ing the action of tocopherols, or otherwise influencing the course of oxidation. These substances may be developed by oxidation, but are not peroxides, since they are stable toward steam deodorization.

Summary

1. Molecularly distilled concentrates of peanut oil antioxidants and pure alpha-tocopherol were tested at 110° C. as agents for the stabilization of lard and abnormal peanut oil products of poor stability.

2. Neither the peanut oil concentrates nor alpha-tocopherol were effective in improving the stability of either raw or hydrogenated peanut oils. In some cases, the addition of these substances materially reduced the stability of the oils. The results indicate that where poor keeping quality is encountered in hydrogenated peanut oils it is not in general due simply to a deficiency in tocopherols or related antioxidants.

3. Both alpha-tocopherol and peanut oil antioxidants were effective stabilizers for lard in concentrations up to approximately 0.06 percent. Above this concentration, the addition of alpha-tocopherol did not materially extend the keeping time of the lard, and the addition of peanut oil antioxidants decreased the keeping time. Essentially similar relationships between antioxidant concentrations and effectiveness were observed at the lower levels of concentration of the two antioxidants.

4. An investigation was made of the kinetics of peroxide formation in lard containing various percentages of alpha-tocopherol. With increasing tocopherol concentration, the peroxide level at which rapid oxidation begins was found to increase constantly, whereas the initial rate of peroxide formation passed through a minimum. This accounts for the antioxidant effect of low concentrations of alpha-tocopherol. At higher tocopherol levels the rate at which the peroxide level rises is balanced by the rate at which peroxide formation is accelerated and there is consequently no stabilizing effect.

5. No correlation was observed between the rate of tocopherol disappearance and either peroxide concentration or rate of peroxide formation in accelerated tests of lard containing 0.5 percent peanut oil tocopherols or 0.5 percent alpha-tocopherol. In these tests there was a considerable residue of unoxidized tocopherols remaining after the fat had become strongly rancid.

6. The experimental results strongly suggest the presence of distillable substances in vegetable oils which are capable of inhibiting the action of tocopherols, or otherwise acting as pro-oxidants. It is possible that such substances are developed by oxidation, but they do not consist of peroxides.

Acknowledgment

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Fatty Acid Esters of Furfuryl Alcohol

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Recently, during some partial saponification experiments using furfuryl alcohol as the solvent, it was observed that the unsaponified oil possessed a much higher iodine number than the original oil. For example, linseed oil of iodine number 170 gave an unsaponified fraction having an iodine number of 214-220 (Rapid Hanus method) (1). Since this high degree of unsaturation could not be due to a selective saponification of saturated glycerides, as evidenced by the iodine number of the saponified material, the formation of furfuryl esters by alcoholysis was suspected. Experiments to confirm this suspicion were initiated in view of the possible enhanced drying properties of such esters, because of their content of conjugated double bonds, known to be especially susceptible to oxidation and polymerization.

A search of the literature revealed that furfuryl palmitate had been used by Japanese workers in some tests described in a journal unavailable to the present authors (2). Other furfuryl esters had been prepared, however; namely the acetate (3), phthalate (4, 5), acetate through valerate (6), furoate (7), p-nitrobenzoate (8) and formate (9). These preparations involved (a) the use of the acid anhydride and mild heat, (b) ester interchange or (c) the use of an acyl halide in pyridine. Direct esterification catalyzed by mineral or strong organic acids must be avoided because of the violent polymerization of furfuryl alcohol in the presence of these acids.

In our first experiment linseed oil was treated with a furfuryl alcoholic solution containing 70% of the amount of potassium hydroxide necessary for complete saponification of the oil. The unsaponified material was extracted with petroleum ether, washed with water to remove furfuryl alcohol, and the petroleum ether removed under reduced pressure. Distillation yielded a product having a saponification equivalent of 358.8 and an iodine number (Rapid Hanus method) of 220.0, compared to the calculated values for linseed furfuryl esters of 358.9 and 219.9, respectively. The method of calculation is described in the experimental section.

In subsequent experiments it was found that much better yields of furfuryl esters could be obtained by

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alcoholysis using 0.5% metallic sodium as a catalyst and a reaction temperature of about 60° C.

A preliminary drying test of linseed oil furfuryl esters without driers gave some indications of enhanced drying properties. Therefore, a series of tests were made under control conditions (75° F. and 50% R. H.) using a drier combination of 0.5% lead, 0.05% manganese and 0.01% cobalt as the linoleates. These tests showed furfuryl esters to be definitely inferior to the linseed oil from which they were prepared (Table I). This could be due to (a) the lack

TABLE I

Comparative Drying Time of Linseed Oil Furfuryl Esters

	Tacky to touch (hours)	Dry to touch (hours)
Linseed oil	>96	>96
Linseel oil + driers	4½	5
Linseed oil furfuryl esters	>96	>96
Linseed oil furfuryl esters + driers	48	96
Linseed oil furfuryl esters + heat bodying in N_2 to R. I. of 1.4780 at 30° C.	120	>216
Linseed oil furfuryl esters + heat bodying in N_2 to R. I. of 1.4780 at 30° C. + driers	54	>216
50-50 linseed oil-linseed furfuryl esters + driers	7	7-24

of sufficient functional groups for polymerization (i.e., the methyl esters of the fatty acids do not dry to hard films as do the corresponding glycerides) and/or (b) the possibility that, as indicated by Dunlop and Peters (10), furfuryl alcohol itself does not polymerize by reaction of the double bonds but rather by intermolecular dehydration to produce mainly dimers and trimers still containing the double bonds originally present (equations 1 and 2).

The hypothesis of Dunlop and Peters is in conformity with the observation that furfuryl esters of fatty acids may be polymerized using acidic materials such as maleic anhydride, p-toluenesulfonic acid, concentrated HCl, or cold concentrated H_2SO_4 to give a hard, black, resinous material. Conceivably, the esters polymerize by the splitting out of a mole of fatty acid (instead of water as in the case of furfuryl alcohol) from two ester molecules, as illustrated by equation 3.

A preliminary experiment in which linseed furfuryl esters were heated in nitrogen at 290° C. to effect polymerization showed that free fatty acids were produced. However, the iodine number (Rapid Hanus) decreased greatly indicating that double bonds were also concerned in the polymerization. Results are shown in Table II.

TABLE II

Heat-Polymerization of Furfuryl Esters of Linseed Oil Fatty Acids at 290° C.

Heating time (min.)	I. N. (Rapid Hanus)	R. I. (30° C.)	Time for 100 revolutions in Stormer viscosimeter at 22° C. (sec.)	Acid number
0	226.0	1.4780	10.5	0
60	158.9	1.4902	42	....
140	118.9	1.5042	1200	111.5

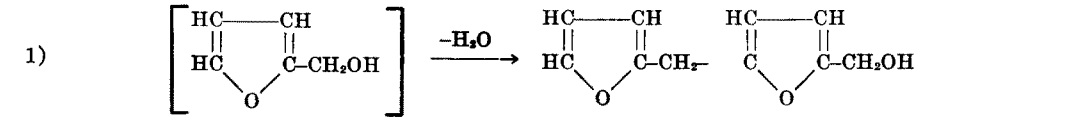
In order to eliminate the possibility of changes in unsaturation resulting from the reactions of double bonds in the fatty acid part of the molecule, furfuryl palmitate was polymerized as above with the results as shown in Fig. 1. The Woburn iodine number method was used in place of the Rapid Hanus method since the former is claimed to give a quantitative measurement of both conjugated and nonconjugated unsaturation and would, therefore, be most sensitive to minor unsaturation changes. The results show that although acidity increases with heating time, the total unsaturation decreases, proving that appreciable reaction occurs at the double bonds in the furfuryl part of the molecule.

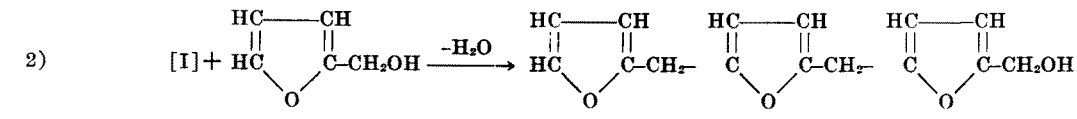
The foregoing may be interpreted to mean that, given the proper functionality, compounds containing the furfuryl nucleus might dry in air. However, our experiments (Table I) show conclusively that linseed furfuryl esters, bodied or unbodied, are inferior to the linseed oil from which they were made. This applies in the presence or absence of driers.

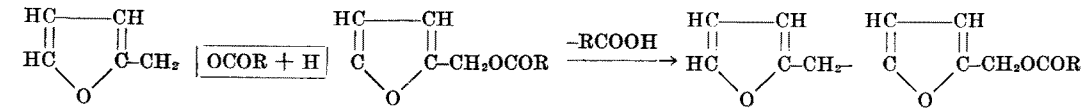
A final check on the ability of the furfuryl nucleus to polymerize by air drying would be a drying test on trifurfuryl tricarballylate since this is a compound more analogous to an unsaturated triglyceride with respect to functionality. A preliminary experiment in this connection was unsuccessful because alcoholysis of trimethyl tricarballylate with furfuryl alcohol could not be accomplished by the methods at hand.

Experimental

Preparation of linseed oil furfuryl esters by partial saponification. One hundred gms. of linseed oil plus 13.3 gms. of KOH (70% of theoretical) dissolved in







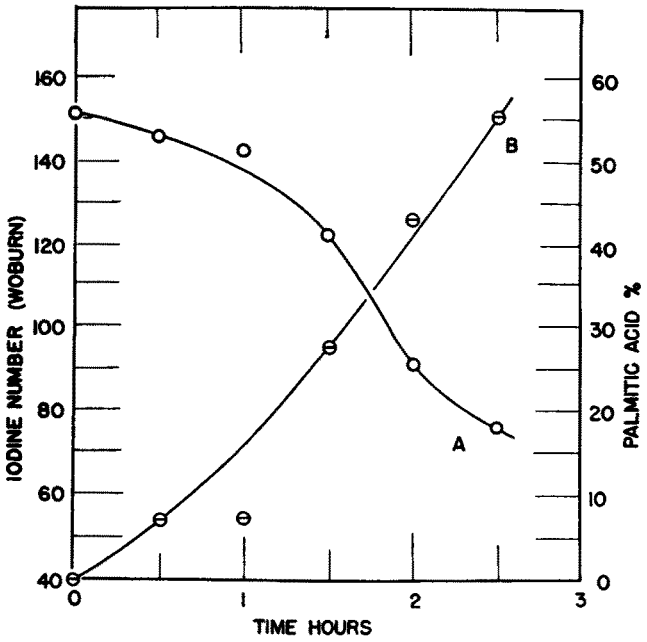


FIG. 1. Heat polymerization of furfuryl palmitate.
A = iodine number vs. heating time.
B = palmitic acid vs. heating time.

7 gms. of water were added to 200 ml. furfuryl alcohol. After heating to 80° C. for 15 minutes 200 ml. of water was added, and the furfuryl esters extracted with petroleum ether (30-60° C.). The petroleum ether solution was washed with water until the washings were neutral and the furfuryl esters then isolated by vacuum distillation after the removal of the solvent at atmospheric pressure. Forty-three grams of esters were obtained, S.E. found 358.8, calculated 358.9; I.N. (Rapid Hanus) 220.0, calculated 219.9.

Preparation of linseed oil furfuryl esters by sodium catalyzed alcoholysis. Four hundred gms. of linseed oil and 800 gms. of furfuryl alcohol in which 2 gms. of metallic sodium had been dissolved were heated with good agitation for 3 hours at 60 ± 5° C. The reaction mixture was then homogeneous. The addition of 300 ml. of water caused stratification, permitting the removal of an ester layer. This layer was washed with 1% acetic acid, dried, and vacuum distilled, giving a 96.5% yield of esters of S.E. 361.0, calculated 358.9, I.N. (Rapid Hanus) 219.4, calculated 219.9. Boiling point 170 ± 5° C. at 1 mm.

Preparation of furfuryl oleate from methyl oleate. A 70% saponification of methyl oleate [S.E. 290.9, I.N. 81.7 (Rapid Hanus)], yielded furfuryl oleate which after distillation had an S.E. of 357.7 (calculated 356.9) and I.N. (Rapid Hanus) 150.4, calculated 149.6).

Preparation of furfuryl palmitate by sodium catalyzed alcoholysis. Ninety-five and five-tenths gm. of methyl palmitate (0.354 mole) was stirred for 2 hours with 196 gm. (2.0 moles) of furfuryl alcohol containing 0.5 gram of sodium. Temperature was maintained at 60-68° C. Three volumes of distilled water were then added and the upper layer was washed several times with distilled water. The ester was then taken up in petroleum ether, the solution washed with water and dried over anhydrous sodium sulfate. After removal of the solvent the crude product was fractionally distilled into three fractions. The first two (53 grams) were contaminated with unreacted methyl palmitate as evidenced by their boiling points. The third fraction (31 grams) had an S.E. of 335.1 (calculated 336.3) and a Rapid Hanus iodine number of 88.2 (calculated 88.2). The Woburn iodine number of this fraction was 152.0, compared to the theoretical of 153.9.

Heat polymerization of furfuryl palmitate. About 25 grams of furfuryl palmitate were heated at 290-300° C. in air. Samples were withdrawn at one-half hour intervals and analyzed for acid number and iodine number (12). The Woburn reagent was used for the iodine number determinations since this reagent, unlike the standard reagents, supposedly measures total unsaturation, both conjugated and nonconjugated, and, therefore, is most sensitive to any small changes in unsaturation.

Iodine number determinations and calculations. Furfuryl alcohol (theoretical iodine number 517.4) was found to give iodine numbers of 272.7, 270.8 and ca. 515, with Rapid Hanus, Rapid Wijs, and Woburn methods, respectively. Excess of reagent was found to be important, so theoretical excess of 350-500% were used with the Rapid Hanus and Rapid Wijs methods, since this excess range gave the most consistent results. A 600-900% excess was used with the Woburn reagent as suggested by the originators of this method.

It was found that esterification of the hydroxyl group in furfuryl alcohol increased the iodine number of the furfuryl residue as measured by Hanus and Wijs reagents. Thus furfuryl alcohol alone had a Rapid Hanus I.N. of 272.7, whereas when combined as an ester, the furfuryl residue ($C_5H_5O_2$) had an I.N. of 305.6. This behavior is at present unexplained but was observed in all preparations. For this reason the Rapid Hanus I.N.'s of all furfuryl esters were calculated assuming the I.N. of the furfuryl residue exhibited in its ester combination with palmitic acid. The formula used was as follows:

$$\frac{\text{I.N. of furfuryl residue x mol. wt.} + \text{I.N. of fatty acid residue x mol. wt.}}{\text{Mol. wt. of furfuryl ester}} = \text{I.N. of furfuryl ester.}$$

Complete analytical data are shown in Table III.

TABLE III

Iodine Numbers and Saponification Equivalents of Furfuryl Esters

Furfuryl ester of	Iodine number (Rapid Hanus)		Saponification equivalent	
	Observed	Calculated	Observed	Calculated
Linseed oil (Partial saponification)	220.0	219.9	358.8	358.9
Linseed oil (Alcoholysis)	219.4	219.9	361.0	358.9
Oleic acid	150.4	149.6	357.7	356.9
Palmitic acid	88.2	88.2	335.1	336.3

Summary

Furfuryl esters were prepared from linseed oil and methyl palmitate by alcoholysis using metallic sodium as the catalyst. They were also prepared from linseed oil and from methyl oleate by partial saponification in furfuryl alcohol. These esters, although containing conjugated double bonds, did not possess any increased drying power.

Iodine numbers were determined by several methods, and, except with the Woburn reagent, the furfuryl group was found to exhibit a higher iodine number when combined as an ester than when present as the free alcohol.

Furfuryl esters were found to polymerize to products of greatly decreased iodine number and increased acidity, showing that polymerization involved both deacylation and reaction at the double bonds of the furan ring.

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Report of the Bleaching Methods Committee 1942-1943

This Committee was formed last year with the express purpose of studying the A.O.C.S. Bleach Test as applied to refined soybean oil, and the outcome of last year's work was the adoption as tentative of a slight modification in the method which had generally been used on cottonseed oil, as a result of which the method now shows two procedures for the bleach test, one for cottonseed and other oils and one for soybean oil.

This year there were two points presented for consideration by this Commtitee: (1) the desirability of wording the bleach test procedure to insure that the oil filtered for the color reading be absolutely clear and free from turbidity and (2) the question of yellow-to-red ratio.

1. *Clarity.* At least two Society members called attention to the fact that the oil might not be entirely clear when making the color reading, thus resulting in an inaccurate reading—higher than it should be. This apparently has obtained in spite of the wording of the method: "after sufficient oil has passed the filter to insure clearness . . ." It was the unanimous opinion of those of the Committee reporting on this that the insertion of the words "close textured" before the words *filter paper* would be a desirable change in the wording of the method which would lessen the likelihood of colors being read on slightly turbid test-bleached oil. Hence the direction which now reads, ". . . and filter through filter paper," would then read: ". . . filter through an unused close textured filter paper." The Committee did not consider this point to be of sufficient importance to warrant a laboratory study of various filter papers leading to the designation of specific types or brands.

It should be pointed out to those who have been accustomed to using a fast-filtering paper that while the use of a more retentive paper in this application might appear at first sight to slow the outturn of results, it must be recalled that the large-pore, fast-filtering paper requires that a fairly large amount of oil be passed before it begins to come with sufficient clarity to yield an accurate color reading, so that it is doubtful if any appreciable time is lost. Moreover, the fuller's earth-oil mixture is poured into the filter paper at a temperature of 105°C. or higher, at which the filter rate is fairly rapid even through a highly retentive paper.

2. *Yellow-to-red Ratio.* The Committee was practically unanimous in the opinion that bleach colors on soybean oil cannot be satisfactorily read using the ten-to-one yellow-red ratio now designated in our methods for colors under 3.5 red or using the fixed 70 yellow value for colors higher than 3.5 red, especially in times when the oil contains appreciable chlorophyll, or when it is off-hue due to other causes.

[This question has assumed an enhanced importance commercially within recent weeks as the result of the recommendations of a Task Committee convened by the Office of Price Administration, providing a scale of discounts for off-bleach color on crude soybean oil. The yellow-to-red ratio was considered by the oil chemists present (representing the soybean oil industry), and the scale of bleach colors was given in terms of the red reading, with the yellow color being read *as is*, in other words, with the *yellow which affords the best match.* This action was considered by the Finished Materials Standards Committee and the Rules Committee of the National Soybean Processors' Association and approved by both groups.]

A careful reading of our method Section (b) *Determination*—under the section REFINED OILS—COLOR (pg. 16f) reveals that the method as written now provides for the contingencies of oils not conforming to type and also where "Rules specify the yellow and/or red to be used in determining given grades." Thus

"The ratio of yellow to red in determining color shall be as follows, except where rules specify the yellow and/or red to be used in determining given grades:

Soybean Oil—10 yellow to 1 red, up to 3.5 red
70 yellow for 3.5 red or higher

"If the above ratios fail to give a satisfactory match, this fact should be noted and a second reading made, using the amount of yellow required for a good match. Report both readings."

Nevertheless, the Committee recommends the addition of the following paragraph to follow the last paragraph in the directions just quoted:

"Note—Soybean Oils are subject at times to abnormalities in the composition of their pigment contents resulting in the occurrence of hues which cannot be matched even approximately using the fixed yellow or yellow-to-red ratio designated above. In the case of such oils, report only the reading with the yellow required to give the best match."

This recommendation is made with the thought that the reporting of two different color readings under such circumstances can serve no useful purpose and is likely to lead to confusion.

Consequent upon this action, the Committee further recommends that the first paragraph quoted above be changed to read as follows: "The ratio of yellow-to-red in determining color shall be as follows, except where Rules specify 'yellow affording the best match,'