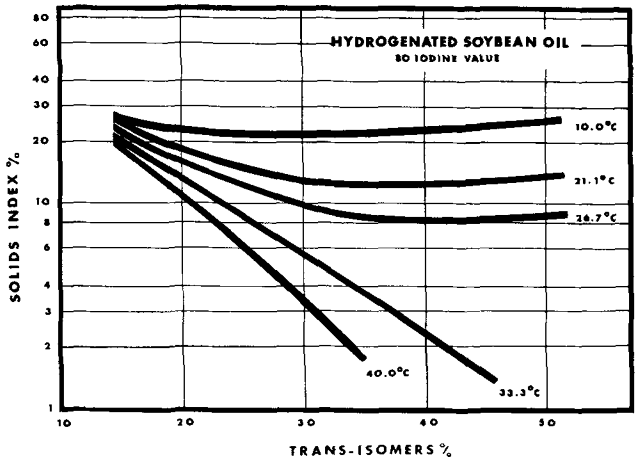

Fig. 5.

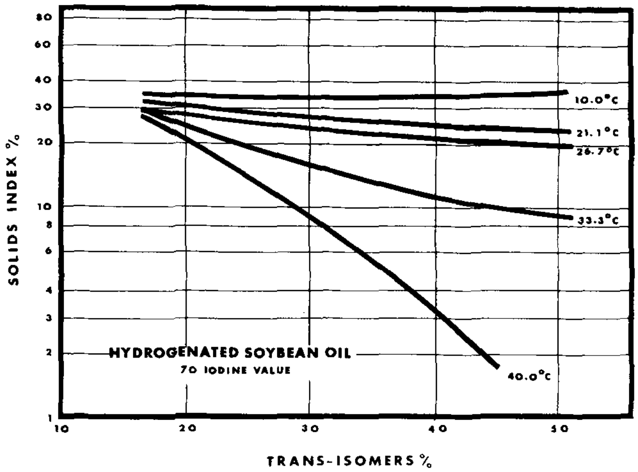

Fig. 6.

TABLE V

Effect of Pressure and Temperature on Hydrogenation Index of Hydrogenated Cottonseed and Soybean Oils

Pressure p.s.i.	Temp. °F.	Hydrogenation index							
		Cottonseed oil[a]				Soybean oil[a]			
		90	80	70	60	90	80	70	60
10	260	34.4	37.1	37.0	36.0	34.7	35.2	35.2	32.7
	340	47.3	53.0	52.8	51.8	48.9	51.3	52.0	50.2
	485	58.0	64.7	64.0	60.5	67.9	76.8	72.9	58.3
40	260	31.3	33.5	33.1	32.9	29.6	30.2	30.3	29.8
	340	40.4	43.9	44.3	44.2	43.4	44.8	45.9	42.1
	485	56.6	62.7	62.8	60.5	67.9	73.6	71.5	53.7
70	260	22.7	23.8	24.2	25.3	21.0	21.6	22.2	22.2
	340	33.0	35.7	35.7	36.5	41.4	48.8	51.4	40.8
	485	55.8	61.8	62.8	60.5	62.2	70.5	70.2	52.6

[a] 90, 80, 70, and 60 iodine value.

in determining the type of reaction. Soybean oil, because of its higher concentration of reactable double-bonds, hydrogenates faster than cottonseed oil until its unsaturation is reduced to a comparable figure. The temperature of the soybean oil, particularly at 70 p.s.i., was also more difficult to control. It is the opinion of the investigators that the few divergent results resulted from the poor temperature control possible at the higher temperatures with the experimental apparatus that was employed.

Acknowledgment

The authors wish to thank C. W. Hoerr for making the infrared spectrophotometric determinations and F. S. Kosco for the other analytical work.

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[Received May 21, 1959]

Aliphatic Urethanes. Effect of Chain Length on Some Physical Properties[1]

SOL SHULMAN,[2] MARVIN W. FORMO, and ALFRED E. RHEINECK,[3]
Archer-Daniels-Midland Company, Minneapolis, Minnesota

During a study of the thixotropic behavior of certain fatty materials a series of alkyl esters of substituted carbamic acids was prepared, and some of the physical properties were examined. Highly purified fatty alcohols and fatty isocyanates were reacted to give urethanes with from 8 to 22 carbon atoms in both the O-alkyl and N-alkyl groups.

The melting points of the urethanes were dependent not only on the number of carbon atoms in the molecule but also on the symmetry of the moiety. In an homologous series the melting point increases with the number of carbon atoms. When symmetry is reached, there is a sharp increase in the melting point. After this the increase is less pronounced.

The urethanes give thixotropic gels with ethyl alcohol, soybean oil, solvent-thinned resins, and other similar materials at concentrations as low as 0.5%. In general, better-defined crystal structure and poorer thixotropic properties were observed with an increase in symmetry.

Chemicals which impart thixotropic character are important in the manufacture of greases, paints, polyester resins, adhesives, and other classes of products. Polyamide resins, for instance, are used in paint vehicles (7), and bentonites modified with

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[1] Technical Paper No. 177, Archer-Daniels-Midland Company.

[2] Present address: College of Chemical Technology, North Dakota State University, Fargo, N.D.

[3] Present address: Coatings Technology Department, North Dakota State University, Fargo, N.D.

TABLE I

Melting Points, °C.,[a] of n-Alkyl Esters of N-n-Alkyl Carbamic Acid, $RNHCOOR^1$ [b]

O-Alkyl, R^1	N-Alkyl, R						
	n-Octyl, C_8	n-Dodecyl, C_{12}	n-Tetradecyl, C_{14}	n-Hexadecyl, C_{16}	n-Octadecyl, C_{18}	n-Eicosyl, C_{20}	n-Docosyl, C_{22}
n-Octyl, C_8	36–38	48–49	54–55	61–62	66–68	70–71	74–76
n-Decyl, C_{10}	41–43	58–60	59–61	64–66	69–71	72–74	76–78
n-Dodecyl, C_{12}	49–50.5	65–67	67–69	68.5–70.5	72–74	75.5–76.5	78–80
n-Tetradecyl, C_{14}	58–60	64–66	74–76	76–77	76–77	77.5–78.5	80–82
n-Hexadecyl, C_{16}	63–64.5	69–71	70–72	80–81	80–82	80–81	82–84
n-Octadecyl, C_{18}	68–70	74–76	76–78	76–78	85–87	85.5–86.5	84–86
n-Eicosyl, C_{20}	74–75.5	77.5–79	79–81	81–83	83–84	90–93	90–93
n-Docosyl C_{22}	76.5–78.5	79–81	80.5–82.5	82.5–84	84.5–85.5	85.5–87.5	92–94

[a] All melting-points are uncorrected for stem exposure.

[b] Percentage N (Kjeldahl) for these compounds was within experimental error (± 0.4%) of the theoretical value. Infrared data indicated the compounds were essentially free from impurities.

fat-derived quaternary salts are used for paints and greases (1).

Preliminary experiments demonstrated that aliphatic carbamic acid esters (urethanes), prepared from commercial fatty alcohols and isocyanates derived from commercial fatty amines, were effective in imparting thixotropy to a variety of materials. However performance varied widely, depending upon the relative, average size of the alkyl groups contributed by the starting alcohols and amines. Accordingly it was of interest to use highly purified fat derivatives to evaluate the effect of size and position of alkyl substituents on melting points and thixotropic behavior.

Fatty amines containing from 8 to 22 carbon atoms were converted to the corresponding isocyanates by the conventional phosgene synthesis. Urethanes were then prepared from the isocyanates and fatty alcohols containing from 8 to 22 carbon atoms.

The structures and melting points of the resulting alkyl carbamates are summarized in Table I. Capillary melting-points vary from 38°C. for the n-octyl N-n-octyl carbamate up to 94°C. for n-docosyl N-n-docosyl carbamate. Polymorphic behavior of these compounds has not been investigated.

Experimental

Fatty amines and fatty alcohols were obtained by careful fractional distillation of commercially available materials,[4] using a Podbielniak still. Table II shows some of the properties of these purified compounds.

The fatty amines were converted to the corresponding isocyanates by using the well-known phosgene synthesis (2). Table III summarizes some of the properties of the fatty isocyanates. The NCO content of the isocyanates was determined by a modification of the method of Siggia and Hanna.

TABLE III

Starting Materials. Fatty Isocyanates[a]

Compound	BP °C.	% NCO	
		Calc'd	Found
n-Octyl isocyanate	201–203/740.3 mm.	27.0	25.7
n-Dodecyl isocyanate	79–81/0.1–0.2 mm.	19.87	19.72
n-Tetradecyl isocyanate	133–135/0.7–0.9 mm.	17.5	16.8
n-Hexadecyl isocyanate	157/4 mm.	15.7	15.9
n-Octadecyl isocyanate	154–156/0.3–0.4 mm.	14.2	14.7
n-Eicosyl isocyanate	174–0/3 mm. (MP = 34°C.)	12.98	12.96
n-Docosyl isocyanate	182/0.15 mm. (MP = 42°C.)	11.95	12.13

[a] Percentage of N (Kjeldahl) for these compounds was within experimental error (± 0.4%) of the theoretical value.

Procedure. Add 40 ml. of dry toluene to a flask. Weigh 1.000 g. of sample into the flask. Immediately add 25 ml. of approximately 0.5 N dibutylamine in toluene by pipette. Stopper the flask loosely, and warm on hot plate until the first indication of boiling is observed. Remove from the hot plate, and allow to stand at room temperature for 1.0 hr. Add 25 ml. of isopropyl alcohol and 1 ml. of bromcresol green indicator solution. Titrate with standard 0.5 N HCl in isopropyl alcohol to the disappearance of blue color. At the same time run a blank.

Calculation

$$\text{R NCO} = \frac{(\text{ml. B} - \text{ml. S}) \times \text{N HCl} \times 4.2}{\text{sample wt.}}$$

B = blank titration

S = sample titration

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[4] Adogens and Adols, Archer-Daniels-Midland Company.

TABLE II

Starting Materials. Fatty Alcohols and Amines[a]

Compound	MP, °C.[b]	BP, °C.	Purity by Chromatography[c, d]
Octanol-1	......	194–195	99+% C_8
Decanol-1	......	119–120/12 mm.	99.5+% C_{10}
Dodecanol-1	......	132.5–133.5/9.5 mm.	99.5+% C_{12}
Tetradecanol-1	37.0	172/20 mm.	99.5+% C_{14}
Hexadecanol-1	49.2	162–162.5/2.7 mm.	99.5+% C_{16}
Octadecanol-1	57.8	177/2 mm.	99.5+% C_{18}
Eicosanol-1	66.0	190/1.3 mm.	98.8% C_{20}, 1.2% C_{18}
Docosanol-1	70.0	208/1.3 mm.	88.1% C_{22}, 11.9% C_{20}
n-Octyl amine	......	178–179	99+% C_8
n-Dodecyl amine	28.5	139–143/20–21 mm.	99.6% C_{12}
n-Tetradecyl amine	38.0	96/0.15 mm.	98.0% C_{14}
n-Hexadecyl amine	47.0	157/4 mm.	97.6% C_{16}, 2.4% C_{18}
n-Octadecyl amine	53.5	139/0.2 mm.	99.0% C_{18}, 1.0% C_{16}
n-Eicosyl amine	58.5	180/1.5 mm.	89.9% C_{20}, 3.7% C_{22}, 4.8% C_{18}[e]
n-Docosyl amine	64.5	200/1.5 mm.	85.4% C_{22}, 14.6% C_{20}

[a] Infrared and other analytical data indicated these materials to be essentially pure.

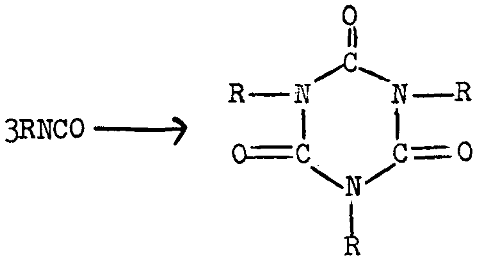
[b] Uncorrected for stem exposure.

[c] Gas-liquid chromatography method for alcohols was that of Link, W.E., *et al.*, J. Am. Oil Chemists' Soc., *36*, 300–303 (1959).

[d] The method for amines was that of Link, W.E. *et al.*, J. Am. Oil Chemists' Soc., *37*, 364 (1960).

[e] Unidentified peaks accounted for the remainder.

It is of interest to note that, on standing, the higher isocyanates deposit a precipitate. Initially it was surmised that the precipitate which appeared in the distilled isocyanate over a period varying from several days to several weeks was caused by traces of water, which reacted with the isocyanates to form N-alkyl carbamic acids. Precipitation was still observed in redistilled isocyanates and in repeat preparations, using extreme precaution to eliminate traces of water, followed by storage of the vacuum-distilled products in sealed containers. It is postulated that the precipitate is a cyclic trimer:



The carbamic esters were made by treating freshly prepared isocyanates with alcohols. A trace of anhydrous pyridine was used as a catalyst.

General Procedure

Equimolar (0.01 m.) quantities of the isocyanate and the alcohol were heated at 90–110°C. for 4 hrs. in the presence of a trace of pyridine. The products were recrystallized from ethanol and air-dried, followed by further drying for 24 hrs. at 0.1 mm. and a temperature of 10 to 20°C. below their melting points. Table I summarizes the melting points of the carbamates as determined by the capillary method.

The urethanes were checked for thixotropic behavior by heating the given compound in various solvents until solution occurred and cooling to room temperature. The thixotropic effect was then noted.

Discussion

The melting points of most classes of fatty compounds containing an even number of carbon atoms in the alkyl chain fall on ascending curves. Examples of such behavior are the fatty alcohols (3,4), fatty acids (3,4), fatty amines (4), thiol esters of long-chain fatty acids (5), etc.

In general, the melting points of the fatty urethanes are dependent not only on the number of carbon atoms in the molecule but also on the symmetry of the moiety. In an homologous series, in which the alkyl chains contain an even number of carbon atoms, the melting points increase with the number of carbon atoms. When symmetry is reached, there is a marked increase in the melting point. After this the increase is less pronounced. Figure 1 compares the melting points of alkyl carbamates with several fatty derivatives which show the normal ascending melting behavior. Figure 2 compares the melting points of tetradecyl and hexadecyl esters of N-substituted carbamic acid against the number of carbon atoms in the N-alkyl group. It can be seen that the melting points in each homologous series increase gradually until symmetry is reached. At this point the melting point rises markedly. The next two members of the homologous series have melting points very close to that of the symmetrical urethane. The melting points again rise gradually with the increase in the number of carbon atoms. Similar curves were obtained for other carbamates. The octyl esters apparently do not follow this pattern.

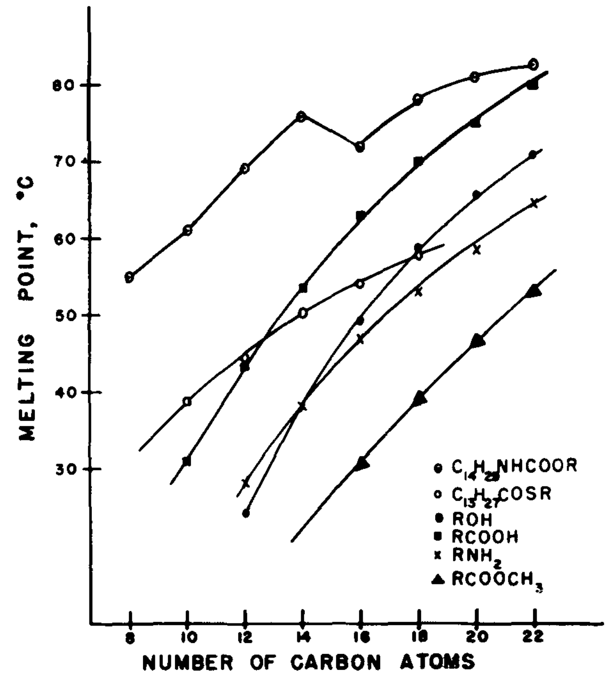


Fig. 1. Melting-point curves for several classes of fatty derivatives.

Figure 3 compares the melting points of alkyl tetradecyl and hexadecyl carbamates against the number of carbon atoms in the O-alkyl group. In this case there is also an increase in melting points with an increase in the number of carbon atoms until symmetry is reached. The next member has a lower melting-point than the symmetrical urethane. The melting points resume their gradual rise with the increase in the number of carbon atoms. Similar curves

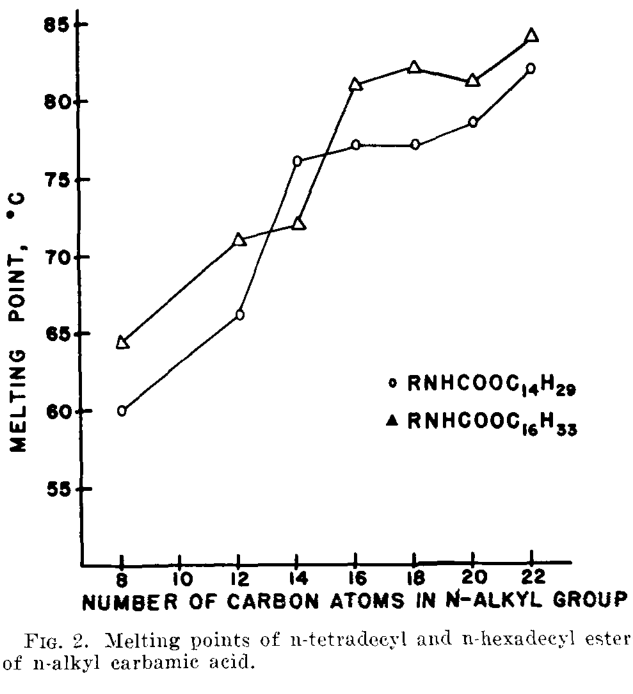


Fig. 2. Melting points of n-tetradecyl and n-hexadecyl esters of n-alkyl carbamic acid.

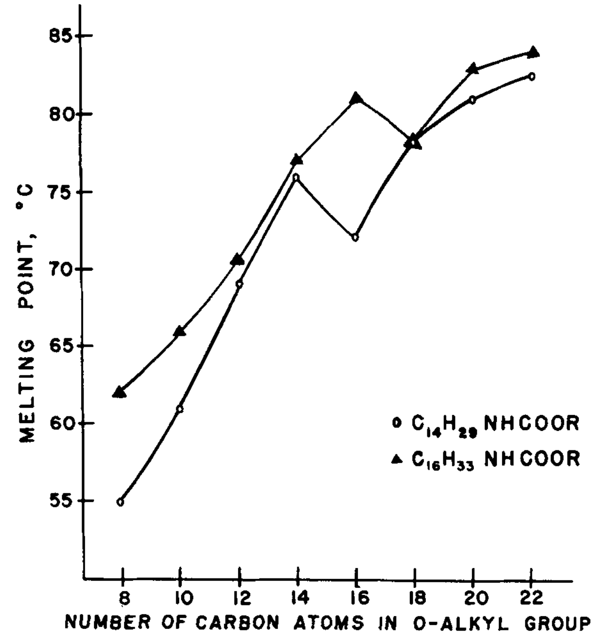


FIG. 3. Melting points of alkyl esters of N-n-tetradecyl and N-n-hexadecyl carbamic acid.

with transition points at symmetry were obtained for the other carbamates.

The urethanes give thixotropic liquids or nonflowing gels with soybean oil, solvent-thinned vehicles, ethanol, and other similar materials at concentrations as low as 0.5%. Better-defined crystal structure and poorer thixotropic properties were observed with an increase in symmetry. Best thixotropic behavior is observed when the N-alkyl group differs from the O-alkyl by 4 to 8 carbon atoms. For example, in the eicosyl series of N-alkyl carbamates the best thixotropic properties were observed when the N-alkyl group contained 14 to 16 carbon atoms.

It would be interesting to examine other fatty derivatives to determine whether a similar peaking at point of symmetry is observed. Systems which might demonstrate similar properties include N-alkyl fatty amides, N-N-dialkyl fatty amides, symmetrical and unsymmetrical disubstituted ureas, etc. There is scattered melting-point information available in the technical literature for several different classes of compounds, but questionable purity of the materials or paucity of data makes analyses of the information difficult. Possibly even simple alkyl esters might show such behavior, but again the literature information on compounds of known purity is inadequate for evaluation.

Acknowledgment

The authors wish to acknowledge the cooperation of the Analytical Section of the Archer-Daniels-Midland Company Research Laboratory, especially to W.E. Link, W.F. McKusick, and R.A. Morrissette, in the analysis of compounds and products used in this study.

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[Received October 12, 1959]

Hydrogenation of Linolenate. II. Hydrazine Reduction[1]

C.R. SCHOLFIELD, E.P. JONES, JANINA NOWAKOWSKA, E. SELKE, and H.J. DUTTON,
Northern Regional Research Laboratory,[2] Peoria, Illinois

Observations by Aylward and Rao that hydrazine is a reducing agent for a number of unsaturated fatty acids were extended. The hydrazine reaction on linolenic acid was followed by periodic sampling until methyl esters prepared from the reduced acids had an iodine value of 162. These esters were shown by countercurrent distribution to consist of 26% triene, 43% diene, 26% monoene, and 5% stearate and by infrared analysis to contain no *trans* bonds.

Oxidation of the separated monoene and diene fractions by permanganate-periodate mixtures and gas chromatography of the dibasic acids showed that the double bonds were in the original 9, 12, and 15 positions and that the double bonds farthest from the carboxyl were reduced at a slightly faster rate. Gas chromatography of the monoene fraction indicated three components that were identified in the order of elution from the column as 9, 12, and 15 monoenes; in the diene fraction three components were identified in the order of elution as 9,12; 9,15; and 12,15 dienes. After alkali isomerization of this diene fraction, the conjugated material was reacted with maleic anhydride; the unreacted 9,15 diene isomer was separated by distillation.

THE REDUCTION of a number of unsaturated fatty acids with hydrazine has been described by Aylward and Rao (1–6). Their earlier work on the hydrazine reaction is summarized in their first paper. A detailed study of the reduction of linolenic acid seemed pertinent to research on the selective hydrogenation of linolenates (7) for two reasons.

First, catalytic hydrogenation of methyl linolenate produces a complex mixture of *cis* and *trans* monoene and diene isomers with widely different double bond locations. In work at this laboratory nine monoenes and four diene components were separated by gas chromatography (7). By contrast the all *cis* product of hydrazine reduction might be expected to provide a relatively simple mixture for the characterization and identification of the all *cis* monoenes and dienes present and thereby afford some insight into the composition of more complicated mixtures from catalytic reduction.

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[1] Presented at fall meeting, American Oil Chemists' Society, New York, October 17–19, 1960.

[2] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.