price-depressing effect. But considering the great production potential in tropical regions, it is possible that by 1955 or 1960 world production of fats may be over-large in terms of prices considered by producers to be fair and reasonable.

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Notes on the Stabilization of Oxidized Fats by Steam Deodorization With Phosphoric Acid or Commercial Lecithin[1]

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Introduction

COMMERCIAL lecithin has long been known as an antioxidant for fats and oils, having been patented for this purpose by Bollman (1) in 1926. Olcott and Mattill (7) have demonstrated that cephalin rather than lecithin is the active substance in the commercial product, and have attributed its activity to an ionizable hydrogen atom in the phosphoric acid group. Phosphoric acid itself is recognized as an antioxidant in the patents issued to Eckey (2), and Richardson, Vibrans, and Andrews (9). It has been shown by various investigators (4, 6, 10) that antioxygenic activity is not peculiar to phosphoric acid, but is a property of acidic substances in general.

It has been well established that acids are not antioxidants when present alone in fats, but are capable of enhancing the antioxygenic activity of tocopherols or other antioxidants of the phenolic type. Recently Golumbic (3) has advanced a logical explanation of the synergistic action of certain acid-type antioxidants with tocopherols. Since tocoquinones, one group of the oxidation products of tocopherols, may be recyclized to tocopherols by treatment with mineral acids (5), it is suggested that phosphoric acid and other acidic antioxidants are able to prolong the induction period of oxidizing fats by continuously regenerating tocopherols during the course of oxidation. Conversion of tocoquinone to tocopherol by phosphoric acid was actually observed by Golumbic in a fat to which tocoquinone had been added, but not in a natural oxidized fat.

The present investigation was prompted by certain observations relative to the effect of commercial lecithin on the stability of deodorized shortenings and other fats. It was observed by one of the authors some years ago, and is probably generally known in the industry, that lecithin added to fat before it is steam deodorized is equally as effective as lecithin added after deodorization. Actually, it is advantageous to incorporate the lecithin before deodorization. By this procedure the lecithin can contribute no flavor or odor to the fat and, since the surface-activity of the lecithin is destroyed in deodorization, the treated fat is not inclined to foam. Recently it has been noted in this laboratory that vegetable fats of poor stability respond somewhat more favorably to lecithin treatment in the deodorizer than fats of good stability. Since the poorer-keeping fats generally contain relatively large amounts of tocopherol oxidation products, this naturally suggests the possibility of tocopherol regeneration occurring in the deodorizer.

In this communication are reported certain observations made during an investigation of combined deodorization and treatment with lecithin or phosphoric acid, particularly for the stabilization of oxidized fats.

Preparation of the Samples and Methods of Testing and Analysis

THE vegetable oils used in these experiments were commercially refined and bleached, but hydrogenated and deodorized in the laboratory. The oxidized samples were prepared by aerating the oil at 105° to 110° C. until the desired peroxide value was reached. All deodorizations were carried out at 400° F. (204° C.), with a deodorization time of 45 minutes. Stability tests were conducted by the Swift aeration method, at 110° C., keeping-times being recorded in terms of the number of hours required for the sample to develop a rancid odor. Where small amounts of phosphoric acid were to be added to oils before deodorization, the acid was first absorbed on an acid-washed grade of diatomaceous earth, according to the method of Eckey (2). The general procedure

[1] Presented before the American Oil Chemists' Society Meeting, New Orleans, Louisiana, May 10 to 12, 1944.

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followed in conducting stability tests and analyzing the oils has been outlined in a previous publication (8).

Effect of Deodorization on the Stability of Oxidized Oils

Steam deodorization will restore a considerable degree of stability to a vegetable oil which has been oxidized even to the point of incipient or actual rancidity. Deodorization of course destroys peroxides and removes all volatile products of oxidation. The effect of deodorization on a typical oxidized hydrogenated peanut oil is shown graphically in Figure 1.

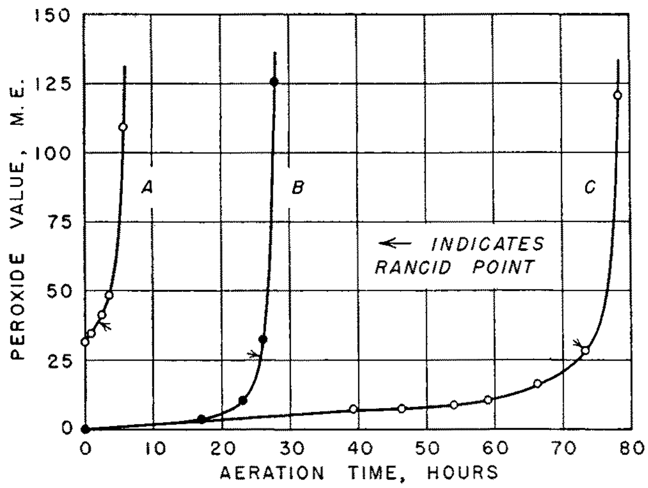

FIG. 1. Stability of (A) an oxidized hydrogenated peanut oil, (B) the same oil after deodorization, and (C) the hydrogenated oil before oxidation.

Addition of Lecithin and Phosphoric Acid Before Deodorization vs. Addition After Deodorization

A number of comparative experiments were carried out in which normal and oxidized hydrogenated peanut oils were treated with lecithin and with phosphoric acid both before and after the oils were deodorized. Results of typical experiments are shown in Table 1. In the case of the unoxidized oils it was found that the stabilizing effect of these substances was substantially the same whether added before or after deodorization. However, in oxidized oils, these antioxidants were relatively ineffective unless present in the oils during deodorization (cf. Table 1 and Figure 2).

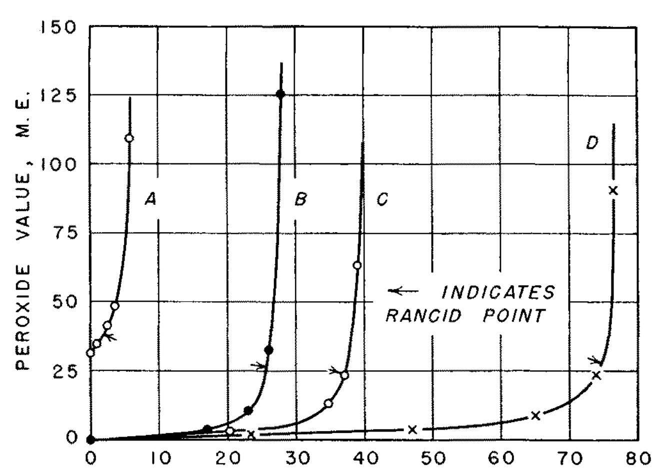

FIG. 2. Stability of (A) a hydrogenated and oxidized peanut oil, PO-38, (B) the same oil after deodorization, (C) the same oil after deodorization but with 0.1 percent lecithin added, and (D) the oxidized oil after deodorization with 0.1 percent lecithin in the deodorizer.

TABLE 1

Comparative Effects of Lecithin and Phosphoric Acid on the Stability of Normal and Oxidized Hydrogenated Peanut Oils When Added Before and After Deodorization (Amounts Added: Lecithin, 0.1 Percent; H_3PO_4, 0.004 Percent).

Fat used in test	Anti-oxidant used	Stability of deodorized oils, hrs.	
		Antioxidant added before deodorization	Antioxidant added after deodorization
PO-37	None	56	56
PO-37, oxidized to peroxide value of 66*	None	9	9
PO-37, oxidized to peroxide value of 66*	Lecithin	25	12
PO-38	None	73	73
PO-38	Lecithin	162	151
PO-38	H_3PO_4	120	......
PO-38, oxidized to peroxide value of 31*	None	26	26
PO-38, oxidized to peroxide value of 31*	Lecithin	74	37
PO-38, oxidized to peroxide value of 31*	H_3PO_4	66	......
PO-39	None	35	35
PO-39, oxidized to peroxide value of 30*	None	16	16
PO-39, oxidized to peroxide value of 30*	Lecithin	44	34
PO-39, oxidized to peroxide value of 30*	H_3PO_4	39	20

* Peroxide value in terms of milliequivalents per 1,000 g. oil.

Relative Effectiveness of Lecithin and Phosphoric Acid and Optimum Amounts of Each

IN Table 2 are shown the results of a series of tests made to determine the relative effectiveness of lecithin and phosphoric acid in the stabilization of oxidized hydrogenated peanut oil, and the optimum amounts of each substance. The optimum amounts of lecithin and phosphoric acid appear to be in the neighborhood of 0.1 percent and 0.004 percent, respectively. Since the two materials contain about 2.6 percent and 31.6 percent of phosphorus, respectively, the optimum amounts of the two are of the same order of magnitude, on the basis of phosphorous content.

TABLE 2

Tests to Determine the Relative Effectiveness of Lecithin and Phosphoric Acid in the Stabilization of Oxidized Hydrogenated Peanut Oils, and the Optimum Amounts of Each.

Fat used in test	Anti-oxidant (A.O.) added	A.O. added, percent	Time at which A.O. was added	Stability of fat, hrs.
PO-38, oxidized	Lecithin	0.004	Before deodorization	48
PO-38, oxidized	Lecithin	0.02	Before deodorization	48
PO-38, oxidized	Lecithin	0.10	Before deodorization	74
PO-38, oxidized	Lecithin	0.50	Before deodorization	67
PO-38, oxidized	H_3PO_4	0.0008	Before deodorization	56
PO-38, oxidized	H_3PO_4	0.004	Before deodorization	66
PO-38, oxidized	H_3PO_4	0.02	Before deodorization	28
PO-38, oxidized	H_3PO_4	0.10	Before deodorization	7
PO-39, oxidized	H_3PO_4	0.0002	After deodorization	24
PO-39, oxidized	H_3PO_4	0.0004	After deodorization	25
PO-39, oxidized	H_3PO_4	0.0008	After deodorization	22
PO-39, oxidized	H_3PO_4	0.004	After deodorization	20
PO-39, oxidized	H_3PO_4	0.02	After deodorization	14
PO-39, oxidized	H_3PO_4	0.10	After deodorization	20
PO-39, oxidized	H_3PO_4	0.50	After deodorization	*

* Sample charred and did not develop peroxides in 100 hrs. aeration.

Effect of Deodorization with Lecithin and Phosphoric Acid on the Color of the Oils

Deodorization with phosphoric acid up to the optimum amount (0.004 percent) had no adverse effect on the color of the oils. However, deodorization with the optimum amount of lecithin (0.1 percent) darkened the oils quite markedly. Comparative effects of the two substances on the color are shown in Table 3. Amounts of lecithin equivalent to 0.02 percent or less had no effect on the color of the deodorized oils.

TABLE 3

Effect on the Color of Oils of Lecithin and Phosphoric Acids Added to the Oils Before Deodorization.

Oil	Color (yellow and red Lovibond units)
Hydrogenated peanut oil, PO-39	15Y– 1.7R
Same oil, deodorized alone	10Y– 1.8R
Same oil, deodorized with 0.1 percent lecithin	35Y–10.5R
Same oil, deodorized with 0.004 percent H_3PO_4	10Y– 1.7R
PO-39 oxidized	35Y– 4.1R
Same oil, deodorized alone	15Y– 2.3R
Same oil, deodorized with 0.1 percent lecithin	35Y– 6.4R
Same oil, deodorized with 0.004 percent H_3PO_4	15Y– 1.9R

Retention of Phosphoric Acid or Lecithin in the Oil During Deodorization

Phosphorous determinations were made on samples of oil after deodorization with lecithin and phosphoric acid, to determine the extent to which these antioxidants are retained by the oil during deodorization. Results of these determinations are shown in Table 4. It is evident that most of either material is retained during deodorization.

TABLE 4

Phosphorous Content of Hydrogenated Oils Containing Added Lecithin and Phosphoric Acid, Before and After Deodorization.

Oil	Phosphorous content
Cottonseed oil:	*percent*
Original oil, found	0.00009
Added in form of H_3PO_4, 0.004%, calculated	0.00126
Original oil plus added H_3PO_4	0.00135
After deodorization, found	0.00120
Peanut oil:	
Original oil, found	0.00008
Added in form of lecithin, 0.1%, calculated	0.00260
Original oil plus added lecithin	0.00268
After deodorization, found	0.00180

Effect of Deodorization with Lecithin and Phosphoric Acid on the Tocopherol Content of the Oils

In spite of the superior stability of oxidized fats treated with acids in the deodorizer, there was no evidence of the regeneration of tocopherols during deodorization. In most cases the tocopherol content of the oils, as measured by the Emmerie-Engel test, actually decreased during deodorization with lecithin or phosphoric acid, although there was no change in the content of total chromans, as measured by the Furter-Meyer test. The tocopherol and total chroman contents of representative oils, before and after deodorization with these materials, are listed in Table 5.

Summary

1. If a normal fat containing tocopherols is ~~to be~~ stabilized by the addition of lecithin or phosphoric acid, these substances are as effective if added before deodorization as if added afterwards. However, if such a fat is oxidized until nearly rancid, these antioxidants are much more effective if added before the fat is deodorized.

2. Lecithin and phosphoric acid are equally effective for the treatment of oxidized fats in the deodorizer. There is an optimum amount of each to be used; the most effective stabilization is obtained with about 0.1 percent lecithin and 0.004 percent phosphoric acid. The optimum amounts of the two are approximately equal, on the basis of the phosphorous content of the materials.

3. Oils deodorized with the optimum amount of lecithin (0.1 percent) darkened in color in the deodorizer, although there was no darkening when 0.02 percent lecithin was used. The optimum amount of phosphoric acid (0.004 percent) had no adverse effect on the color.

4. Phosphorous, in the form of either lecithin or phosphoric acid, is not removed from oils to any large degree by steam deodorization.

5. In spite of the fact that lecithin and phosphoric acid have a superior stabilizing effect if added to oxidized fats before deodorization, there is no evidence of ~~their being~~ any regeneration of tocopherols from tocoquinone in the deodorizer. On the contrary, deodorization with these materials appears to partially convert tocopherols to tocoquinones or other nonreducing chromans, since it invariably lowers the Emmerie-Engel assay of the oil without materially affecting the Furter-Meyer assay.

Acknowledgment

The authors are indebted to Carroll Hoffpauir for the tocopherol assays, to Walter A. Pons for the phosphorous determinations on the oil, and to W. S. Singleton for assistance in carrying out some of the stability tests.

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TABLE 5

Tocopherol and Total Chroman Contents of Oils Before and After Deodorization With Lecithin and Phosphoric Acid.

Oil tested	Substance added	Tocopherol content,* percent		Total chroman content,† percent	
		Before deodorization	After deodorization	Before deodorization	After deodorization
Hydrogenated peanut, PO-38	None	0.040	0.040	0.045	0.043
Hydrogenated peanut, PO-38	0.1% lecithin	0.040	0.012	0.045	0.050
PO-38, oxidized to 31 peroxide value‡	0.1% lecithin	0.025	0.007	0.025	0.028
PO-38, oxidized to 31 peroxide value‡	0.004% H_3PO_4	0.025	0.002	0.025	0.025
Hydrogenated cottonseed, CO-52	None	0.085	0.090	0.090	0.090
Hydrogenated cottonseed, CO-52	0.004% H_3PO_4	0.085	0.049	0.090	0.091
Lard with 0.12 percent α-tocopherol added	0.004% H_3PO_4	0.120	0.075	....	....
Lard with 0.12 percent α-tocopherol added, oxidized to 90 peroxide value*	0.004% H_3PO_4	0.050	0.055	....	....

*By the modified Emmerie-Engel method.
†By the modified Furter-Meyer method.
‡Peroxide value in terms of milliequivalents per 1,000 g. of oil.