2. Molecular weight increases progressively more rapidly for a given extent of a bifunctional or higher order polymeric addition reaction, as the extent of reaction increases.
3. Methods of measurement of extent of reaction of polyunsaturated acids such as by iodine number, polybromide number, and spectral analysis become less accurate as the extent of reaction increases, giving lower than true values, due to interference by trans double bonded isomers and by cyclic monomers.

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Summary

1. Linseed oil has been polymerized at 300° for 1.5, 3, and 6 hours. The polymeric glycerides have been separated from the monomeric glycerides, and the derived methyl esters of each fraction have been analyzed for monomer, dimer, and trimer.

2. The monomeric glycerides show very little intradimerization, ranging from 1.3 to 6% of their acid groups, or 3 to 4% of the total polymeric acid groups in the whole oil.

3. The polymeric glycerides show appreciable intradimerization, from 10 to 20% of their total polymeric acid groups.

4. There is no evidence that a shift from intra- to interdimerization is the major cause of the sudden increase in viscosity in the later stages of thermal polymerization.

5. The rapid rise in viscosity is due to the nature of the relationship of viscosity to molecular weight and of molecular weight to extent of reaction in the difunctional polymerization system present.

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Effects of High Temperature Storage Upon Lard as a Raw Material for Shortening Manufacture[1]

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IT is well known that the meat food fats, in contrast to the vegetable oils, contain a minimum of natural antioxidants (1, 2). As a result, prior to the development of the use of phenolic antioxidants (3, 4, 5, 6), lard was low in keeping quality. Therefore it was of interest to study the effect of storing lard upon its quality as a raw material for the manufacture of stabilized shortenings.

It is known that lard develops strong flavors during aging. We have found in some cases that samples with peroxide values near 20 me./kg. (7, 8) were considered objectionable by panel members.[2] Analytically, the only other difference between fresh and rancid samples noted was an increase in the percentage of conjugated dienes.

Colors of the aged lards after deodorization were found to be considerably darker than those of the fresh, and the flavor stabilities of the former were poorer. Stabilization with synergistic combinations of antioxidants was not fully effective in preventing the development of peroxides in the aged, deodorized lards. Consequently the fresh, deodorized, and stabilized lards had higher A.O.M.'s.

Partial hydrogenation did not stabilize the aged lards nearly as markedly as the fresh lards. The former had darker colors, lower A.O.M.'s and poorer flavor stabilities.

Each experiment described here was repeated at least twice, and in some cases three or four tests were run to establish with certainty that the results could be reproduced. Although data from only one representative series of tests are reported here, the same trends with respect to color, A.O.M., and flavor stability were observed each time a test was repeated.

Experimental

A 200-lb. sample of prime steam lard was centrifuged, using a laboratory model Sharples centrifuge to remove suspended solids and excess moisture. Then 100 lbs. of this lard were stored at −22°C.(−8°F.) to retard deterioration.

The remaining 100 lbs. were aged at 35°C.(95°F.) in a covered can until its peroxide value had increased from an initial figure of 2.0 to 10.0 me./kg. This re-

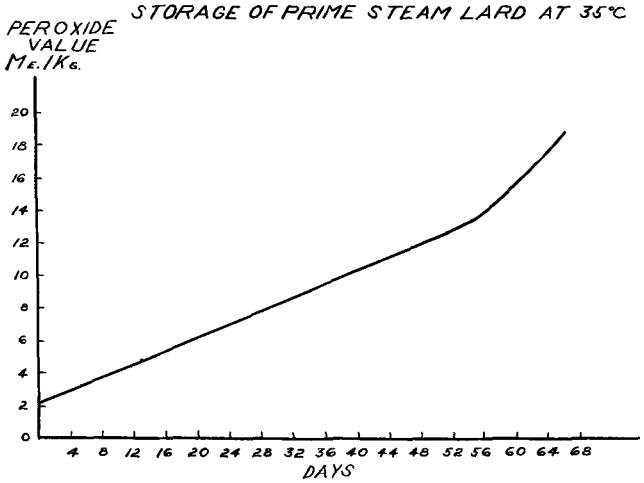
[1] Presented at the 27th annual fall meeting, American Oil Chemists' Society, Nov. 2-4, 1953, in Chicago, Ill.
[2] Lard with a peroxide value of 20 or greater is considered rancid.

quired a period of 42 days. Further storage at 95°F. increased this to 19.7 in a total of 65 days. (See Graph I and Table I.)

It is noted that, after 65 days at —22°C., the fresh lard had increased in peroxide value only by 0.3 unit, from 2.0 me./kg. to 2.3. None of the other analytical

GRAPH I

STORAGE OF PRIME STEAM LARD AT 35°C



constants showed any significant change during this period at —22°. After it had been melted for sampling, it was returned to storage at —22°C. and was held there for an additional 28 days. By this time its peroxide value had reached 4.6 me./kg. Deterioration of the partially oxidized samples (P.V.'s 10.0 and 19.7 me./kg.) could not be arrested even at this low temperature. When they had been sampled (after 42 and 65 days at 95°F., respectively), they were also returned to storage at —22°C. They continued to oxidize rapidly, reaching peroxide values of 21.2 and 36.8 me./kg., respectively, after 28 days at this temperature.

TABLE I

Analyses of Stored Lard

	65 days (—8°F.)	42 days (95°F.)	65 days (95°F.)
Peroxide Value (me./kg.) (7, 8)	2.3	10.0	19.7
Moisture (%)[1]	0.04	0.10	0.01
Free Fatty Acids (%)[2]	0.48	0.54	0.54
Iodine Value[3]	66.5	66.7	66.6
Melting Point (F.A.C.)[4] °F	112	111	113
Softening Point (F.A.C.)[4] °F	86	86	86
Lovibond Color[5]	7Y-1.0R	7Y-1.3R	7Y-1.0R
A.O.M. (hours)[6]	3	....	....
Linoleic (%)[7]	9.0	9.3	9.2
Linolenic (%)[7]	0.31	0.38	0.45
Arachidonic (%)[7]	0.24	0.35	0.31
Conjugated Diene (%)[7]	0.17	0.33	0.71

[1]A.O.C.S. Official Method Ea 8-50, Karl Fischer Volumetric Method.
[2]A.O.C.S. Official Method Ca 5a-40.
[3]A.O.C.S. Official Method Cd 1-25, Wijs Method.
[4]A.O.C.S. Official Methods Cc 1-25, and Cc 3-25.
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[7]A.O.C.S. Tentative Method Cd 7-48.

A. *Stability of Undeodorized Lards.* Samples 1, 2, and 3 at the three levels of oxidation mentioned above (P.V.'s 2.3, 10.0, and 19.7, respectively), were each stabilized with 0.05% by weight of a solution consisting of 20% butylated hydroxyanisole, 4% citric acid, and 6% propyl gallate in propylene glycol. The stabilized lards were then evaluated organoleptically by a panel of 10 trained tasters.

Sample	A.O.M. (hours)	Panel Median
1	41	Good
2	14	Fair
3	3	Poor

These samples were stored at 60°C.(140°F.), following the development of peroxides as shown below:

Days at 60°C.	Sample 1	Sample 2	Sample 3
	Peroxide Values (me./kg.)		
0	2.0	9.2	18.1
2	2.0	8.6	19.0
6	2.8	8.7	.....
14	2.6	8.8	.....
20	3.4	15.4	.....
30	3.8	19.4	.....

B. *Stability of Deodorized Lards.* Samples 1, 2, and 3 (P.V.'s 2.3, 10.0, and 19.7, respectively) were then deodorized with steam for five hours at 220°C. and 1 mm. pressure in all glass laboratory equipment. Each was cooled to 60°C. before admitting air. Then 0.05% of a solution of 20% butylated hydroxyanisole, 4% citric acid, and 6% propyl gallate in propylene glycol was used to stabilize each sample.

Sample	P.V. (me./kg.)	A.O.M. (hours)	Lovibond Color
1	<0.1	58	7Y 1.7R
2	<0.1	38	20Y 2.2R
3	<0.1	33	21Y 2.1R

Each sample was evaluated organoleptically by a panel of 10 trained tasters before and after aging at both 60°C.(140°F.) and 24°C.(75°F.). The scoring system used was that developed at the Northern Regional Research Laboratory (9), showing media in each case.

Days at 60°C.	Sample 1		Sample 2		Sample 3	
0	8		8		8	
1	8		8		7	
2	7		7		6	
3	7		7		6	
5	7		6		5	
Days at 24°C.	Flavor	P.V.	Flavor	P.V.	Flavor	P.V.
0	8.0	<0.1	8.0	<0.1	8.0	<0.1
14	6.0	0.4	7.0	0.5	7.0	0.7
42	7.5	0.4	7.5	0.7	8.0	1.7
76	6.5	0.7	6.0	1.2	6.0	1.9

C. *Stability of Partially Hydrogenated, Deodorized Lards.* Samples 1, 2, and 3 (P.V.'s 2.3, 10.0, and 19.7, respectively) were hydrogenated in a mechanically stirred, electrically heated, carbon steel converter of the "dead end" type. A temperature of 200°C. and a hydrogen pressure of 30 P.S.I. were used with 0.2% by weight of a commercial reduced nickel catalyst (containing about 25% Ni.). After hydrogenation each oil was cooled to 80°C. under vacuum, opened to the air, and filtered with a neutral bleaching clay and diatomaceous earth to remove nickel. Iodine values on the hardened oils are shown below:

Sample	Hydrogenation Time (min.)	Iodine Value
1	8	58.6
2	6	58.6
3	9	58.0

These oils were deodorized concurrently for five hours at 220°C. and 1-mm. pressure, treated with 0.005% citric acid, and cooled under vacuum.

Sample	A.O.M. (hours)	Lovibond Color	Flavor Panel Scores, Days at 60°C.	
			0	1
1	8	4Y 0.9R	9	8
2	10	10Y 3.0R	8	5.5
3	1	75Y 7.6R	7	5.0

The hydrogenation of samples 1 and 2 was then repeated, stabilizing the hardened, deodorized oils with 0.05% by weight of a solution of 20% butylated hydroxyanisole, 4% citric acid, and 6% propyl gallate in propylene glycol.

Sample	Hydrogenation Time (min.)	Iodine Value	P.V. me./kg.	A.O.M. (hours)	Lovibond Color
1	4	50.6	<0.1	>400	2Y 0.2R
2	4	50.7	<0.1	250	3Y 0.3R

Flavor panel scores on these two stabilized oils are shown below:

Days at 60°C.	Sample 1	Sample 2
0	9	9
1	7.5	7
2	7.5	7
3	8	7
4	8	7

D. *Rate of Hydrogenation.* No significant differences in rate were observed during the partial hydrogenations described in section C. However, when samples 1, 2, and 3 were hydrogenated to nearly complete saturation, there were considerable differences. The data below demonstrates that peroxides are active catalyst poisons.

The three lard samples were hardened at 200°C. and 30 P.S.I. of hydrogen with 0.2% by weight of a commercial reduced nickel catalyst (containing about 25% Ni.). Then they were cooled under vacuum and filtered with a neutral bleaching clay and diatomaceous earth.

Sample	Hydrogenation Time (min.)	Iodine Value	Lovibond Color
1	115	6.5	2Y 0.5R
2	165	7.0	20Y 3.2R
3	330	6.3	9Y 1.5R

Summary

Storage of lard at 95°F. with the resultant development of peroxides had a detrimental effect on its flavor. Colors of the stored lards after deodorization were considerably darker than those of the fresh, and the flavor stabilities of the former were poorer. Partial hydrogenation did not stabilize the aged lards nearly as markedly as the fresh lards. The former had darker colors, lower A.O.M.'s, and poorer flavor stabilities.

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

• Oils and Fats

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Oxidation changes in lard in the process of production. N. S. Drozdov, N. P. Materanskaya, and N. Trofimova (Moscow Chem.-Technol. Inst. Meat Ind.). *Myasnaya Ind. S. S. S. R.* 24 (4), 82-5(1953). This is principally a review and discussion of past work. The course of the acid no., peroxide no., and epihydrinaldehyde, and oxy-acid contents of 2 lards during production are graphically presented. (*C. A.* 48, 901)

l-Lysine content of some oilseed cakes. V. S. Govindarajan and B. V. Ramachandran. *J. Sci. Ind. Research, India* 11B, 477-9 (1952). The *l*-lysine content of some Indian oil seed cakes was determined by Gale's method (measuring the carbon dioxide liberated from lysine by the specific *l*-lysine decarboxylase of a strain of *Bacterium cadaveris*). Cottonseed and groundnut cakes proved to be useful sources of lysine. An exceptionally high content of lysine was found in the seed cake of papri *(Holoptelea integrifolia)*. (*Food Sci. Abs.* 25, 3392[1953])

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The determination of the fat content of cream (comparison of the modified butyrometer method with the Röse-Gottlieb method). H. Hostettler and W. Lehmann. *Proc. 13th Intern. Dairy Congr.* (The Hague) 3, 1216-21(1953). A description of a modified butyrometer method which compares well with the Röse-Gottlieb method. (*C. A.* 48, 297)

Chlorophyll for colouration of vanaspati. *Indian Forester* 72, 635(1952); *J. Sci. Ind. Research* 12A, 196(1953). A simple, inexpensive method has been developed for coloring vanaspati (hydrogenated peanut oil) with leaves of Indian plants without requiring the previous separation of chlorophyll extracts. The attractive green color is difficult to remove and can be detected even in traces spectroscopically or by a micro test for Mg.

The constitution of the polyenic acids occurring in the liver oils of cod and blue skate. E. Klenk and W. Bongard (Univ. Cologne, Germany). *Hoppe-Seyler's Z. Physiol. Chem.* 292, 51-8(1953). In order to decide whether the polyunsaturated fatty acids of fish-liver oils belong to the divinylmethane (CH: $CHCH_2CH$: CH) or the divinylethane (CH: $CHCH_2CH_2$-CH: CH) type, liver oils from cod and blue skate were submitted directly to ozonization in order to avoid isomerization by previous alkaline hydrolysis. Under these conditions 18-28% malonic and a trace of succinic acid were formed, indicating that the fish-oil fatty acids are of the divinylmethane type. The monocarboxylic acids obtained during oxidation had the following mole % composition: propionic 14.6; caproic 9.8;