

ABSTRACTS . . . . E. S. Lutton, Editor

• Oils and Fats

Ralph W. Planck, Abstractor
Dorothy M. Rathmann, Abstractor

Lecithin in food processing. F. Aylward. *Food Manuf.* **27**, 285-7, 311-4, 355-7, 395-7, 411(1952). Commercial lecithin, which is obtained from soybean, corn, peanut, and rapeseed oils, is a mixture of phosphatides. The properties of pure lecithin are described. The use of commercial lecithin in the manufacture of bread, flour, confectionery, biscuits, prepared mixes, food pastes, cake icings, fillings, and tin-greasing agents is reviewed. The applications of phosphatides in the production of other foods, such as chocolate and sugar confectionery, ice cream, and edible fats, are outlined. (*Food Sci. Abs.* **25**, No. 3196[1953])

Esterified and interesterified fats. A. E. Bailey. *Proc. Research Conf., Council on Research, Am. Meat Institute, Univ. Chicago* **5**, 11-17(1953). The inability of lard shortening to retain air is corrected by interesterification, making it comparable to hydrogenated vegetable-oil shortenings. Means of interesterification are discussed. (*C. A.* **58**, 901)

The role of surface phenomena in the butter-formation process. A. Belousov. *Molochnaya Prom.* **14** (9), 28-34(1953). Rahn's foam theory, its Zaikovskiĭ version and the flotation theory, proposed for the formation of butter from cream during churning, are discussed together with some of the contributing factors, namely, the physical chemical properties of the fat-globule-stabilizing membrane, the breakdown of the membrane, the air dispersion, and the influence of the surface-active agents. Evidence supports the flotation theory, according to which, during churning, the fat globules are drawn into the air-liquid interface and concentrated on the surface of the air bubbles. Albumin, lecithin, and saponin prolong, while isoamyl alcohol hastens, the churning process. (*C. A.* **48**, 900)

So-called vitamin F-active fatty acids. Karl Bernhard and Urs Gloor (Univ. Basel, Switzerland). *Helv. Physiol. et Pharmacol. Acta* **11**, 323-8(1953) (in German). Addition of stearolic, 9,10-dihydroxystearic, or 9,10-diketostearic acid to a diet devoid of essential fatty acids given to lactating rats had a curative effect on the growth and the life expectancy of the offspring. A possible formation of linoleic acid from these compounds is discussed. (*C. A.* **48**, 827)

Effect of cooking upon the vitamin A content of ghee. I. S. Bhatia. *Bull. cent. Food Tech. Research Inst., Mysore* **2**, 72-4 (1952). All processes of cooking applied to ghee caused a loss of vitamin A. When ghee was used for frying, all vitamin A was destroyed after 15 minutes. (*Food Sci. Abs.* **25**, 3194)

Vitamin A content of cow's butter fat. I. S. Bhatia. *Bull. C. F. R. I.* (Mysore) **2** (7), 178(1953). The content of vitamin A of cow's butter fat in the Punjab varies between 17.5 and 61.0 I.U./g. This content decreases during the lactation period. (*Oléagineux* **8**, 899[1953])

The deodorization of edible oils. J. L. Boyle. *Food* **21**, 372-6 (1952). The deodorization of oils is accelerated by low pressures, high temperatures (up to 250°), and a large area of contact between the steam and the oil. Designs and flow diagrams for several commercial deodorizers are given.

A new index for butter analysis. Bruno Cadrobbi and Franco De Francesco. *Boll. lab. chim. provinciali* (Bologna) **3**, 7-10 (1952). The critical temperature of solubility in nitrobenzene of the nonvolatile fatty acids (T.S.N.) can be used to reveal adulteration of butter. One ml. of the nonvolatile fraction of the extracted fatty acids is added, in a test tube of 16 mm. diameter, to 2 ml. commercial nitrobenzene. A thermometer is immersed in the mixture and the test tube is heated over a flame until the solution becomes clear (30°-40°). Then the solution is allowed to cool while being shaken. The temperature at which the solution starts to become turbid is considered the T.S.N. index. For genuine butter the index is 27.2°-28.2°; for margarine, made from coconut fat, below 16°; for lard, below 28°; for the official stearic acid, 46.8°. (*C. A.* **48**, 899-900)

Preparation of linolenic acid by the bromination-debromination method. Georges N. Catravas. *Compt. rend.* **257**, 1250-2(1953). Purified, powdered hexabromide was suspended in acetone and the solution refluxed with frequent additions of powdered Zn and conc. HCl. When the hexabromide had disappeared, the solution was diluted with a large amount of water and the linolenic acid extracted with petroleum ether. The petroleum ether solution was washed with water, dried over Na_2SO_4, and the solvent removed under CO_2. Yields and purity were higher than when alcohol was used as solvent, for there was less formation of trans-isomers of linolenic acid during the debromination process.

The antibiotic action of polyunsaturated fatty acids in sterilized milk. H. Cornelissen, M. Loncin, and D. Jacqmain. *Proc. 13th Intern. Dairy Congr.* (The Hague) **3**, 1098-1101(1953). Total soaps of linseed oil showed a partial inhibition by 100 p.p.m. and practically complete at 1000 p.p.m., the action being due to linolenic acid in the oil. Unsaturated acids with 4 or 5 unsaturated bonds gave more activity. The inhibition is nearly the same in broth and skimmed milk and less in whole milk. Because of the taste this method of preservation is not practical. (*C. A.* **48**, 296)

Synthesis of phospholipides during absorption of different fats. P. Favarger (Univ. Geneva, Switzerland). *Helv. Physiol. et Pharmacol. Acta* **11**, C14-16(1953) (in French). Chiefly discussion. (*C. A.* **48**, 244)

Feeding experiment on young calves with flaxseed residues which split off hydrogen cyanide. A. Orth and F. Mohr (Landwirtschaft. Hochschule, Hohenheim, Germany). *Arch Tierernähr.* **3**, 31-9(1953). The danger involved in the splitting of the flaxseed glycoside into HCN, grape sugar, and acetone was studied in young calves. Although HCN is an extremely toxic material, flaxseed and flaxseed products such as flaxseed cakes and extraction residues are used as nutrient materials in animal nutrition. Four kg./day of flaxseed cakes, and extraction salvage were fed to cattle in doses which theoretically exceeded the lethal doses of HCN with no toxic effects other than retarded appetites. A basic difference was demonstrated between animals with a simple digestive tract and those animals with a thick forestomach. In the former the activity of the flaxseed enzymes is destroyed by the gastric acidity, preventing the breakdown of the glycoside, whereas in ruminants the HCN is split off in 6-8 hr., quickly resorbed from the mucus of the forestomach and taken care of through detoxification by the liver and expiration. No evidence of accumulation of HCN has been presented. (*C. A.* **48**, 824)

Method for retention stability of margarine in vacuum. Ya. I. Paliĭ (N. I. Pirogov Medical Inst., Odessa). *Masloboĭno-Zhirovaya Prom.* **18** (9), 9-10(1953). Milk or cream and nonmilk varieties of margarine which were held in a vacuum chamber