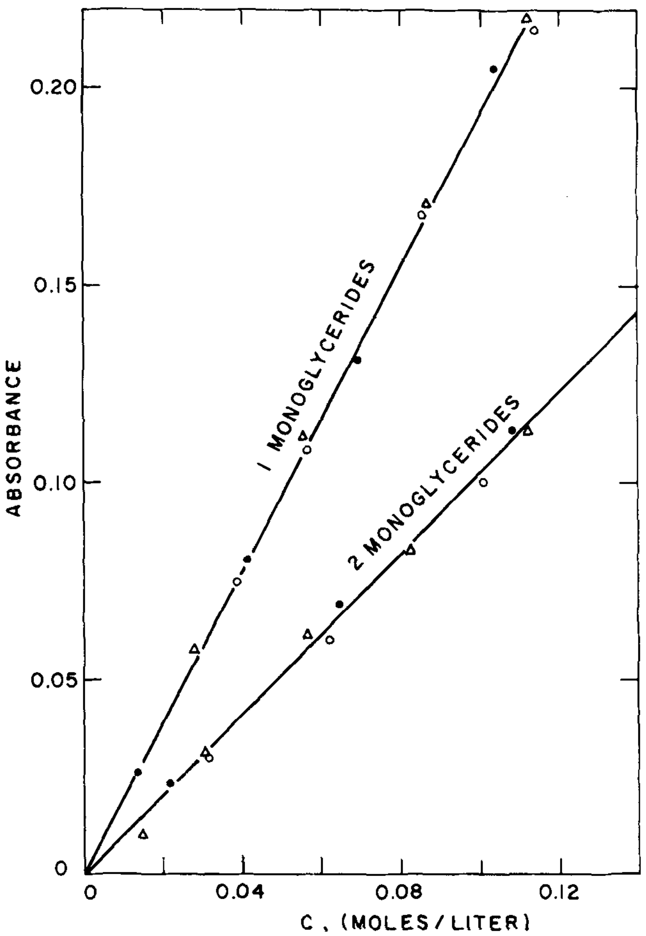

FIG. 4. Absorbance of 1-monoglycerides and 2-monoglycerides at 1.430 microns as a function of concentration. Open circles—monopalmitins; closed circles—monostearins; triangles—monooleins.

A is the total absorbance; c_1 and c_2 are the molar concentrations of 1-monoglycerides and 2-monoglycerides; k_1 and k_2 are the molar absorptivities of 1-monoglycerides and 2-monoglycerides; b is the path length in cm. Rearrangement and substitution yields:

$$(3)\quad \%\ \text{monoglyceride} = (c_1/c)\ 100 = (A - ck_2\,b)\ 100/(k_1 - k_2)\ bc$$

Figure 4 leads to $k_1 = 0.39$ and $k_2 = 0.20$. The path length, b, was 5.0 cm.

TABLE I

Known and Computed Composition of Mixtures of 1- and 2-Monoglycerides

Glyceride mixture	Total concentration (moles/liter)	Known amount of 1-monoglyceride (%)	Amount of 1-monoglyceride by eq. (3) (%)
1- and 2-monostearin...........	0.1093	26.8	23.2
	0.1073	47.8	48.1
	0.1052	69.8	73.0
1- and 2-monopalmitin.........	0.1110	16.4	18.0
	0.1127	40.3	42.0
	0.1139	57.6	57.2
	0.1154	78.9	79.6

Table 1 presents composition data calculated by equation (3) for mixtures of 1- and 2-monopalmitins and 1- and 2-monostearins of known composition. The agreement between the known composition and the spectroscopically measured composition is seen to be within a few per cent. This represents good agreement, considering the small absorbance differences between the two classes of compounds. The computed data are more exact than could be expected from measurements in the fundamental infrared region and approach the accuracy attainable in the ultraviolet region on samples with comparable differences in absorbance. While the procedure is not suitable for trace analysis, it constitutes a rapid method for rather accurate estimation of the abundance of position isomers in mixtures of 1- and 2-monoglycerides.

Acknowledgment

The authors wish to express their gratitude to Sherman S. Pazner, who performed many of the spectroscopic measurements.

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The Effect of trans-Isomers on the Physical Properties of Hydrogenated Oils

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Data have been presented which indicate a positive relationship between the *trans*-isomer content of a hydrogenated oil and the congeal point, Wiley melting-point, and solids index. It has also been shown that cottonseed oil and soybean oil undergo substantially the same type of reaction under identical hydrogenating conditions. This conclusion is based on the relationship of *trans*-isomer formation to total reduction in unsaturation up to the point that equilibrium is reached and saturation of the *trans*-isomers occurs. This equilibrium was noted at between 60–70 iodine value.

The relationship of *trans*-isomer formation to the total reduction in double bonds can be expressed as the hydrogenation index. This is a reliable indication of the type of reaction taking place up to the point where appreciable hydrogenation of the *trans*-isomers occur.

THE LITERATURE contains many references to the hydrogenation reaction as applied to hydrogenating vegetable oils for use in shortening and margarine. Bailey (1) gives an excellent summary of the background work prior to 1951, and a number of investigators including Sims (2), Allen and Kiess

TABLE I

Hydrogenation of Cottonseed Oil.
Effect of *trans*-Isomers on Congeal and Wiley Melting-Point

Pressure and temperature	90 I.V.			80 I.V.			70 I.V.			60 I.V.		
	% *trans*	°C. Cong.	°C. WMP	% *trans*	°C. Cong.	°C. WMP	% *trans*	°C. Cong.	°C. WMP	% *trans*	°C. Cong.	°C. WMP
10 p.s.i.												
260°F.	7.6	21.5	34.8	12.5	26.0	39.0	16.8	31.0	42.5	20.5	36.5	45.6
340°F.	10.4	20.0	31.7	17.8	24.0	35.0	24.0	29.0	38.2	29.5	34.5	41.0
485°F.	12.8	Soft	31.0	21.8	23.0	34.0	29.0	27.0	37.0	34.5	32.0	39.5
40 p.s.i.												
260°F.	6.9	23.0	34.8	11.3	26.5	38.5	15.0	30.5	43.8	18.7	35.0	46.5
340°F.	8.9	22.0	32.0	14.8	25.0	36.0	20.1	28.5	39.5	25.2	32.5	41.8
485°F.	12.5	20.5	30.6	21.1	23.4	34.5	28.5	26.5	37.9	34.5	30.6	40.0
70 p.s.i.												
260°F.	5.0	26.0	38.0	8.0	31.5	43.5	11.0	38.0	48.0	14.4	43.0	51.0
340°F.	7.3	23.0	33.0	12.0	28.0	39.0	16.4	33.0	43.5	20.8	40.0	47.0
485°F.	12.3	Soft	29.0	20.8	21.6	34.0	28.5	26.0	38.0	34.5	31.5	41.0

(3,4,5,6), and Eldib and Albright (7) have materially increased our knowledge in this field. In the present study the authors have employed analytical tools not available to previous investigators and, as a result, were able to develop information on the effect of *trans*-isomers on the physical properties of hydrogenated oils, which materially aids in determining the type and degree of hydrogenation required for a specific finished product.

Experimental Procedure and Data

Refined cottonseed oil (109.0 I.V.) and refined soybean oil (133.6 I.V.) were hydrogenated at 10, 40, and 70 p.s.i. hydrogen pressure and at temperatures of 260°F., 340°F., and 485°F.; a total of nine hydrogenations were made on each oil. Hydrogen pressures were controlled by means of an automatic reducing-valve, and temperatures were controlled manually to within a few degrees of the primary temperature desired, usually ±10°F.

The hydrogenating vessel used was a one-gallon black iron converter equipped with a constant-speed agitator. A reduced nickel formate catalyst was used at a level of 0.04% nickel in all tests. The hydrogenating system employed is commonly known as a "dead-end" system since vacuum was used to evacuate the hydrogen from the converter when desired.

Hydrogenated products with iodine values of approximately 90, 80, 70, and 60 were desired from each run, and these were withdrawn, based on refractive index values as determined with a Bausch and Lomb, Abbe type of refractometer at 45°C.

All samples were analyzed for iodine value, congeal point, Wiley melting-point, and dilatometric solids index. A.O.C.S. methods were employed with the exception of congeal point, for which a method under consideration by the Fat Analysis Committee was selected. *Trans*-isomer content was determined by use of an infrared spectrophotometer with tri-elaidin as a primary standard.

Since it was obviously not possible to hydrogenate the samples to the exact iodine value desired, each series of analytical data was plotted and then cross-plotted to develop a family of curves, from which comparative information at 90, 80, 70, and 60 iodine value was interpolated to arrive at the conclusions reported in this paper.

In Table I the effect of a variation in temperature and pressure on the formation of *trans*-isomers during the hydrogenation of cottonseed oil is shown, as is also the effect of *trans*-isomers on the congeal point and Wiley melting-point.

These data are presented graphically in Figures 1 and 2.

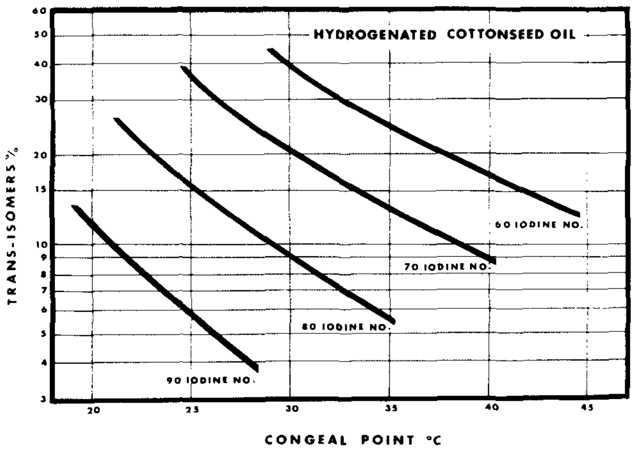

FIG. 1.

TABLE II

Hydrogenation of Soybean Oil.
Effect of *trans*-Isomers on Congeal and Wiley Melting-Point

Pressure and temperature	90 I.V.			80 I.V.			70 I.V.			60 I.V.		
	% *trans*	°C. Cong.	°C. WMP	% *trans*	°C. Cong.	°C. WMP	% *trans*	°C. Cong.	°C. WMP	% *trans*	°C. Cong.	°C. WMP
10 p.s.i.												
260°F.	17.6	32.0	45.0	22.0	37.5	48.0	26.0	42.0	52.0	28.0	46.0	55.0
340°F.	24.8	21.0	32.0	32.0	26.2	37.0	38.5	32.5	42.0	43.0	40.0	49.0
485°F.	34.5	Soft	28.0	48.0	23.5	33.0	54.0	30.0	38.5	50.0	38.0	46.5
40 p.s.i.												
260°F.	15.0	31.0	48.0	18.8	36.0	51.0	22.4	42.0	54.0	25.5	47.0	57.0
340°F.	22.0	22.0	36.0	28.0	28.0	39.5	34.0	34.0	44.0	36.0	42.0	50.0
485°F.	34.5	Soft	27.5	46.0	Soft	32.5	53.0	29.0	39.0	46.0	38.0	47.0
70 p.s.i.												
260°F.	10.6	43.0	52.0	13.5	46.0	55.0	16.4	49.0	56.5	19.0	52.0	58.0
340°F.	21.0	26.0	42.0	30.5	31.0	45.0	38.0	36.5	48.0	35.0	42.0	53.0
485°F.	31.5	Soft	28.0	44.0	Soft	32.5	52.0	30.0	38.0	45.0	37.0	46.0

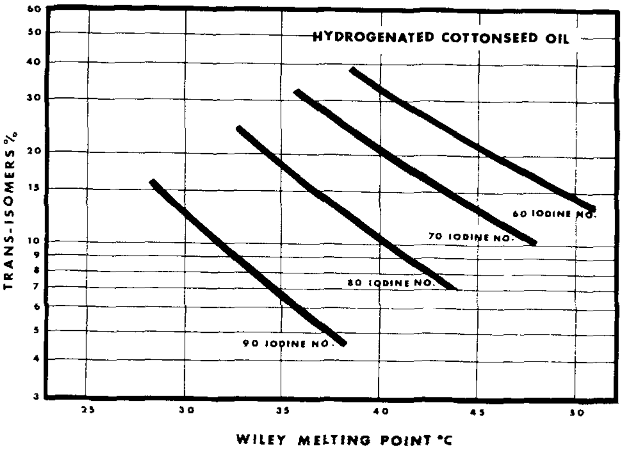

Fig. 2.

These figures illustrate very clearly the effect of *trans*-isomers on congeal point and Wiley melting-point and show that, as the *trans*-isomer content is increased, a reduction in congeal point and Wiley melting-point occurs for a given iodine value.

In Table II data on the hydrogenation of soybean oil comparable to that reported in Table I for cottonseed oil are given.

In Table III the effect of *trans*-isomer content on the solids index of cottonseed oil is shown.

Figures 3 and 4 illustrate these data for 70 and 80 iodine value hydrogenated cottonseed oils. In a like manner Table IV and Figures 5 and 6 show the results obtained with soybean oil.

Both cottonseed oil and soybean oil show very similar patterns in which increased *trans*-isomer content at any given iodine value results in a materially lower solids index (saturated acid content) at 33.3°C. and 40.0°C.

Discussion

In obtaining the data outlined in this report, extreme care was taken to maintain conditions as constant as possible with the exception of the single variable under study. Reactions were carried out at constant pressure and at varying temperatures, and *vice versa* the temperature was held constant, and the pressure was varied. Soybean oil and cottonseed oil were investigated under identical conditions, thus providing information on the effect of hydrogenating oils with different degrees and types of unsaturation.

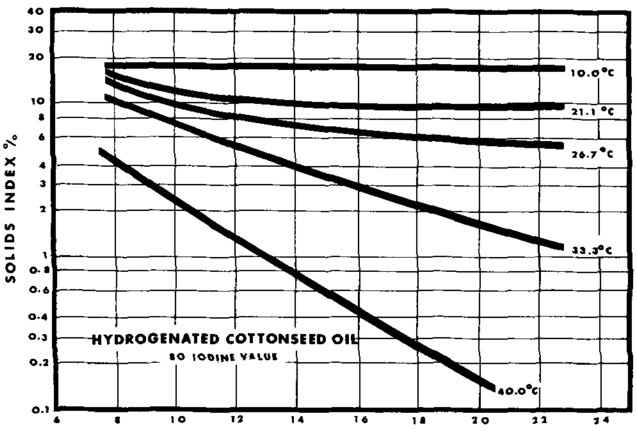

Fig. 3.

TABLE III

Hydrogenation of Cottonseed Oil.
Effect of *trans*-Isomer Content on Solids Index

	% *trans*	Solids Index, Percentage of Solids at				
		10.0°C.	21.1°C.	26.7°C.	33.3°C.	40.0°C.
a) 90 Iodine Value						
10 p.s.i.						
260°F.	7.6	9.0	5.1	4.4	2.1	Nil
340°F.	10.4	9.0	4.3	3.3	0.8	Nil
485°F.	12.8	9.0	4.3	2.7	0.3	Nil
40 p.s.i.						
260°F.	6.9	9.8	6.0	4.3	2.0	0.25
340°F.	8.9	9.8	4.4	2.9	0.8	Nil
485°F.	12.5	9.8	4.4	2.4	0.2	Nil
70 p.s.i.						
260°F.	5.0	10.0	8.7	7.4	5.3	1.5
340°F.	7.3	10.0	7.0	4.8	2.1	0.35
485°F.	12.3	10.0	4.6	2.4	0.1	Nil
b) 80 Iodine Value						
10 p.s.i.						
260°F.	12.5	18.4	11.0	9.4	5.4	0.5
340°F.	17.8	18.4	9.5	7.5	2.7	Nil
485°F.	21.8	18.4	9.5	6.3	1.5	Nil
40 p.s.i.						
260°F.	11.3	17.5	12.0	9.8	5.8	1.2
340°F.	14.8	17.5	9.5	7.0	2.7	Nil
485°F.	21.1	17.5	9.5	6.2	1.5	Nil
70 p.s.i.						
260°F.	8.0	18.5	15.3	14.0	10.8	4.8
340°F.	12.0	18.5	13.0	10.2	5.8	1.5
485°F.	20.8	18.5	9.5	6.2	1.5	0.2
c) 70 Iodine Value						
10 p.s.i.						
260°F.	16.8	31.0	20.0	18.0	11.4	3.3
340°F.	24.0	31.0	18.0	15.5	7.0	0.1
485°F.	29.0	31.0	18.0	13.5	5.2	Nil
40 p.s.i.						
260°F.	15.0	28.0	21.4	18.2	12.0	4.0
340°F.	20.1	28.0	18.3	13.8	7.0	1.0
485°F.	28.5	28.0	18.3	12.5	5.2	Nil
70 p.s.i.						
260°F.	11.0	29.0	24.5	23.5	19.0	12.0
340°F.	16.4	29.0	21.5	18.7	13.0	5.2
485°F.	28.5	29.0	17.3	14.0	5.2	0.5
d) 60 Iodine Value						
10 p.s.i.						
260°F.	20.5	44.0	33.0	30.5	21.0	9.8
340°F.	29.5	44.0	30.0	28.0	15.0	2.9
485°F.	34.5	44.0	30.0	26.0	12.5	1.4
40 p.s.i.						
260°F.	18.7	39.0	34.0	30.4	22.0	9.6
340°F.	25.2	39.0	30.5	25.0	15.0	3.7
485°F.	34.5	39.0	30.5	23.0	13.0	1.5
70 p.s.i.						
260°F.	14.4	40.0	36.0	35.5	30.0	22.8
340°F.	20.8	40.0	33.0	31.0	25.0	14.0
485°F.	34.5	40.0	33.0	26.5	14.0	3.2

Known factors which were not included in this study were the effect of different catalysts, varying the amounts of catalyst, and agitation. Both catalyst and agitation are specific factors; thus any data obtained would apply only to a specific catalyst and/or specific piece of equipment. Other investigators, notably Eldib and Allbright (7), have reported in detail on the effect of operating factors.

It has been known for many years that the physical constants of a hydrogenated oil (congeal point, Wiley melting-point, solids index, etc.) varies over wide limits, depending upon the conditions of hydrogenation. Recently the work of Allen and Kiess (3,4,5,6) has provided us with what appears to be a valid explanation of the various types of reactions which occur during hydrogenation. Since this information is largely of theoretical interest, no attempt will be made to apply it to the interpretation of the data contained in this report. We are, though, listing below the various reactions which are known to occur during hydro-

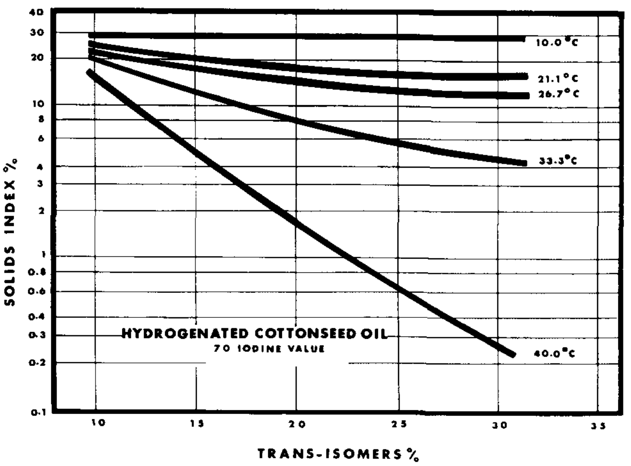

FIG. 4.

genation: a) addition of hydrogen (H_2) to an unsaturated bond to produce a saturated bond; b) geometrical isomerization at the double bond, resulting in formation of *trans* acids; and c) migration of the double bonds, which appears to take place equally in each direction, resulting in the formation of positional isomers.

All three of the above reactions appear to take place at varying rates under all conditions of hydrogenation although "nonselective" hydrogenation (high pressure-low temperature) favors reaction (1) whereas "selective" hydrogenation (low pressure-high temperature) materially accelerates reactions (2,3).

Based on the best information available, it would appear that these three reactions are controlled by two primary factors which we will refer to as hydrogen demand and hydrogen availability.

Hydrogen demand, which may be defined as the potential rate at which a fat will combine with hydrogen to form saturated bonds, appears to be mainly controlled by temperature although the amount and activity of the catalyst are known factors. However, once the activity of any given catalyst is established, control of the hydrogen demand by temperature variation is relatively simple. A third factor in determining reaction rate may be the amount and kind of unsaturation of the oil being hydrogenated. However evaluation of the data obtained for cottonseed and soybean oils seems to rule this out as a major factor. This will be discussed later.

The second factor controlling the course of the hydrogenation reaction appears to be hydrogen availability. This factor, for all practical purposes, is controlled by pressure since for any given hydrogenation unit the factor of mass transfer of hydrogen from the gas to the oil phase, as determined by agitation and equipment design, will stand as a constant for the particular unit.

If, as we have concluded above, the type of reaction on hydrogenation is the result of the ratio of hydrogen availability to hydrogen demand, it should therefore be possible within practical limits to establish a series of pressure-temperature relationships which would result in the same type of reaction.

In order to determine this relationship, calculations were made, based on the ratio of *trans*-isomer formation to the total iodine value reduction. These results appear in Table V and will be referred to as the hydrogen index.

The following formula was employed in these calculations:

$$\frac{\%\ \textit{trans}\text{-Isomers} \times 86}{\text{Original oil I.V.-hydrogenated oil I.V.}} \times 100 = \text{hydrogenation index}$$

Since the *trans*-isomer results are reported as percentage of tri-elaidin (iodine value = 86.0), it is evident that the hydrogenation index must be defined as the percentage of double bonds isomerized to the *trans* position, per unit of double-bond reduction.

From Table V it is evident that a series of pressure-temperature relationships exist which will result in the same type of reaction (hydrogenation index).

It is also significant that a comparison of the hydrogenation indices of hydrogenated cottonseed oil and soybean oil for the same pressure-temperature relationships (Table V) indicates a close similarity in the type of reaction which occurs. This leads to the conclusion that the degree of unsaturation of an oil is or at least the differences in unsaturation between soybean oil and cottonseed oil are not a major factor

TABLE IV

Hydrogenation of Soybean Oil.
Effect of *trans*-Isomer Content on Solids Index

	% *trans*	Solids Index, Percentage of Solids at				
		10.0°C.	21.1°C.	26.7°C.	33.3°C.	40.0°C.
a) 90 Iodine Value						
10 p.s.i.						
260°F.	17.6	15.0	11.8	10.7	6.3	5.2
340°F.	24.8	13.1	5.0	2.7	0.3	Nil
485°F.	34.5	13.2	4.5	1.7	Nil	Nil
40 p.s.i.						
260°F.	15.0	17.0	13.8	13.0	9.8	6.3
340°F.	22.0	15.0	7.2	5.5	2.0	0.1
485°F.	34.5	14.8	5.4	2.3	0.1	Nil
70 p.s.i.						
260°F.	10.6	21.8	21.3	20.5	18.5	16.8
340°F.	21.0	19.0	10.6	9.7	4.7	1.3
485°F.	31.5	15.2	5.8	3.7	0.3	Nil
b) 80 Iodine Value						
10 p.s.i.						
260°F.	22.0	22.0	18.7	17.2	12.0	9.1
340°F.	32.0	22.5	11.7	7.9	2.3	0.1
485°F.	48.0	25.5	14.8	10.0	1.2	Nil
40 p.s.i.						
260°F.	18.8	25.0	21.0	20.5	17.0	12.0
340°F.	28.0	24.0	14.0	12.0	5.6	1.1
485°F.	46.0	26.0	13.0	7.6	1.5	Nil
70 p.s.i.						
260°F.	13.5	28.0	26.2	25.5	24.0	22.0
340°F.	30.5	27.5	19.0	17.5	9.5	3.4
485°F.	44.0	24.0	13.0	10.0	1.8	0.1
c) 70 Iodine Value						
10 p.s.i.						
260°F.	26.0	31.5	28.0	26.4	20.8	15.6
340°F.	38.5	35.0	24.6	20.7	11.0	3.2
485°F.	54.0	40.5	31.0	26.4	9.0	0.6
40 p.s.i.						
260°F.	22.4	34.0	30.0	29.0	26.4	20.0
340°F.	34.0	35.0	28.4	23.0	14.6	5.7
485°F.	53.0	39.5	25.5	19.4	9.7	0.8
70 p.s.i.						
260°F.	16.4	34.5	32.0	31.0	30.0	28.0
340°F.	38.0	36.0	29.4	28.0	18.0	9.3
485°F.	52.0	37.0	26.0	22.0	9.3	1.0
d) 60 Iodine Value						
10 p.s.i.						
260°F.	28.0	45.0	39.0	37.0	32.0	25.0
340°F.	43.0	51.0	44.0	41.5	33.0	17.5
485°F.	50.0	57.0	51.0	48.0	35.5	13.8
40 p.s.i.						
260°F.	25.5	45.0	39.5	38.0	36.5	30.0
340°F.	36.0	48.0	42.0	38.0	33.0	19.5
485°F.	46.0	56.0	50.0	40.5	34.0	10.8
70 p.s.i.						
260°F.	19.0	42.0	38.0	37.0	36.0	35.0
340°F.	35.0	48.0	42.0	40.0	31.0	21.5
485°F.	45.0	53.0	44.5	40.0	29.0	10.4

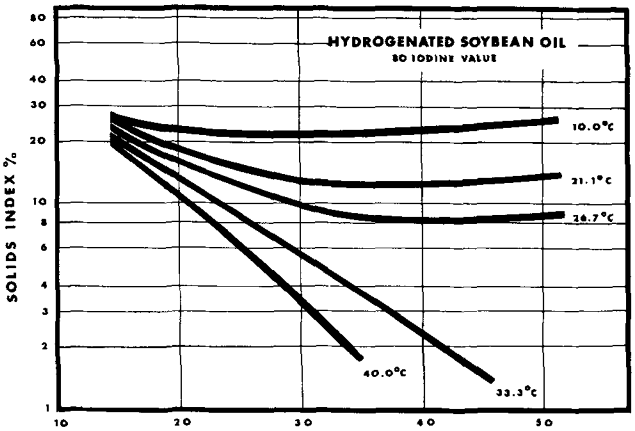

FIG. 5.

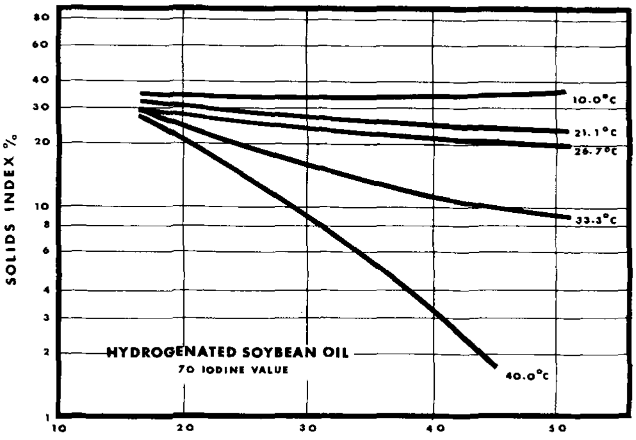

FIG. 6.

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.

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

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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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