The Elimination of Flavor Reversion in Linseed Shortening by Heat Polymerization and Solvent Segregation of the Oil*

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THE problem of flavor reversion in linseed shortenings has recently been reviewed by Lemon (4) and by Armstrong and McFarlane (1) who also tried to produce a more acceptable shortening by modifying the customary steps in processing and by special treatments including the use of antioxidants. Improved products were obtained, but flavor reversion was never entirely eliminated. The special treatments employed by the latter workers included attempts to bring about the isomerization of the linolenic acid, which is believed to be the constituent in linseed oil responsible for flavor reversion. For example, the oil was heated at 230° C. for 12 hours in an atmosphere of hydrogen, but the quality of the shortening obtained was not improved.

We have repeated this experiment at higher temperatures and with carbon dioxide bubbling through the oil during the heating period, thereby eliminating volatile products with an obnoxious odor. The shortening prepared from this oil does not exhibit flavor reversion. Believing that the high polymer fraction of this oil would be less nutritious or even injurious to health, we have subjected the polymerized oil to fractionation with immiscible solvents such as acetone. The acetone soluble fraction makes a most acceptable shortening. However, the quality of the shortening obtained depends on the conditions of polymerization as also does the yield of the acetone soluble oil.

The heat polymerization, solvent segregation, and hydrogenation of alkali-refined linseed oil were carefully studied, as described below, to establish the optimum conditions for the production of the highest yield of shortening of the best quality.

Methods

I.—Heat Polymerization

The heating medium is a salt mixture, composed of 55 parts potassium nitrate and 45 parts sodium nitrate, which melts at 227° C. It is contained in an enamel sauce-pan (8″ wide x 5″ deep), which is set in a shallow sand bath on a 1,000-watt, insulated hotplate. The molten salt is stirred with an electric stirrer, and temperature is controlled to within ±2° C. by a bimetallic thermoregulator connected to a 250-watt immersion heater. About 275 g. of the oil are weighed into a 500 ml. Erlenmeyer flask fitted with glass tubing connections to permit the passage of carbon dioxide through the sample. Carbon dioxide is bubbled through at a rate sufficient to agitate the oil. When the bath is at the required temperature, the flask is immersed in the bath so that when the oil has reached the bath temperature the surface will be approximately at the same level as the surface of the heating medium. This precaution is necessary to avoid the charring of volatile products on the surface of the flask, which occurs when the flask is too deeply immersed.

It requires about 30 minutes heating for the oil to reach the bath temperature. Samples, amounting to a few drops of the oil, are taken at 45-minute intervals and cooled rapidly to avoid oxidation. The refractive index of each sample is determined at 25° C. using an Abbe refractometer with the prism temperature regulated by water from a Höppler Ultra-Thermostat. At the end of the heating period the flask is raised from the bath, and the passage of carbon dioxide is continued until the oil has cooled to room temperature.

II.—Solvent Segregation

Acetone was chosen as the solvent. After experimenting with various methods of fractionation, we adopted the following procedure: The polymerized oil is poured into 1,500-1,700 ml. (six volumes) of acetone in a round-bottomed flask and the oil completely dissolved by bringing to boiling temperature on a steam bath. The solution is allowed to cool and stand overnight at room temperatures. The supernatant is decanted from the insoluble oil, the acetone distilled off, and the last traces removed under reduced pressure. Extracting the polymerized oil with acetone at room temperatures in a separatory funnel was less satisfactory because of the formation of a cloudy emulsion of oil in the extract.

III.—Hydrogenation and Deodorization

The shaker-type apparatus and the catalyst (reduced nickel on silica-gel base), and the general conditions of hydrogenation and steam deodorization are the same as employed by Armstrong and McFarlane (1). To facilitate the removal of small samples during the course of hydrogenation the reaction chamber is fitted with a piece of 4 m.m. copper tubing inserted through the stopper and with a valve on the outlet. The course of hydrogenation is indicated by the hydrogen consumption and from the refractive indices (60° C.) of samples of the filtered oil. The catalyst contains 28% nickel. At a level of 4% catalyst and a temperature of 170° C. the hydrogenation time is generally about 45 minutes. The catalyst is removed by suction filtration on paper in a Buchner funnel.

We have recently used an all-glass apparatus for steam deodorization at 180° C. and 5 mm. pressure. The process is completed within three hours. Sometimes it is necessary to refilter the oil to remove the last traces of the catalyst.

IV.—Quality of Shortening

Each sample of linseed shortening is tested by baking pie crust and judging on the basis of flavor and

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general quality as compared to samples prepared from commercial shortenings. The grading is done by a panel, usually 10 experienced judges.

Experimental

Small samples of 250-275 g. of commercial alkali-refined linseed oil were subjected to the heat polymerization process at various temperatures from 260-300° C. for periods up to 30 hours. The results presented in Figure 1 show that in the earlier stages of isothermal polymerization a linear relationship exists between the refractive index and the time of heated whereas in the later stages the reactions proceed in a stepwise manner. This is especially apparent at the lower temperatures when the reaction rate is slower.

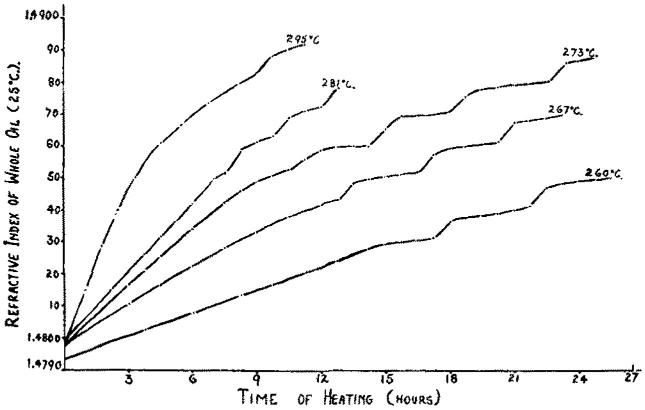

Fig. 1. Polymerization of alkali-refined linseed oil at various temperatures.

The temperature at which the polymerization process is carried out is especially important in obtaining the desired oil for the preparation of shortening. If the polymerization is carried out at temperatures above 280°C. or at temperatures so low that the period of heating is unduly prolonged, the shortenings obtained are of poor quality. Some improvement is obtained by using the acetone soluble fraction of these polymerized oils, but they still do not make good quality shortenings. *Our experience indicates that the best oil is obtained by heating at 270-275°C. for 12-15 hours. At this stage (Fig. 1) the whole oil has a refractive index of 1.4858-1.4861 and yields 60-65% of acetone soluble oil with a refractive index of 1.4830-1.4834.*

The continuous passage of carbon dioxide through the oil is an essential condition in the process as volatile decomposition products including free acids are eliminated in this manner. The product is characterized by a low acid value (0.5-1% as oleic acid) and a very pale yellow color. The color of the product is a criterion of the efficiency with which the decomposition products have been removed. The volatile products comprise about 5% of the original oil. The results obtained with nitrogen have not been as good as with carbon dioxide. If the oil is simply heated under carbon dioxide, the acid value of the product may be as high as 12% (as oleic acid), and obviously it will contain all the decomposition products. The shortenings obtained from such oils are of very poor quality.

A small portion, about 4%, of the polymerized oil is soluble in 95% methanol at room temperatures. This oil has a fishy odor and a deep brown color. It has a relatively low refractive index (1.4778 at 25° C.) and a low acid value of about 0.7%, as oleic acid. Insofar as the quality of the shortening is concerned, no apparent advantage accrues from separating this fraction prior to acetone segregation.

No special process is required for the hydrogenation; all of the commercial nickel catalysts which we have tried gave satisfactory results. The course of hydrogenation at various temperatures, as indicated by refractive indices, is illustrated in Figure 2. These results were obtained by the procedure described above and using our own catalyst, i.e. reduced nickel on silica-gel base. The best shortenings were obtained

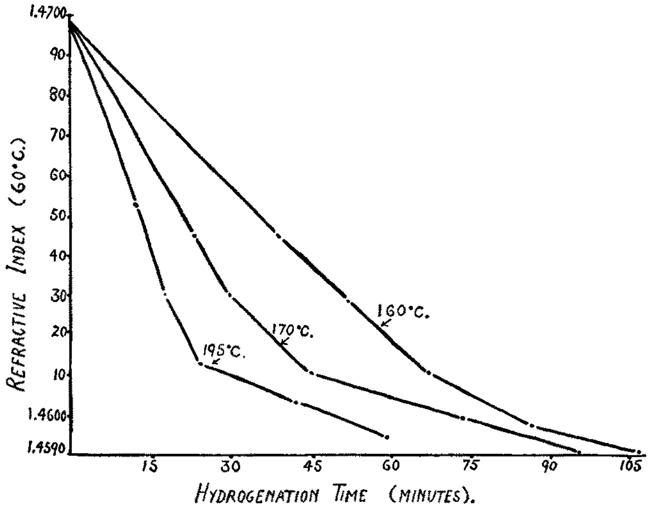

Fig. 2. Hydrogenation at various temperatures of the acetone soluble fraction of polymerized linseed oil.

TABLE I.

Summary of Experimental Data on the Processing of Linseed Oil.

(Alkali refined linseed oil, refractive index 1.4795, polymerization at 272-275°C. for 14 hours; hydrogenation at 170°C. to different refractive indices.)

Run No.	Whole oil R. index (25°C.)	Polymerized oils				Shortenings			Judgment of pastry	
		Acetone soluble		Acetone insoluble		R. index (60°C.)	Color[2]	Consistency	Flavor reversion	Grade compared to controls[4]
		Yield[1]	R. index (25°C.)	Yield[1]	R. index (25°C.)					
1	1.4859	60	1.4830	32	1.4890	1.4621	Slight yellow	Too soft	None[3]	Not as good
2	1.4860	62	1.4834	33	1.4892	1.4619	Very slight yellow	Soft	None[3]	No discernible difference
3	1.4859	63	1.4832	32	1.4889	1.4612	Pure white	Good	None[3]	No discernible difference
4	1.4858	63	1.4831	32	1.4890	1.4608	Pure white	Good	None[3]	Better than controls
5	1.4859	62	1.4830	33	1.4888	1.4604	Pure white	Slightly hard	None[3]	No discernible difference

[1] Percentage of original oil.

[2] Not decolorized with adsorbent clays nor creamed.

[3] The decision of the panel was unanimous.

[4] Two commercial samples of shortening included as standard of reference. The pastry was judged simultaneously for flavor, odor and texture by a panel of 10 judges made up of graduate dieticians, housewives, and cooks.

by hydrogenating to a refractive index of 1.4615-1.4605 (60°C.).

The data obtained in five typical runs is summarized in Table I. Preliminary trials indicate that the digestibility of these linseed shortenings, as tested with rats, compares favorably with commercial shortenings. However, further experiments are planned to assess more accurately the relative nutritive values.

The high polymer, acetone insoluble fraction comprises about 30-35% of the polymerized oil (Table I) and has a refractive index of about 1.4890 at 25° C. This should make an excellent paint and varnish oil since it represents the most highly unsaturated fraction in linseed oil.

General Discussion

The aim of this investigation has been to establish the optimum conditions of polymerization and solvent segregation of linseed oil for the production of a "non-reverting" edible shortening and an improved drying oil. The presence of linolenic acid in the edible fraction is most undesirable whereas it is obviously advantageous to have a high content in the drying oil fraction. Therefore the conditions of polymerization should be such as will permit the highest degree of selectivity in the solvent segregation.

TABLE II.

Polymerization of Linseed Oil at 295°-300°C. and Solvent Segregation With Acetone.

Time of heating	Refractive index of whole oil	Yield of acetone soluble oil	Refractive index of acetone soluble oil
hours		%	
1	1.4824	100	....
1½	35	100	....
4	59	95	1.4850
6	72	78	1.4850
8	80	60	1.4850
10	88	49	1.4850

The nature of the curves in Figure 1 indicate that the reactions involved in heat polymerization take place in a definite sequence which is most apparent in the results obtained at the lower temperatures. The theoretical implications of these results may be more apparent when data are available on the chemical composition of the oil at the various stages of polymerization. However, it is well established that conjugation precedes polymerization and that conjugate trienoic acids have a higher refractive index than their polymers (2, 3, 5). The initial rise in the refractive index suggests conjugation and the flat portions of the curves may represent a state of equilibrium where intramolecular rearrangement is taking place prior to polymer formation. One advantage of heating at the lower temperatures is that polymerized oils of uniform composition are most readily obtained since the "steady state" may persist for as long as two to three hours.

These results also suggest that the polymerization is more selective at the lower temperatures. This is supported by the observation that when two samples of linseed oil are polymerized at different temperatures but to the same refractive index, the acetone soluble fraction of the sample polymerized at the lower temperature has a lower refractive index. For example, at 272-275° C. when the refractive index of the whole oil is 1,4859, 60-65% is soluble in acetone and the refractive index of this fraction is 1.4832; whereas at 295-300° C. and at the same refractive index for the whole oil, 95% is soluble in acetone and the refractive index of this fraction is 1.4850. The latter results are included in Table II which also shows that the refractive index of the acetone soluble fraction reaches a maximum thus indicating that there is a fixed limit of polymer aggregate which is soluble in acetone.

It seems a reasonable assumption that under the conditions of polymerization employed in this process the major change in the linseed oil is in the linolenic acid component which is more readily polymerized than linoleic or oleic acid. It is not known to what extent the acetone soluble oil has undergone chemical change. However, it is probable that the linolenic acid in this fraction is at least changed to a conjugated isomer. This would account for the refractive index of the acetone soluble oil being slightly higher than that of the original linseed oil. This point is being investigated by conducting detailed analysis of the acetone soluble fraction.

Summary

The optimum conditions have been established for the high temperature polymerization and solvent segregation of linseed oil to produce a "non-reverting" edible shortening and an improved drying oil. The best oil is obtained by heating at 270-275° C. for 12-15 hours while carbon dioxide is continuously passed through the oil. Under these conditions the polymerized oil has a refractive index of 1.4858 to 1.4861 at 25° C. and yields 60-65% of acetone soluble oil with a refractive index of 1.4830 to 1.4834 at 25° C. and an acid value of less than 1%, calculated as oleic acid. Pie crusts containing shortenings made from the acetone soluble fraction of the oil have been judged to be of good quality. The best shortenings were obtained by hydrogenating to a refractive index of 1.4615-1.4605 (60° C.).

Acknowledgments

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