Characteristics of Deodorized-Polymerized Oils[1]

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POLYMERIZATION increases the flavor stability of highly unsaturated oils (10, 19), but the application of this process to food fats may be undesirable from a nutritional standpoint (4, 14, 18). Deodorization-polymerization of fish oil has been used in Germany (3) and Norway (11, 12). In the German method herring oil was alkali refined and bleached, and then deodorized at 280°-300°C. at 10-15 mm., for 8-12 hr. in an electrically heated vessel of acid-proof steel equipped with a turbine stirrer. Although the process resulted in a lowering of the iodine number and the nutritional value of the oil, the product was said to be suitable for canning sardines and other fish, and it was also used as a salad oil (3).

This paper describes the physical and chemical characteristics and the organoleptic qualities of a number of deodorized-polymerized oils.

Materials and Methods

Crude herring, linseed, weed seed screenings and rapeseed oils, and commercially refined cottonseed and peanut salad oils were used. The crude oils were alkali-refined with 10° Bé. sodium hydroxide at 60° C., then bleached with 2% Superfiltrol for 20 min., at 100°C., under nitrogen. The bleached oils (except herring) and the commercial salad oils were deodorized-polymerized at 280°C. for 1, 2, 4, 8, 14, and 20 hr., in an all-glass apparatus (16). Herring oil was treated for 10 and 20 hr. only. The treated oils were compared with the commercial salad oils as purchased, and with bleached linseed, screenings, and rapeseed oils given a standard deodorization in the same apparatus (1 hr. at 240°C.).

Measurements. Measurements included color (light transmission relative to mineral oil in the Evelyn photoelectric colorimeter) (15), kinematic viscosity (1), refractive index (2), and free fatty acid (2). Iodine values were done by the Hunter and Hyde modification of the Wijs method (9), also by the Rosenmund-Kuhnhenn method as modified by Benham and Klee for conjugated oils (13). The latter procedure was selected because polymerization in oils is considered to be preceded by conjugation (21). Stability to oxidation was determined by measurements of peroxide oxygen (6) on samples stored at 60°C. in the dark. Average molecular weights were determined cryoscopically (20) on approximately 3.5% solutions by weight of the oils in cyclohexane. As the oils were substantially neutral, no correction for presence of free fatty acids was applied.

Organoleptic Studies. Assessments were made by a 24-member panel of odor of portions of the oils heated to 200°C. for 15 min. in a rapid heat test, and of odor and flavor of doughnuts fried in other portions of the oils. Herring oils and oils treated for 14 or 20 hr. were not tested. Appraisals were scored by assigning the integers from −5 through zero to +5 to gradations of subjective reaction ranging from "gross deficiency" through "preferred level" to "gross excess" of odor or flavor (7, 8).

Hydrogenation of Polymerized Oils. Linseed control and polymerized oils were hydrogenated in a glass liner in a Parr high pressure hydrogenator. The gas volume (measured by water addition) was 380 ml. Nickel formate catalyst (1%) was added to each oil sample (26.9 g.). The system was evacuated and gradually heated, and at 140°C., hydrogen was introduced at a pressure of 70 p.s.i. gauge. Readings of pressure with time were taken. When the pressure dropped to 20 p.s.i., the hydrogen was vented and the bomb quenched in cold water. After addition of about 1% diatomaceous earth, the oil was filtered with suction through No. 2 Whatman paper.

Results

Measurements. The following general effects of increasing deodorization-polymerization were noted, and only the more important of these are illustrated:

Color—decreased initially
Viscosity—increased
Refractive index—increased
Iodine value—decreased
Free fatty acid—remained at low value (less than 0.1% as oleic)
Stability to oxidation—slightly increased for linseed, no detectable change for others
Average molecular weight—increased

The changes in color (relative transmission at 440 mμ), viscosity, refractive index, and iodine value (Wijs) are illustrated in Figure 1. Polymerization time is shown on a condensed scale to avoid crowding of points near the origin. The lines for herring oil, based on three points only, are dotted to indicate their tentative nature. The greatest changes, except for color, occurred in the more unsaturated oils (linseed, herring, and screenings); the more saturated oils (rapeseed, peanut, and cottonseed) showed marked alteration only after prolonged treatment.

The greatest change in light transmission (color) with time of polymerization occurred in rapeseed oil; the least in peanut oil. Light transmission appeared to increase to a maximum at about 8 hr. and then decrease.

Increase in viscosity was most marked for linseed oil. Values of 221.8 and 556.0 centistokes at 54.7°C. were attained in 14- and 20-hr.treatment, respectively. Viscosities for herring oil were: 0 hr., 19.8 centistokes; 10 hr., 97.3 centistokes; and 20 hr., 103.5 centistokes.

Refractive index curves for screenings and cottonseed oils varied slightly from the simpler curves for the other oils. Values for linseed oil at 8, 14, and 20 hr. were 1.4720, 1.4750, and 1.4762. Increases in refractive index were paralleled by decreases in iodine value.

Changes in average molecular weight were greatest for linseed oil (linseed oil values are shown in Table II). The molecular weights of rapeseed and cotton-

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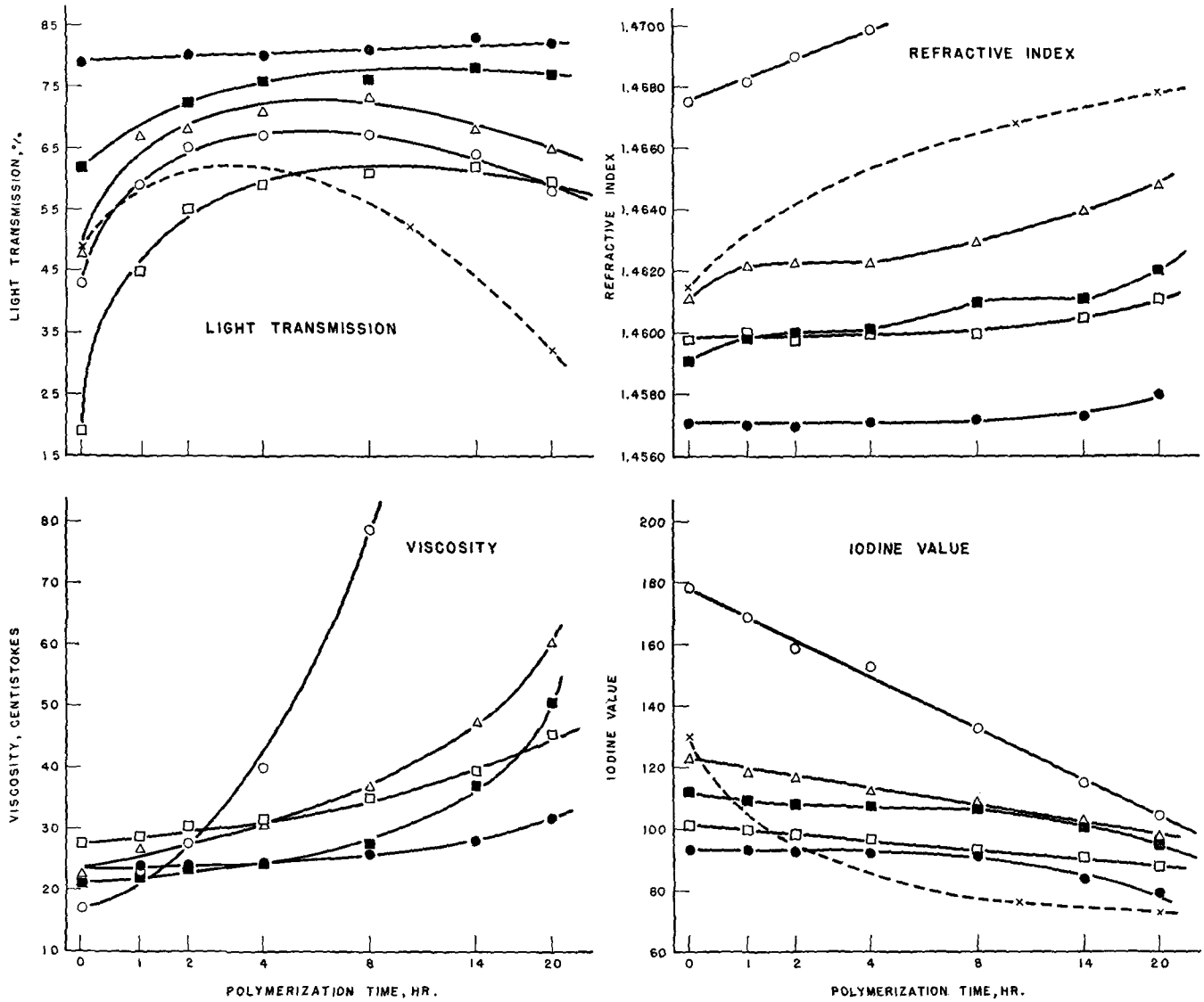

FIG. 1. Changes in light transmission, viscosity, refractive index, and iodine value of oils with increasing time of deodorization-polymerization. Light transmission, % at 440 mμ and 54.7°C. Viscosity, centistokes at 54.7°C. Refractive index, at 54.7°C.
× Herring. ○ Linseed. △ Screenings □ Rapeseed. ■ Cottonseed. ● Peanut.

seed oils increased to 1,025 and 1,125, respectively, after 20-hr. treatment. Changes in molecular weight were approximately linear.

The trap products from the deodorization-polymerization of these oils had free fatty acid contents of 60-90%, and their refractive indices and iodine values were lower than those of the original oils.

Taste Panel. On the average, the linseed control oil *per se* was rated as moderately to decidedly too strong in odor following the heat test at 200°C. (Table I). Deodorization-polymerization, particularly for 8 hr., reduced this excessive odor markedly. The average scores for both the screenings and rapeseed oil series were in agreement in indicating a perceptible reduction in strength of odor following deodorization at 4 and 8 hr. duration, but the result for screenings oil treated 1 hr. was anomalous. In the peanut and cottonseed oil series, on the other hand, no reduction in strength of odor was noted following treatments for 4 and 8 hr., and there was a slight indication of increase in odor after the 1- and 2-hr. treatments.

There was a general tendency for strength of doughnut odor to decrease with deodorization-polymerization of linseed, screenings, and rapeseed oils. None of the detected differences in odor of doughnuts fried in cottonseed and peanut oils was significant.

Linseed, screenings, and rapeseed oils normally deodorized were judged to have imparted slightly to moderately excessively strong flavors to the test doughnuts. These flavors were generally reduced by deodorization-polymerization, except for the 4-hr. treated linseed oil. Treated peanut and cottonseed oils were rated as producing uniformly bland doughnuts.

Nutritional work reported elsewhere (4) indicates that the duration of treatment (4-8 hr.) required to improve definitely the flavor stability of a reverting oil, such as linseed, may also lower the nutritive value of the oil.

Hydrogenation. Examination of changes in hydrogen pressure with time for the polymerized linseed oils by various approaches did not establish the order of the reaction. The reaction rate decreased with

TABLE I

Average Taste Panel Scores Showing Odor and Flavor Changes in Deodorized-Polymerized Oils

Test oils	Polym. 0 hr.	Polym. 1 hr.	Polym. 2 hr.	Polym. 4 hr.	Polym. 8 hr.	Nec. diff., 5% level
Odor of Oil Alone						
Linseed	+2.2	+1.5	+1.5	+0.9	+0.3	1.0
Screenings	+2.0	+0.8	+1.8	+1.1	+0.6	0.8
Rapeseed	+1.6	+1.3	+1.6	+0.6	+0.2	0.8
Peanut	+1.1	+1.7	+1.2	+1.2	+0.8	0.4
Cottonseed	+0.3	+1.2	+1.3	+0.7	+0.9	0.8
Odor of Doughnuts						
Linseed	+1.9	+1.5	+0.5	+1.5	+0.8	1.0
Screenings	+0.8	+0.2	+0.4	+0.2	0.0	0.8
Rapeseed	+0.6	+0.4	+0.6	+0.1	0.0	0.6
Peanut	+0.2	0.0	0.0	0.0	0.0	0.3
Cottonseed	+0.3	+0.2	0.0	−0.3	0.0	0.8
Flavor of Doughnuts						
Linseed	+2.5	+1.9	+.08	+1.9	+1.2	1.1
Screenings	+0.9	0.0	+0.6	0.0	0.0	0.7
Rapeseed	+1.6	+0.8	+0.6	−0.1	−0.4	1.0
Peanut	−0.1	0.0	−0.1	−0.1	−0.4	0.6
Cottonseed	0.0	0.0	+0.3	−0.3	−0.2	0.7

increasing polymerization, presumably because there were fewer double bonds, and also perhaps because of increasing unavailability of the remaining double bonds. In general, the measured rate appeared to build up to a maximum in the early stages of hydrogenation and then fall off logarithmically (Fig. 2).

Hydrogenation led to viscous oils or fats which were difficult to filter. The viscosity could be controlled by the extent of hydrogenation. The hardened 14- and 20-hr. polymerized oils were solid at room temperature, but the material tended to be amorphous without a definite melting point. According to Dittmer (5), polymerized oils first depolymerize and then hydrogenate to form the stearate. However molecular weight determinations of polymerized linseed oils before and after hydrogenation did not provide any evidence of breakdown of polymers (Table II).

TABLE II

Characteristics of Deodorized-Polymerized Linseed Oils Before and After Hydrogenation

Linseed oil	Molecular wt.		Decrease in refractive index at 54.7°C.*	Calculated decrease in iodine value (from pressure decrease)	Ratio of observed to calculated decrease in iodine value*
	Before	After			
Control	877	834	0.0050	37.8	1.18
Polym. 1 hr.	894	888	0.0047	37.1	1.16
Polym. 2 hr.	906	928	0.0050	36.5	1.11
Polym. 4 hr.	954	998	0.0049	36.0	1.16
Polym. 8 hr.	1,151	1,189	0.0048	36.4	1.10
Polym. 14 hr.	1,390	1,418	0.0050	36.5	1.11
Polym. 20 hr.	1,745	1,798	0.0049	38.3	1.13

* See Fig. 1 for values before hydrogenation.

Calculated changes in unsaturation for the hardened oils were closely paralleled by observed decreases in iodine value and refractive index (Table II). The two iodine value methods showed similar changes in the oils but gave initial and final results of differing magnitudes. This observation will be discussed in a subsequent paper (17).

Summary

Deodorization-polymerization of oils at 280°C. for times up to 20 hr. decreased iodine value and color and increased viscosity, refractive index, and mean molecular weight. Free fatty acid remained at a low

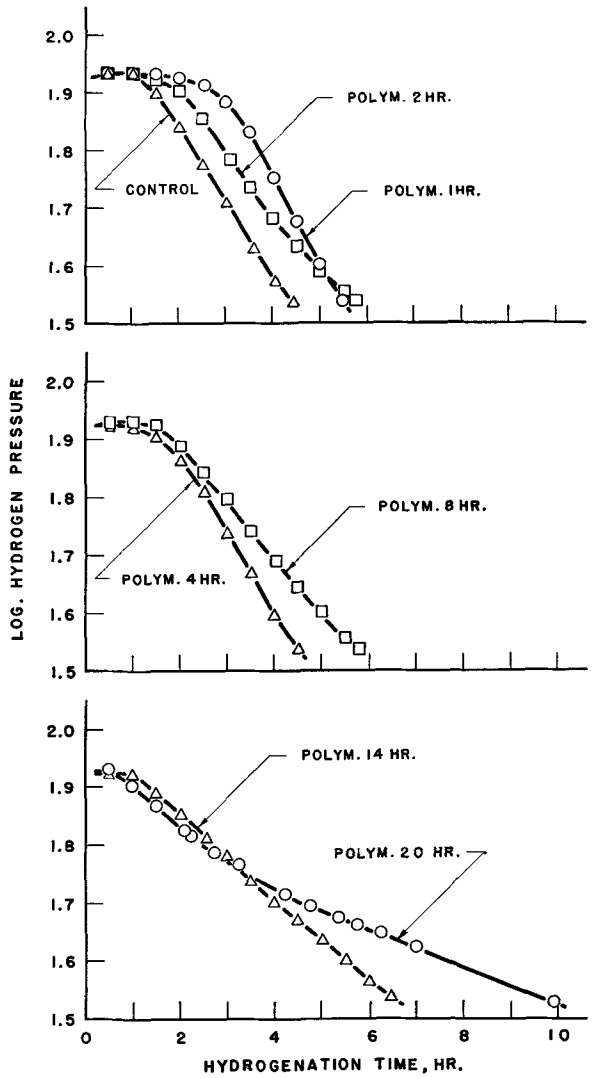

FIG. 2. Course of hydrogenation of deodorized-polymerized linseed oils at 140°C. and initial pressure at 70 p.s.i. gauge, with 1% nickel formate catalyst.

value. Stability to oxidation was increased slightly for linseed oil. Organoleptic qualities were improved for linseed, weedseed screenings, and rapeseed oils but were unchanged or slightly deteriorated for cottonseed and peanut oils.

The rate of hydrogenation of deodorized-polymerized linseed oils decreased with increased polymerization. Hydrogenation produced amorphous fats and did not appear to be accompanied by depolymerization. Calculated changes in unsaturation were paralleled by decreases in iodine value and refractive index.

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Effect of Moisture on the Rate of Solvent Extraction of Soybeans and Cottonseed Meats

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THE effect of variation in the moisture content of oil-bearing seeds upon the rate at which oil is extracted from them by solvents has not been well established. Fan, Morris, and Wakeham (2) found in the extraction of peanuts with a hexane fraction (Skellysolve-B) that an increase from 10 to 22% in the moisture content decreased the extraction rate. Measamer (3), using trichloroethylene as a solvent, found very little difference in the extraction rate of soybean flakes containing zero moisture and 10% moisture. Yates (6) reported a decrease in the amount of oil extracted in a Sohxlet apparatus from soybean flakes by trichloroethylene with an increase in moisture content from 5.63 to 27.95%. Milner (4), in a study of the method for the determination of oil in soybeans, found that the amount of oil extracted with a mixture of approximately 80% hexane and 20% pentane increased with an increase in the moisture content from 3 to 12%. The beans had no heat treatment. Bull (1) in a similar study showed the amount of oil extracted from beans with moisture contents between 8.2 and 11.4% to be practically constant with a slight increase between 11.4 and 23.4%.

In the present study two solvents were used: extraction grade of trichloroethylene and a "hexane" fraction (Skellysolve-B) having a boiling point of 146° to 157°F. Two oil seeds were used: dehulled cottonseed meats and soybeans. Cottonseed meats and cracked soybeans containing 7 to 8% moisture were heated to 160°F. in a steam-jacketed tempering screw and rolled into flakes in a set of laboratory flaking rolls. Samples of flakes from a common batch were adjusted in moisture content by adding distilled water and leaving for two days in a closed container or by drying in a desiccator. The exact moisture content was determined at the time of extraction. The soybean flakes had an average thickness of 0.011 in. and the cottonseed flakes an average thickness of 0.016 in. The equipment used for measuring extraction rates was a jacketed glass extraction tube (Fig. 1) 1 in. in diameter connected to a 110°F. constant-temperature water bath.

The extraction procedure was as follows: The extraction tube was filled with a weighed quantity of cottonseed (equivalent to 18.4 g. on dry basis) or soybean (14.4 g.) flakes. The solvent was run into the bottom of the tube at such a rate that 10 milliliters per minute overflowed at the top. The miscella produced during each 5-minute interval was collected separately. The oil content of samples taken from these miscella increments was determined by evaporating the solvent and weighing the residue. The oil content at the end of the extraction was determined by Soxhlet extraction using hexane (Skellysolve-B) as a solvent. The sum of the amounts of oil in each of the miscella increments and in the residual meal was taken as the total oil content of the sample. The oil remaining in the flake sample after 5 minutes, or a multiple of 5 minutes as desired, was calculated by subtracting the total oil extracted in the given time interval from the total original oil. This was converted into percentage by dividing by the original oil content and multiplying by 100.

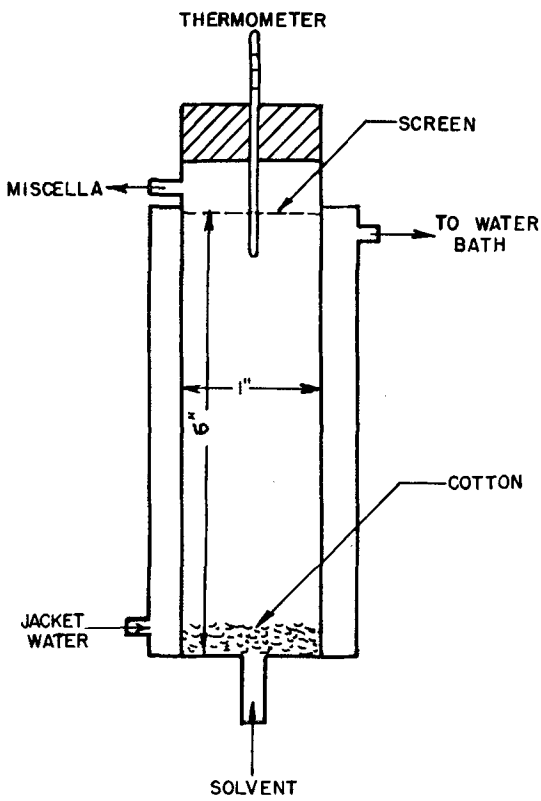

FIG. 1. Extraction rate apparatus.

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