mium oxide, molybdenum oxide, and tungsten oxide. The catalyst carrier may be alumina.

One hundred grams of linseed oil fatty acids, which had previously been distilled and freed from saturated acids by chilling and filtering, were treated with five grams of $\frac{1}{8}''$ chrome- alumina activated catalyst tablets under conditions similar to those described above. The length of time of treatment, however, was varied so as to determine the effect of time of treatment on the relative degree of conjugation obtained. The results are shown in Fig. 1, and they indicate that a reaction time of 6 hours is the optimum duration of treatment under these experimental conditions. No significant change in viscosity or color was observed.

The same catalyst and technique are directly applicable to linseed oil itself, as well as to the fatty acids. However, the direct isomerization of the oil is more difficult, and, under the same catalytic conditions, the magnitude of the effect is less for the oil than it is for the fatty acids.

Oxides of Group IV. One hundred grams of linseed oil fatty acids, which had previously been distilled and freed from saturated acids by chilling and filtering, were treated with five grams of oxides of various metals of Group IV of the Periodic System. The experimental conditions were similar to those described for the alumina catalysis. The results obtained are shown in Table 2.

TABLE 2

Isomerization of Linseed Acids by Oxides of Metals of Group IV

Catalytic Treatment	Refractive Index n_D^{25}	Molecular Refraction, M.R.
None	1.4700	83.64
Germanium dioxide, 4 hours, 250°C	1.4719 (+0.0019)	83.96 (+0.32)
Zirconium dioxide, 4 hours, 250°C	1.4727 (+0.0027)	84.06 (+0.42)
Thorium dioxide, 5 hours, 250°C	1.4742 (+0.0042)	84.27 (+0.63)

These property changes, unaccompanied by significant changes in viscosity or color, indicate in-
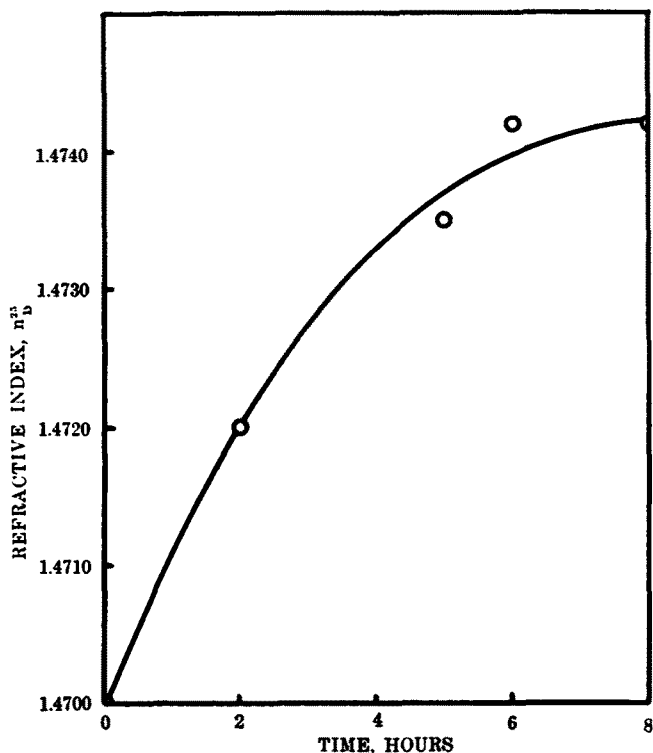

FIG. 1. Isomerization of Linseed Acids by Chrome-Alumina.

creases in the percentage of conjugated constituents, and show that, for the substances and experimental conditions employed, the catalytic effect was greater for the oxides of higher molecular weight.

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Flavour Reversion in Linseed Shortening[1]

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Introduction

THIS study was undertaken in an effort to improve hydrogenated linseed oil for use as an edible fat to help meet the shortage in Canadian supplies. Preliminary work had indicated that although a shortening of apparently good quality could be produced, the products baked with this shortening, e.g., pastry or toasted bread, had a disagreeable flavour, commonly referred to as a reverted flavour.

The term "reverted" has been commonly used to describe a group of "off" odours which develop on heating or storing certain oils. Although it suggests the return of a flavour or odour which has previously been removed, this implication is incorrect and misleading, especially in the case of linseed shortening because the flavour and odour are different from any which were present either in the crude or the refined oil or in the freshly hydrogenated shortening. It should also be pointed out that, while reversion in an oil proceeds through a succession of different odours

described by such terms as "grassy," "painty," etc., the organoleptic sensations of taste and odour associated with reverted linseed shortening seem to be unique and characteristic.

The problem of flavour reversion is not encountered with hydrogenated sunflower and cotton seed oils, so it would appear that reversion in linseed shortening must be associated either with linolenic acid which is present in linseed oil to about 40% and absent from the other oils, or with a constituent of the nonsaponifiable matter of linseed oil which is not present in the other oils. Lemon (4) first suggested that linolenic acid was the responsible constituent and has obtained spectrographic evidence to support his theory that in the hydrogenation of linseed oil the linolenic acid is saturated first at the $\triangle^{12,13}$ double bond to form an isomer of the common linoleic acid which, when heated, gives rise to the odoriferous product.

In this investigation a study has been made of the cause of flavour reversion and the possibility of producing a more acceptable shortening by modifying the customary steps in processing and by special treatments including the use of antioxidants.

Methods

REFINING

ALKALI, bisulphite and adsorbent-refining have been studied. In alkali refining, crude linseed oil was stirred rapidly at room temperature for 45 minutes with a slight excess of a 30% aqueous solution of sodium hydroxide, then stirred slowly at 65-70°C. for 30 minutes; allowed to settle overnight, and the soaps separated by filtration. In one experiment, samples of shortening were refined by carrying out the whole operation at 65°C. Samples of linseed oil were also refined with bisulphite in the same manner as in alkali refining but using 5 ml. of a 10% aqueous solution of sodium bisulphite per 100 g. of oil instead of sodium hydroxide and with less vigorous agitation to avoid emulsions. The oil was separated by decantation and filtration.

Filtrol-carbon and a silica-gel-alumina preparation developed in this laboratory, were employed as adsorbents. The silica-gel-alumina adsorbent was prepared by grinding 100 g. of silica gel[2] to pass a 100-mesh sieve and adding, with stirring, a solution containing 55 g. aluminium nitrate nonahydrate in 500 ml. of absolute ethyl alcohol. The mixture was stirred in a large evaporating dish on a steam bath to remove the alcohol, then dried in an oven at 100°C. and finally heated in a muffle furnace at 750°C. for three hours. Refining with this adsorbent was carried out by allowing about 140 g. of oil to percolate through a one-inch layer of the adsorbent in a 2½-inch Buchner funnel. The Filtrol-carbon adsorbent was a mixture of a special Filtrol and the activated carbon, Darco G-60, in the proportions of 5:1. It was added to the oil at a level of 3.6%; the mixture agitated vigorously for 30 minutes at 65-70°C. and the oil separated by filtration.

HYDROGENATION AND DEODORIZATION

The catalyst was prepared by the method of Hilditch (3) employing the dry reduction of nickel carbonate but with silica gel (100 mesh) instead of kielselguhr for the base, and reducing at about 500°C. instead of at 400-450°C. The catalyst was

stored in a small amount of hydrogenated linseed oil or Blended Shortening. It contained about 28% nickel before mixing with the fat and about 14% after mixing.

An eccentric-driven shaker-type apparatus manufactured by the Standard Calorimeter Co., East Moline, Ill., was used for hydrogenation. The reaction took place in a pyrex glass bottle of 500-ml. capacity heated by a coil of nichrome wire wound around the outside of the bottle between layers of asbestos paper and the reaction temperature was adjusted by a light-bank rheostat. A charge of 100 or 200 g. of oil was placed in the reaction bottle with the catalyst (0.5-0.6% nickel for refined oils and 1.0-1.2% for crude oils) and hydrogenated at 180°C. with a hydrogen pressure of about two atmospheres. Electrolytic hydrogen was admitted from a small storage tank and after calibrating the apparatus the course of the reaction could be followed by noting the fall in hydrogen pressure. The extent of hydrogenation was always checked by determining the iodine number of the product.

Immediately after hydrogenation, all samples were deodorized by passing a jet of steam into the shortening for three hours at 200°C. and about 5 mm. pressure. The vacuum was then released by admitting nitrogen through the steam jet, and the shortening was clarified by filtering through silica gel adsorbent or Super-Cel Standard.

ANALYTICAL PROCEDURES

Acid values were determined by the A. O. A. C. method (8) but using 5 g. samples of the oil dissolved in 15 ml. of ethyl alcohol and titrating with N/100 sodium hydroxide. The method of Rosenmund and Kuhnhenn (9) was employed to determine the iodine number with the exception that carbon tetrachloride was used to dissolve the sample and the brominating reaction time was exactly 10 minutes. Peroxide values were determined by the ferric thiocyanate method of Lips, Chapman and McFarlane (5).

FLAVOUR JUDGMENTS

FOR every sample of shortening prepared in the course of this investigation the success or failure of the process involved lay in the answer to the question, "Does it give a reverted flavour when used in baking?" Whether or not a sample would give the reverted odour on heating in an oven at 100°C. did not seem to be the real criterion of quality. Although such a test would give an indication of what was probably unsuccessful it would lack finality. Accordingly, all samples were used in baking (generally pastry) and the quality of the shortening was then ascertained by the judgments of the baked products.

Most of the samples were judged qualitatively by four or five judges, but in a number of cases a panel of ten to fifteen judges was organized to quantitatively measure the quality of a particular series of samples. In some cases the flavour and in other cases the odour of the samples was judged. In either case, two methods were employed to assign a numerical score to each sample. In the first method a ten-point scale resembling that of Wilson and Slosberg (10) was used with the points on the scale described briefly in the following manner:

10 Excellent
9 Very good
8 Good
7 Slight off flavour (odour)
6 Off flavour (odour)

} Considered suitable for household use.

5 Slight oily or reverted flavour (odour)
4 Definite oily or reverted flavour (odour)
3 Unpleasant flavour (odour)
2 Very unpleasant flavour (odour)
1 Repulsive flavour (odour)

} Considered not acceptable for household use.

Each sample in a series was scored by each of the judges. The scores for each sample were then averaged. The best score possible was thus 10 and the poorest was 1.

In the second method the judges were asked simply to indicate for each sample in flavour judgment whether or not they considered it of satisfactory flavour for household use; and in the case of odour judgments, whether or not they considered it to have a reverted (or worse) odour. Then to give a rating of the "excellence" of each sample the number of judgments declaring it satisfactory (or not reverted in odour) were added and this total divided by the number of judgments, giving scores in fractional quantities. Thus with 12 judges in a panel, a sample judged satisfactory by all judges would have a score of 12/12 = 1, and a sample judged satisfactory by 6 judges would have a score of 6/12 = 0.5. To have these scores more nearly like those obtained by the first method each was multiplied by 10, thus the two samples mentioned would receive final scores of 10 and 5 respectively. In a number of experiments it was desired to follow the progress of reversion by noting the development of the reverted odour. In these cases it was more convenient to record for each sample the percentage of the judgments which considered it reverted. It should be pointed out that both forms of this second method graded the samples on a scale of eleven points because a very poor sample could receive a score of zero if all judges considered it unsatisfactory.

Experimental

CAUSES OF FLAVOUR REVERSION

A 500-g. sample of alkali-refined linseed oil was saponified and the two fractions separated (3). The nonsaponifiable fraction was added, in the same proportion as it was present in linseed oil, to a sample of alkali-refined sunflower seed oil and to a sample of "blended" shortening, containing up to 65% animal fat. The former mixture was then hydrogenated to the consistency suitable for a shortening and finally deodorized. The two shortenings were used in baking pastry but in neither case was a reverted flavour detected. A portion of the mixed component-fatty acids was re-esterified with glycerol (2), and the resulting neutral oil hydrogenated and used to make pastry. This pastry had the characteristic reverted flavour, thus indicating that flavour reversion was caused by a fatty acid component of the oil and not by the nonsaponifiable matter.

Two samples of deodorized-linseed oil shortenings were found to have acid values (as % oleic acid) of 0.10 and 0.18. A portion of each was alkali-refined, reducing the acid values to 0.028 and 0.031, and the four samples used to prepare pastries. As there were no appreciable differences in the pastries it seemed

that the free fatty acids in the shortening were not responsible for reversion.

A sample of ethyl linolenate (B. P. 194°C. at 5.5 mm.) was prepared from linseed oil (7). One portion was blended with sunflower seed oil in the proportions of 40:60 and the mixture hydrogenated. Pastry prepared with this shortening had the characteristic reverted flavour. Another portion was blended with a sunflower seed shortening in the same proportions. The pastry prepared with this blended shortening had an unpleasant flavour but not that characteristic of reversion. It was thus indicated that linolenic acid did cause the reverted flavour, but only after hydrogenation. In this experiment, the flavour imparted by ethyl linolenate itself, could have been misleading. However, we believe this is unlikely as the flavour judgments on the baked products were made by a panel of experienced judges.

MODIFICATIONS IN PROCESSING

Variations in a number of steps in the established methods of processing linseed oil into an edible shortening were studied as follows:

1. Samples of a crude hot-pressed linseed oil were hydrogenated to iodine numbers of about 65 with catalyst concentrations varying from 0.4 to 1.7% nickel.

2. Samples of an alkali-refined hot-pressed linseed oil were hydrogenated to iodine numbers of about 65 with catalyst concentrations varying from 0.3 to 1.6% nickel.

3. Five samples of an alkali-refined hot-pressed linseed oil were hydrogenated to iodine numbers of about 65 at temperatures of 50, 80, 120, 150 and 180°C.

4. Five samples of a hot-pressed linseed oil and five samples of a cold-pressed linseed oil were refined as follows: (a) no refining, (b) alkali refining, (c) alkali refining, then bisulphite refining, (d) alkali refining, then adsorbent refining with silica gel-alumina, (e) alkali refining, then adsorbent refining with Fitrol-carbon. Each sample was hydrogenated to an iodine number of about 70.

5. Eight samples of a crude hot-pressed linseed oil were hydrogenated to iodine numbers of 61, 67, 72, 76, 83, 87 and 89.

6. Two samples of alkali-refined hot-pressed linseed oil were hydrogenated to iodine numbers of 62 and 68 and blended in the proportions of two and three parts respectively of the linseed oil shortening with one part of alkali-refined sunflower seed oil.

7. Two samples of alkali- and adsorbent-refined (silica gel-alumina) hot-pressed linseed oil were hydrogenated to iodine numbers of 67.5 and 69.0 and blended in the proportions of two and four parts respectively of the linseed oil shortening to one part of sunflower seed oil.

8. Seven samples of linseed oil, including one hot-pressed and one cold-pressed oil from each of three seed crushing mills and a sample of a special linseed oil No. 100 from Pittsburgh Plate Glass Co. (iodine number 155) were each divided into four parts, one part hydrogenated directly to an iodine number of 65-70, one part alkali refined and hydrogenated to an iodine number of 65-70 and the other two parts (duplicates) alkali-refined, adsorbent-refined and hydrogenated to iodine numbers of 75-80.

All of the above shortenings were subjected to baking tests. From the results it was concluded that an improved shortening, but which still gave a slight characteristic flavour to pastry, was obtained by hardening to an iodine number below 70 and by a greater degree of refining prior to hydrogenation, although
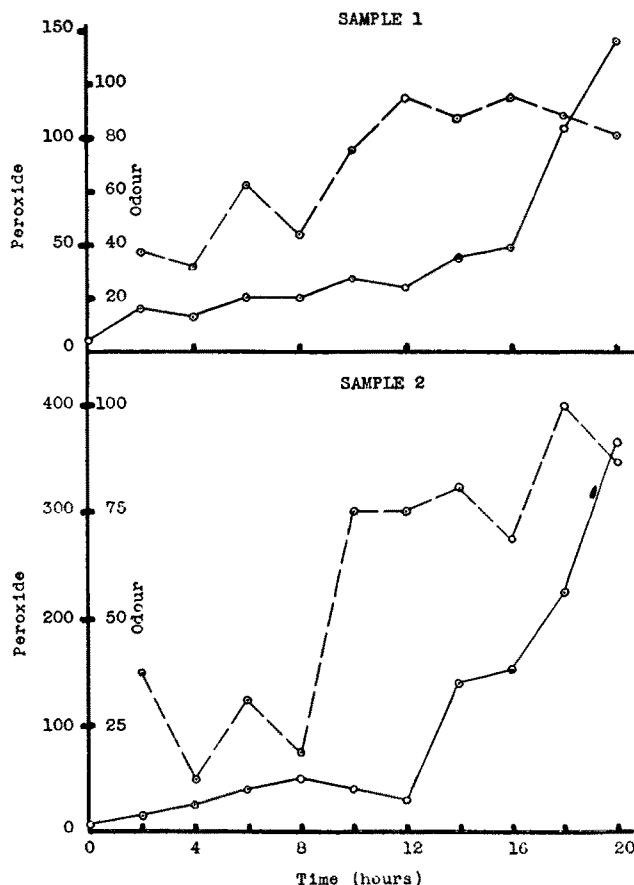
FIG. 1. Showing the relationship between the degree of flavour reversion and the peroxide content.

————————⊙———————— Peroxide-oxygen (milliequivalents per Kg.)

— — — —⊙—— — — — Odour (% of judgments which indicated the sample was reverted)

bisulphite refining gave no improvement. Hot- or cold-pressed oils gave the same results. Larger amounts of catalyst and higher temperatures reduced the hydrogenating time but had little effect on the quality of the product except in the case of crude oil where an increase in catalyst concentration did bring some improvement although this may have been due entirely to the silica gel partially refining the oil by adsorption. The experiments with blends of sunflower seed oil and hydrogenated linseed oil showed that a shortening with desired physical characteristics could be prepared and its presence in fresh or toasted slices of bread could not be detected when used at a level of 4% of the dough. However, the flavour could still be detected when pastry was prepared with these shortenings.

SPECIAL TREATMENTS AND TECHNIQUES

Conjugated Hydrogenation: Two samples of alkali-refined hot-pressed linseed oil were hydrogenated in a pyrex flask in the presence of 1% nickel catalyst at 200°C. while vapours of ethyl alcohol passed continuously through the mixture at approximately atmospheric pressure. There was no apparent difference in the course of the hydrogenation when absolute or 95% alcohol was used, the iodine number being 120 at 3 hours and 100 at 12 hours. Pastry prepared from these shortenings gave the characteristic reverted flavour.

Isomerization: Attempts to bring about isomerization following the hydrogenation of alkali-refined

hot-pressed linseed oil involved the following experiments: (a) heating at 230°C. for 12 hours in an atmosphere of hydrogen using the hydrogenation apparatus to agitate the oil; (b) heating at 230-240°C. for 6 hours with sulphur dioxide bubbled through at a rate sufficient to keep the mixture agitated, and (c) heating at 230-240°C. for 6 hours with one percent selenium using a mechanical stirrer to agitate the mixture. The quality of the shortening was not improved by any of these treatments.

Oxidation Before and After Hydrogenation: A sample of alkali-refined linseed oil was heated for 12 hours at 98-100°C. while agitated with a current of air. This slightly oxidized oil was hydrogenated to an iodine number of 71. Pastry prepared from this product had a more objectionable flavour than the characteristic reverted flavour. A sample of alkali-refined linseed oil was hydrogenated to an iodine number of 69.5, divided into two portions, and air blown through one portion at 150-160°C. for 6 hours and through the other at 180-190°C. for 8 hours. These treatments did not improve the shortening.

However, we have observed that the degree of flavour reversion parallels the increase in peroxide-oxygen during the oxidation of linseed shortenings. The formation of peroxides and the development of reverted odour were followed in two samples of hydrogenated linseed shortenings stored at 100°C. for 20 hours. The first appearance of reverted odour and the rate at which it increased were determined by a panel of judges. The relationship between peroxide-oxygen and reverted odour was found to be essentially the same for both samples. The data presented in Figure 1 indicates that the first appearance of the reverted odour does not coincide with the end of the induction period as detected by peroxide values, but rather that the onset of flavour reversion precedes the point at which there is a marked increase in peroxides.

Fractionation with Acetone: Three samples of alkali-refined linseed shortening of iodine numbers 83, 65 and 54 respectively were fractionated by crystallization from acetone (3) giving three fractions, viz., (I) crystallized at room temperature, (II) soluble at room temperature but crystallized at —15°C., (III) soluble at —15°C. The yields and the iodine numbers of each fraction from the three shortenings are shown in Table I.

TABLE I

Fractionation of Linseed Shortening From Acetone

	Acetone Fractions		
	Fraction No.	Yield (%)	Iodine Number
Shortening No. 1, Iodine Number 83	I	14.0	58
	II	58.7	86
	III	27.3	112
Shortening No. 2, Iodine Number 65	I	39.8	46
	II	45.6	81
	III	14.8	95
Shortening No. 3, Iodine Number 54	I	55.0	39
	II	33.8	74
	III	11.3	87

The development of peroxides and of reverted odour at 100°C. in each of the three fractions of each shortening was studied with the results shown in Figure 2. These results confirm the previous observations that the onset of flavour reversion is accompanied by an increase in peroxide-oxygen. It will be observed that all of the samples showed flavour reversion but in varying degrees, fraction I being the most

stable. However, it was expected from the relative iodine numbers that there would be a greater difference in stability between fractions II and III. It is of interest to note that in each case fraction I showed a marked increase in peroxides before the appearance of the reverted odour, whereas in this respect fractions II and III behaved in a manner typical of the unfractionated shortening (see Fig. 1).

The Use of Antioxidants: Since there appeared to be a relation between flavour reversion and oxidation in linseed shortenings, experiments were next carried out to determine whether antioxidants, known to retard the formation of peroxides in fats, would also retard or prevent flavour reversion in these shortenings. Figure 3 presents the results obtained with "Viobin Antioxidant" (6) alone, and supplemented with isopropyl gallate (1). The antioxidants were added to the deodorized linseed shortening because, in this case, the activity of the antioxidant is greatly reduced if it is added at any earlier stage in processing. It is evident from the results presented that the antioxidants have retarded the formation of peroxides and of the reverted odour. When these samples of shortening were subjected to baking tests some improvement in flavour was noted but the characteristic reverted odour was detectible in every case.

These findings were confirmed in further experiments in which many other commonly used antioxidants were tested singly or in combination and at different levels. It was therefore concluded that antioxidants even at relatively high levels did not entirely prevent the development of a reverted flavour during baking tests.

General Discussion

THE results of this investigation support the theory, developed by Lemon (4), that linolenic acid is responsible for flavour reversion in linseed shortenings. However, the characteristic reverted flavour seems to arise, not from this substance itself, either as a free fatty acid or in glyceride linkage, but from some product formed from it during hydrogenation. Regarding the nature of this product it can only be said that it isn't a free acid and that it does not seem to be offensive in itself, but on heating it produces the substances which are directly responsible for ,the flavour and odour. These latter substances may be removed by deodorization whereas the basic cause may not; it remains and is able, on subsequent heating to form again the odoriferous substances.

In the work here completed the identification of this substance has not been attempted. There are many possibilities, only a few of which can be eliminated: the ordinary oleic, linoleic and linolenic acids . are ruled out, likewise the usually occurring iso-oleic acids cannot be responsible. If linolenic acid were first hydrogenated at the $\Delta^{15,16}$ double bond the ordinary linoleic acid would be obtained and no rever-
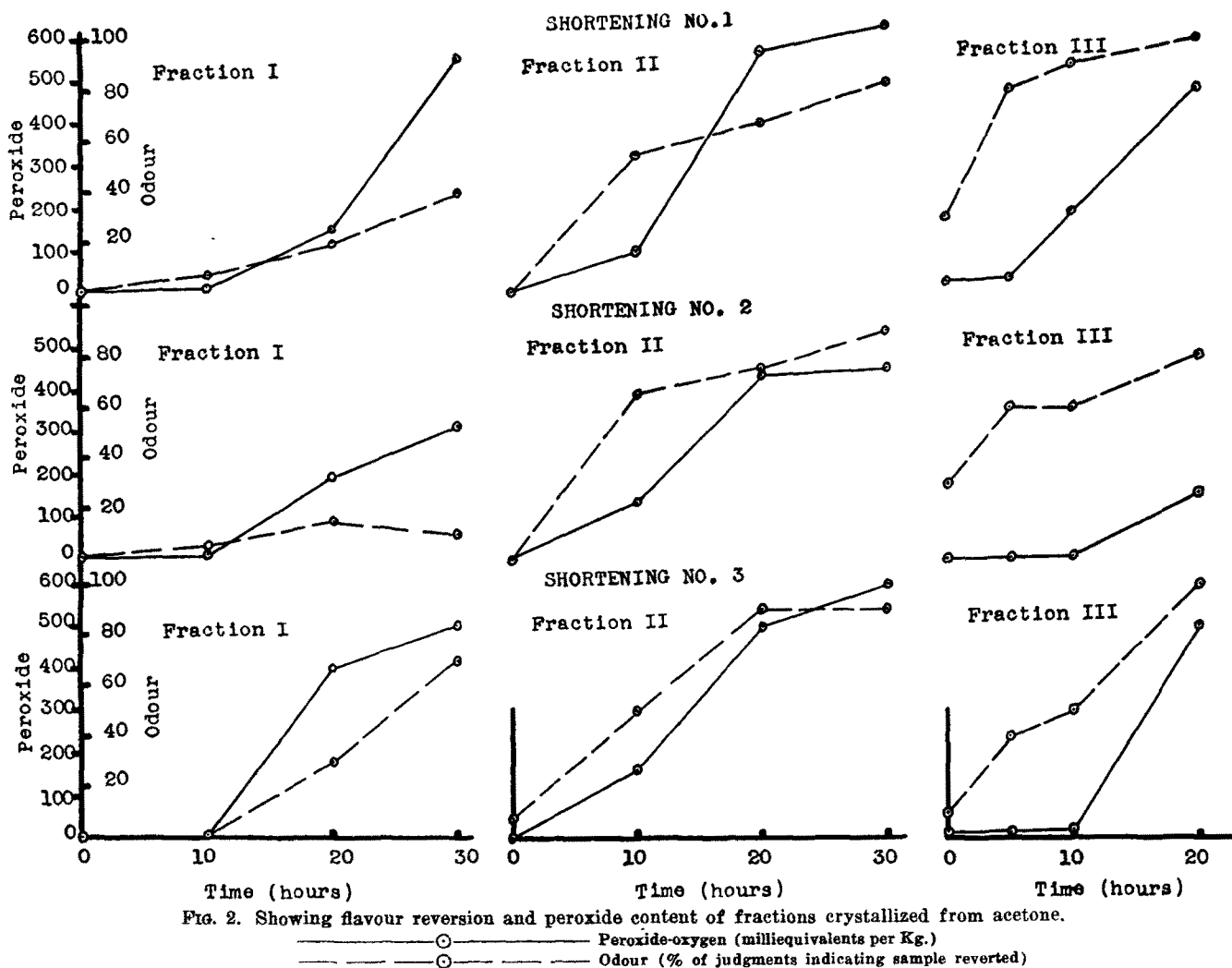

FIG. 2. Showing flavour reversion and peroxide content of fractions crystallized from acetone.
————————⊙———————— Peroxide-oxygen (milliequivalents per Kg.)
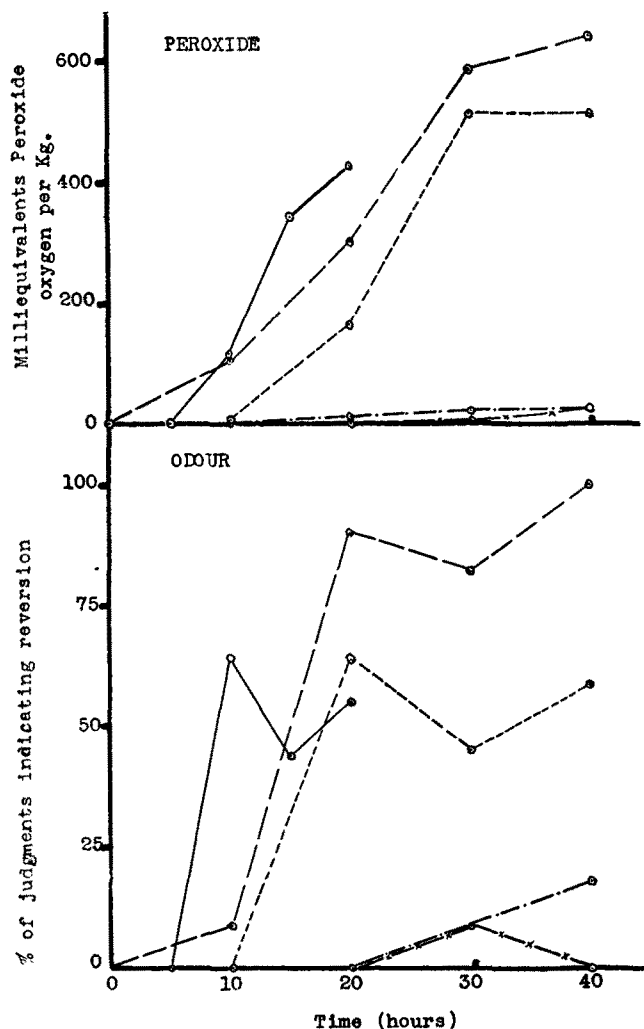— — —— ——⊙—— —— —— Odour (% of judgments indicating sample reverted)

FIG. 3. Showing the effect of antioxidants on flavour reversion and peroxide formation in linseed shortenings at 100°C.

——————⊙—————————— Control—No antioxidant
— — — ——⊙— — — — —— 0.01% Viobin antioxidant
— — — — — —⊙— — — — — — 0.01% Viobin antioxidant
+0.0025% isopropyl gallate
————·————·————⊙————·————·—— 0.10% Viobin antioxidant
——·—x————x————⊙————x————x—— 0.10% Viobin antioxidant
+0.025% isopropyl gallate

sion should occur thereafter. Therefore, at least a part of the linolenic acid must have undergone some other change, which may involve reduction at one of the other double bonds or an isomerization reaction, either of these may be followed by the other and the isomerization may involve migration of the double bonds of cis-trans changes. The possibilities thus created are many and the available methods of study may not be adequate to give a definite answer.

Regarding the reversion some possible solutions may be offered. There is a possibility that hydrogenating conditions may be made so highly selective that all the linolenic acid would be changed into ordinary linoleic before any other change occurred, or that some change, e.g., oxidation, might be made to

occur in the original linolenic acid so that on hydrogenation the reaction would take a more favourable course. Also the hydrogenated product might be changed through a subsequent isomerization to restore the structure to one which is heat-stable and inoffensive, or through a treatment such as prolonged heating (and possibly oxidation) accompanied by deodorization the basic substance might be converted into volatile products which would be removed, or finally certain substances might act as inhibitors to prevent the usual decomposition during baking.

The experiments here described have attempted to investigate these possible solutions but no satisfactory method can be claimed.

Summary

1. The production of an edible shortening by the hydrogenation of linseed oil with dry-reduced nickel catalyst has been studied.

2. A derivative of linolenic acid formed during hydrogenation, is shown to be responsible for flavour reversion in linseed oil shortening. It is believed that this substance decomposes to form the volatile products directly responsible for the reverted flavour and odour.

3. Possibilities of producing linseed oil shortening free of reversion have been investigated as to (a) pretreatment of the oil, (b) changing hydrogenation conditions, (c) changing the hydrogenation product by isomerization, (d) destruction of the offensive product of hydrogenation and removal by deodorization, and (e) the use of antioxidants to inhibit reversion in the hydrogenated product.

4. Improved products have been obtained but flavour reversion has never been entirely eliminated.

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