Steam-Refined Soybean Oil: II. Effect of Degumming Methods on Removal of Prooxidants and Phospholipids[1]

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ABSTRACT

The first paper in this series described the effect of refining and degumming methods on the quality of steam- and caustic-refined soybean oils. Flavor evaluations demonstrated that phosphoric acid-pretreated oils were superior to water-degummed oils particularly in the steam-refining mode. The present study reports observations on the function of the phosphoric acid pretreatment. The effects of iron on the flavor and oxidative stability are reviewed. Data on phosphatide and iron removal during caustic and steam refining are presented and the results discussed. The poor initial quality of the water-degummed, steam-refined oil is attributed to oxidation resulting from incomplete iron removal during the prerefining stage. Significant correlations were obtained between the initial flavor scores of processed oils and their iron contents. Phosphoric acid pretreatment apparently alters iron compounds in crude soybean oil and facilitates their removal during subsequent processing.

INTRODUCTION

The removal of phospholipids and trace metals from crude vegetable oils has long been recognized as an important factor influencing the quality and keeping properties of the finished product (1-3). Avoidance removal and inactivation of trace metals are universally accepted industrial practices (4,5).

Prooxidants and phospholipids occur in soybean oil at levels of parts per million (ppm) and several percent, respectively, and are generally satisfactorily removed during caustic processing (3,6,7). On the other hand, while the need for their removal in physical refining is appreciated and stressed (8,9), little information has been reported on the factors influencing removal of the phosphatides and prooxidants from soybean oil.

The first paper in this series (10) described the effects of degumming and refining methods on the quality of steam- and caustic-processed soybean oil, where it was demonstrated that degumming methods had a significant effect on oil quality. Here we report observations on the function of phosphoric acid as a degumming agent for soybean oil.

MATERIALS AND METHODS

Analytical Methods

Iron was determined by atomic absorption spectroscopy as 25% oil solutions in methyl isobutyl ketone (7). Phosphorus was determined by a modification of the official AOCS method (6). Phosphatides were determined according to a modification of the Acetone Insoluble procedure (L. Crauer, private communication). Phosphatides in the crude oil were also estimated based on partition between auqeous methanol and petroleum ether as described by Nichols (11). Free fatty acids were determined according to the official AOCS method (12). Fatty acid composition was determined by gas liquid chromatography of the methyl esters prepared by sodium methoxide catalyzed transesterification of the triglycerides (13).

Oil Processing Methods

The source of the crude soybean oil and the processing schemes by which it was processed into caustic- and steam-refined salad oils was described in the preceding paper (10).

Preparation and Evaluation of Oils Containing Added Iron

A lot of commercially caustic-refined and bleached soybean oil was used. Two sets of four samples were prepared as follows. With one sample serving as a control, 0.1, 0.5, and 1.5 ppm of iron as the chloride salt in ethanol was added. One set was deodorized as described previously (14), and no citric acid was added. The other set was deodorized, and 0.01% citric acid was added on the cooling side of deodorization. Flavor evaluations were conducted according to methods described by Moser et al. (15,16) and Warner et al. (17). Initial evaluations were made by comparison of the four samples while accelerated storage (4 day, 60 C) data were obtained by comparing the control to an iron-treated sample. Peroxide values were determined by a modification of the 1-min Wheeler method (18). Peroxide development under active oxygen method (AOM) conditions were carried out according to the official AOCS method (12).

RESULTS

Composition of Crude Oil Used in Refining Study

The composition of the commercially extracted crude soybean oil used in the refining study is shown in Table I. Free fatty acids, iron, and phosphorus contents were 0.5%,

TABLE I

Composition of Crude Soybean Oil Used in Refining Study

Free fatty acids %	Iron, ppm	Phosphorus, ppm	Phosphatides, %		
			% P x 30	Acetone insol.	Extraction[a]
0.5	1.4	660	1.98	1.65	2.13

Fatty acid composition, wt % GLC					Calc.
Pal	St	OL	LO	LN	I.V.
11.0	3.9	23.0	54.6	7.5	133.9

[a] Partition between 95% aqueous methanol and petroleum ether.

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[1] Presented in part at the AOCS-AACC Symposium, Current Concepts of Food Ingredients, Chicago, March 1977.

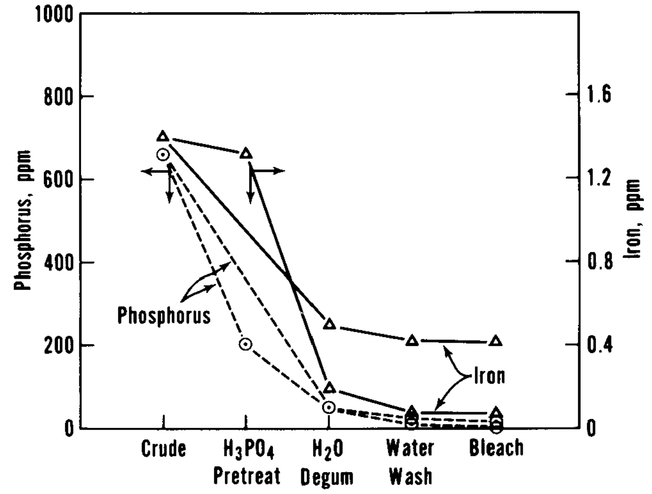

FIG. 1. Effect of phosphoric acid pretreatment on phosphorus and iron content of soybean oil prior to steam refining.

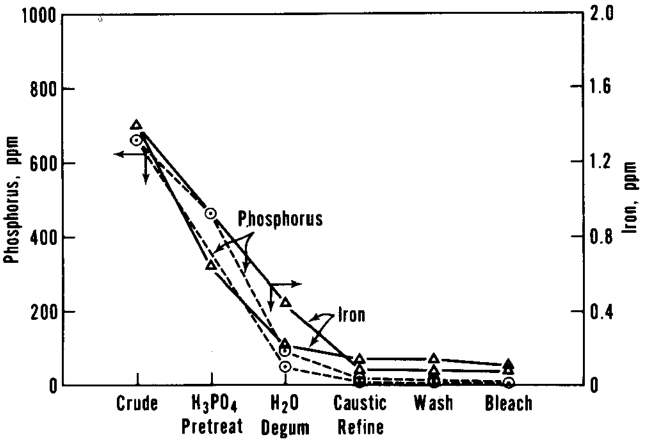

FIG. 2. Effect of degumming methods on phosphorus and iron content of soybean oil during caustic refining.

1.4 ppm, and 660 ppm, respectively. These values are in the range previously reported for good quality crude soybean oil (6). The phosphatide content determined by elemental analysis (%P x 30), acetone insoluble, and extraction shows good agreement between methods, and the average value of 1.92% is in the range previously reported in the literature (19). The fatty acid composition and iodine value are also typical.

Effect of Phosphoric Acid Pretreatment on Removal of Iron and Phospholipids

As cited in the introduction, thorough removal of prooxidants and phospholipids is crucial to preparing quality oils by steam-refining techniques. Accordingly, we monitored their removal during caustic and steam refining. The effect of the phosphoric acid pretreatment in the steam-refining mode is shown in Figure 1. After water degumming, the phosphorus content was reduced from 660 ppm to 53 ppm, which amounts to 92% removal. After several water washings and bleaching, the oil going to the deodorizer had a phosphorus content of ca. 15 ppm. After pretreatment of the crude oil with phosphoric acid and a subsequent water degumming, the amount of phosphorus removed was equivalent to the amount removed by water degumming alone. However, in subsequent processing steps, namely the water washings and bleaching, the phosphorus content was reduced to 3.0 ppm in the oil going to the deodorizer. Thus, phosphoric acid pretreatment had a relatively minor effect on the phosphorus content of the oil prior to steam refining. Both the phosphoric acid-pretreated and the water-degummed oils contained levels of phosphorus in the range of 2-20 ppm reported to be optimum for oxidative stability (20).

The effects of the phosphoric pretreatment are more apparent in the iron removal data. Pretreatment with phosphoric acid, while removing relatively little iron per se, reduced the iron from 1.4 ppm in the crude oil to ca. 0.2 ppm after water degumming. After water washings and bleaching, the oil going to the deodorizer and an iron content of less than 0.1 ppm. The crude soybean oil not receiving the pretreatment (water degumming alone) had an iron content of 0.5 ppm after water degumming. However, unlike the phosphoric acid-pretreated oil, where further iron removal results, little iron was removed in the subsequent water washings and bleaching steps. Changes in phosphorus and iron content of the crude soybean oil during caustic processing are shown in Figure 2. Although some variations were observed from run to run, particularly in the amounts of iron and phosphorus removed during degumming, the overall amounts of these materials left after caustic refining, washing, and bleaching were low and consistent.

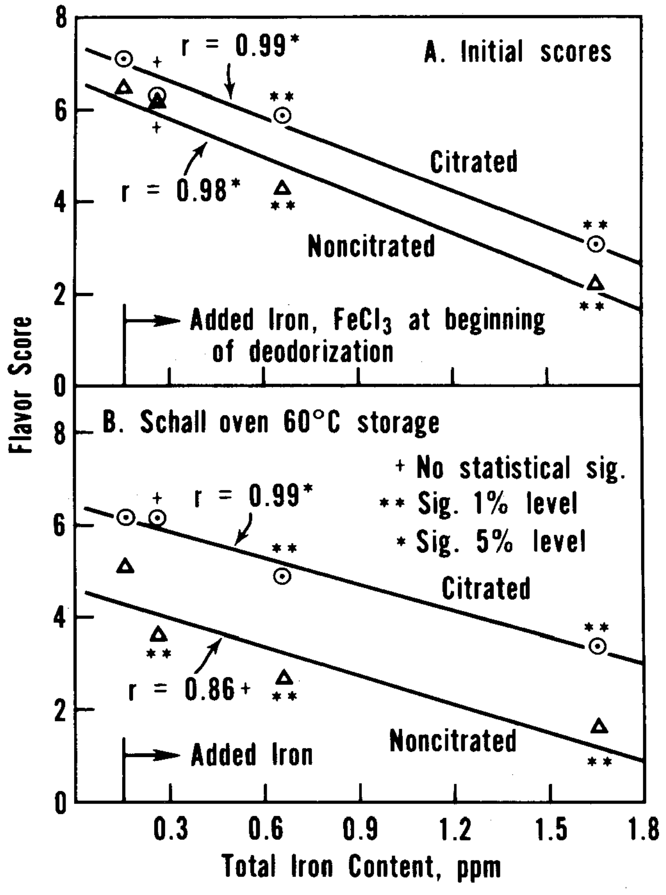

FIG. 3. Effect of iron on flavor stability of soybean oil (A) initial flavor scores, (B) flavor scores under Schall oven storage; 4 days 60 C.

In the caustic refining mode, the value of the phosphoric acid pretreatment is less apparent since the iron and the phosphorus contents of oils so treated were not markedly different than those given a water degumming only. The phoshporus and iron contents of phosphoric acid-pretreated oils going to the deodorizer were 2.7 and 0.11 ppm, respectively. Straight water-degummed, alkali-refined, washed and bleached oils prior to deodorization had phosphorus and iron contents of 4.0 ppm and 0.08 ppm, respectively.

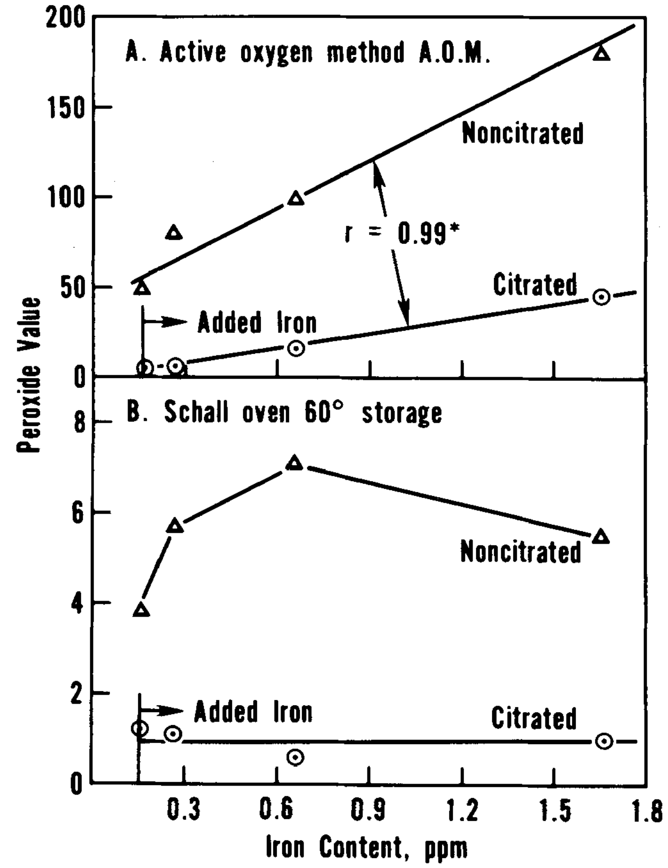

FIG. 4. Effect of iron on oxidative stability of soybean oil (A) active oxygen method (AOM) conditions, (B) Schall oven storage conditions; 4 days 60 C.

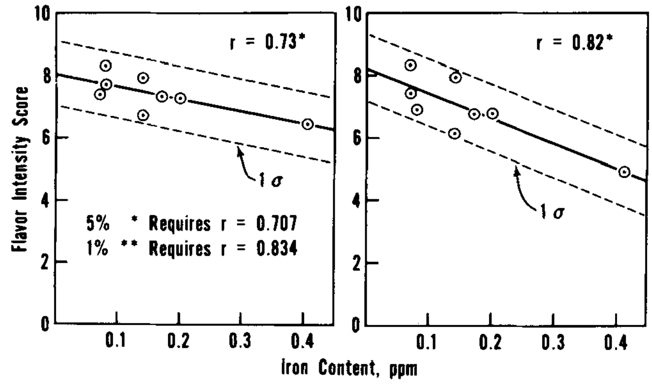

FIG. 5. Effect of iron on initial flavor intensity scores of freshly deodorized soybean oils.

Effects of Added Iron and Citric Acid on Flavor and Oxidative Stability

In light of current results, a review of the effects of iron and citric acid on the flavor of soybean oil is appropriate. Figure 3 shows the effect of iron on the flavor and stability of soybean oil deodorized with and without citric acid. Part A of Figure 3 shows a plot of initial flavor scores vs. the total iron content which includes 0.16 ppm natural iron left from processing and the iron added as the chloride salt.

Iron added at the 0.1 ppm level (0.26 ppm total iron) had no significant effect on flavor scores. However, the difference between the control and the sample containing 0.5 and 1.5 ppm added iron (0.66 and 1.66 ppm total iron, respectively) both were significant at the 1% confidence level.

The stabilizing effect of citric acid is apparent from the results. Oil treated with citric acid scored about one flavor score unit higher than uncitrated oils.

Part B of Figure 3 presents results obtained after 4-day storage under Schall oven accelerated storage conditions. Iron added at the 0.1 ppm level had no significant effect on flavor score in the presence of citric acid, but as discussed above differences between the control and the 0.5 ppm and 1.5 ppm level were significant at the 1% confidence level. In the absence of citric acid all levels of added iron significantly lowered the flavor stability of the oil. In contrast to the 1 unit improvement in initial scores afforded by treatment with citric acid, the improvement under accelerated storage conditions amounts to about 2 units. With the exception of the noncitrated oils under 60 C storage conditions, the correlations between flavor scores and iron content are high (0.98-0.99 and significant at the 5% confidence level.

The effects of iron on the oxidative stability of citrated and noncitrated soybean oil under active oxygen method (AOM) and Schall oven 60 C storage conditions are shown in Figure 4 (Parts A and B, respectively). Under AOM conditions (Part A) oxidative stability is a direct function of iron content. The high correlations (0.99) between peroxide development and iron content are significant at the 5% confidence level. Under Schall oven 60 C storage, peroxide development was erratic and showed no statistical correlations with iron content. At levels of 1.5 ppm added iron, the peroxide value of the noncitrated soybean oil after 4 days' storage was lower than that of the 0.5-ppm sample. Perhaps 1.5 ppm iron exerts such a strong prooxidant effect that considerable breakdown of fat hydroperoxides had occurred.

Results obtained with citrated oils also showed no statistical correlation between iron content and peroxide development under the test conditions. However, it is interesting to note that extensive flavor deterioration (Fig. 3, Part B) has occurred at low levels of peroxide development, i.e., ca. 1.

Nonetheless, despite showing poor correlation between iron content and oxidative stability under Schall oven conditions, the results presented in Part B of Figure 4 show the marked improvement in oxidative stability resulting from treatment with citric acid.

Prooxidant Properties of Iron Compounds in Steam-Refined Soybean Oil

The high correlations between flavor scores and added iron (Fig. 3) suggested that similar relationships might be found for caustic- and steam-refined oils produced in the refining study. Accordingly, the flavor scores were plotted against their iron contents, and the results are presented in Figure 5. The dashed lines represent one standard deviation of the taste panel data, which generally amounts to approximately one flavor score unit. The correlation coefficients of 0.73 and 0.82 for citrated (Part A) and noncitrated oils (Part B), respectively, are significant at 5% confidence level. Significance requires r equal to 0.707. Significance at the 1% level requires r equal to 0.834. Thus, for noncitrated oils the observed correlation borders on statistical significance at the 1% level. Evans et al. (2) found poor correlations between the iron content and stability of commercially processed oils and attributed this to the use of metal-inactivating agents by processors. However, laboratory-refined oils to which known amounts of iron were added showed high correlations between iron content and stability. A similar correlation resulted when iron was added to refined oils known to contain no added metal inactivators. Results presented here (Figs. 3-5) are in accord with these observations.

Evidence gained from evaluations of citrated and non-

TABLE II

Effect of Citric Acid on Flavor and Oxidative Stability of Caustic- and Steam-Refined Soybean Oil

Degumming	Refining	Initial flavor scores and sig[a]			4 Days storage flavor scores and sig[a]		
		Noncitrated		Citrated	Noncitrated		Citrated
Water	Steam	5.6(0.3)	+	6.0(0.1)	5.1(8.9)	+	5.5(0.5)
Water	Caustic	6.1(0.4)	+	6.7(0.5)	4.6(8.7)	**	6.6(1.3)
Phosphoric acid	Steam	7.1(0.1	+	7.9(0.1)	4.9(3.0)	**	6.6(2.0)
Phosphoric	Caustic	6.2(0.4)	**	8.4(0.1)	5.7(1.7)	**	6.9(0.7)

		Peroxide development under active oxygen method (AOM) conditions – 8 hr		
		Noncitrated	Citrated	Iron content, ppm
Water	Steam	41.8	15.8	0.41
Water	Caustic	63.4	5.6	0.08
Phosphoric acid	Steam	25.6	11.6	0.08
Phosphoric acid	Caustic	38.6	8.0	0.14

[a] + Denotes no statistical significance; ** denotes significance at 1% confidence level; values in parentheses are peroxide values at time of tasting.

citrated oils suggests that iron remaining in caustic and steam-refined oils possess different prooxidant properties. Table II presents paired sample evaluations showing the effect of citric acid on the flavor and oxidative stability of steam- and caustic-refined oils. Also included are peroxide values at the time of tasting and those developed under the AOM test (8 hr, 98.6 C, 1.5 ml air/sec). Evaluations of freshly deodorized oil showed only slight improvmenet by citration. The one exception was phosphoric acid-degummed, caustic-refined oil where a highly significant improvement resulted.

In accelerated storage tests citric acid, as would be expected (5), significantly improved the flavor stability for all samples except the water-degummed, steam-refined oil. Lack of improvement afforded by citration of the water-degummed, steam-refined oil is unexpected since its iron content is the highest encountered in the study. A comparison of water-degummed oils in the steam- and caustic-refining mode shows that the former contains 5 times as much iron (0.41 vs. 0.08). However, peroxide levels at the time of tasting (noncitrated) were about equal (8.9 vs. 8.7). Similarly, in the AOM tests, the water-degummed, caustic-refined oil (noncitrated) showed poorer oxidative stability than its steam-refined counterpart. Water-degummed, caustic-refined and phosphoric acid-degummed, steam-refined oils both contained 0.08 ppm iron, yet the caustic-refined oil (noncitrated) had an AOM peroxide value nearly 2½ times as great (63.4 vs. 25.6). These results suggest that, at equal concentrations, iron compounds left in soybean oil after steam refining may be less deleterious than those from caustic refining, particularly in the absence of a metal inactivator, i.e., citric acid.

DISCUSSION

Ziels and Schmidt (1) studied the effects of deodorizing a cottonseed oil shortening (IV 70) in the presence of various metals and alloys. They concluded that (a) all metals with the exception of aluminum and nickel exert some catalytic prooxidant effect. (b) The metal effect as a rule increases with temperature. (c) The formation of soaps was suggested by interaction of the metal with free fatty acids.

Beal and Lancaster (21) extended the study of Ziels and Schmidt to soybean oil and produced more definitive data on the mechanism of iron contamination relative to stability. Their data demonstrated that: (a) lowered stability results from the combination of metal, acid, high temperature, and violent agitation; (b) iron soaps are prooxidants; (c) inorganic iron compounds vary in their prooxidant activity, i.e., ferric citrate or ferrous sulfate are probably not prooxidants, but ferric chloride is; and (d) with mild agitation sobyean oil is not appreciably contaminated by contact with clean steel surfaces unless the free fatty acid content is above 0.1% and the temperature above 150 C.

Interpretation of results on the prooxidant effects of iron compounds in steam-refined oils is complicated by a lack of knowledge of their structure(s). Pokorny (22) has stated that the iron compounds in crude oils are of unknown structure but are not important, since they are removed by caustic refining. Furthermore, the new compounds formed during processing contribute in much higher degree to the reduction of stability toward rancidification. High correlation (6) found between the free fatty acid content of commercially extracted crude soybean oils and their iron content suggests that iron exists in crude oils as soaps formed by reaction of free fatty acids with steel processing equipment. Unpublished data indicate that enzymatic processes occurring within the bean can effect release of iron compounds into the crude oil upon extraction with hexane. Thus iron compounds in crude oil may exist as soaps, known to be prooxidants (21), or may be bound to proteins, phospholipids, or other minor constituents such as tocopherols, sterols, or secondary oxidation products. Because of the particularly detrimental effects of iron at deodorization temperatures (20), it appears that oxidation resulting from incomplete removal of iron compounds during water degumming is the cause of poor quality of such steam-refined oils. The function of phosphoric acid in the degumming of soybean oil appears to be an alteration of the iron compounds so that they are more readily removed in subsequent processing steps.

It should be pointed out that these processing studies were carried out under idealized conditions and in all-glass equipment. In commercial operations use of phosphoric acid-degumming agent may effect release of iron into the oil through corrosion of steel processing equipment. Another factor to be considered in the steam-refining process is the reduction of free fatty acids during deacidification-deodorization. While the free fatty acid content of fully processed caustic-refined oils ranged from 0.02-0.04%, steam-refined oils contained about 0.2% free fatty acids (60% reduction from the crude) under the steam-refining conditions employed (1 hr, 260 C, >1 mm Hg). In general, while these conditions were suitable for removal of flavor-bearing materials, complete reduction of free fatty acids was not achieved. This is not totally unexpected, since published results with high-acid fats like palm kernel and sansa olive oil (23) show that deacidification is rapid during the early stages but levels off during the latter stages of steam refining. Soybean oil containing 0.2% free fatty acids could possibly pick up traces of iron through corrosion of stainless-steel deodorizers (21). Conditions necessary for more complete reduction of free fatty acids of soybean oil during steam refining are currently being investigated.

Studies presented here indicate that improved degumming methods will be required to reduce the content of iron to low levels. While phosphoric acid pretreatment achieves this purpose, its use in commercial operations has several disadvantages. European refiners have sought alternative degumming agents because phosphoric acid contributes to pollution (24). Private reports indicate that use of phosphoric acid poses problems for processors who recover soybean lecithin, since the gums recovered from phosphoric acid-pretreated oils are darker than those obtained from water degumming. A possible way to alleviate this problem would be to reverse the degumming sequences, i.e., degum with water, recover the majority of the lecithin and, finally, degum with phosphoric acid.

ACKNOWLEDGMENTS

K. Warner assisted with the organoleptic evaluations. The NRRC taste panel evaluated the oils. W.F. Kwolek gave statistical assistance.

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[Received October 10, 1977]