Quality of Oil from Damaged Soybeans[1]

G.R. LIST, C.D. EVANS, K. WARNER, R.E. BEAL, W.F. KWOLEK,[2]
L.T. BLACK and **K.J. MOULTON**, Northern Regional Research Center,
ARS, USDA, Peoria, Illinois 61604

ABSTRACT AND SUMMARY

Various processing steps were explored in an attempt to improve the quality of oil from field- and storage-damaged soybeans. A crude soybean oil (5.7% free fatty acid) commercially extracted from damaged soybeans was degummed in the laboratory with different reagents: water, phosphoric acid, and acetic anhydride. Two alkali strengths, each at 0.1 and 0.5% excess, were used to refine each degummed oil. After vacuum bleaching (0.5% activated earth) and deodorization (210 C, 3 hr), these oils were unacceptable as salad oils. A flavor score of 6.0 or higher characterizes a satisfactory oil. Scores of water and phosphoric acid degummed oils ranged from 4.5 to 5.1, while acetic anhydride degummed oils averaged 5.6. Flavor evaluations of (phosphoric acid degummed) single- and double-refined oils (210 C deodorization) showed that the latter were significantly better. Flavor scores increased from 5.0 to about 6.0. To study the effects of deodorization temperature, the crude commercial oil was alkali-refined, water-washed and bleached with 0.5% activated earth, but the degumming step was omitted. Flavor evaluation of oil deodorized at 210, 230, and 260 C showed that each temperature increment raised flavor scores significantly. Further evaluations of specially processed oils (water, phosphoric acid, and acetic anhydride degummed oils given single and double refinings and deodorized at 260 C) showed that deodorization temperature is the most important factor affecting the initial quality of oil from damaged beans. Flavor evaluations showed that hydrogenation and hydrogenation-winterization treatments produced oils of high initial quality, but with poorer keeping properties than oils from normal beans. No evidence was found implicating nonhydratable phosphatides in the oil flavor problem. Iron had a deleterious effect in oils not treated with citric acid during deodorization.

INTRODUCTION

The poor quality of crude and finished salad oils from damaged soybeans has periodically concerned oil processors for many years (1,2). Mature beans remaining in the field during prolonged wet weather can become field or weather damaged (3). Further damage can result if beans with high-moisture contents are placed in storage (3).

Crude oils from damaged soybeans are dark colored and cannot be processed to light-colored salad oils (1). In addition, free fatty acids increase giving rise to high refinery losses (3).

More importantly, finished salad oils processed from such crudes are of inferior quality. Sanders (1) reported that salad oils processed from 30% damaged beans were barely edible. Hutchins' (2) data showed that freshly deodorized oils from damaged beans were of poor to fair quality and had inferior keeping properties.

In 1971 (4,5), much of the southeast portions of the United States during the harvest season experienced wet weather that resulted in damage to much of the soybean crop. Extensive damage to the 1971 soybean crop prompted investigations by the U.S. Department of Agriculture. Robertson et al. (6) have presented chemical evidence that crude oil from field- and storage-damaged beans is of poor quality. Their data showed that phospholipids are progressively destroyed during damage and suggested the formation of nonhydratable phosphatides is the first stage in the rapid deterioration of phospholipids in damaged soybeans.

Studies conducted at the Northern Center have linked poor flavor to oxidation and the high iron content of damaged oil (7,8). We now have found some methods to be effective in improving the quality of salad oils processed from a crude oil from severely damaged beans. These include phosphoric acid degumming, double alkali refining, hydrogenation, and high temperature deodorization.

MATERIALS AND METHODS

A 55-gal drum of crude soybean oil, processed from the 1971 damaged crop, was obtained from a processor located in the southeastern area of United States. The crude oil contained 5.7% free fatty acids, 312 ppm phosphorous, and 5.5 ppm iron. Gas liquid chromatographic (GLC) analyses after transesterification showed the following area percent: Pal 11.2, St 4.4, 01 27.4, Lo 51.0, Ln 6.1. Calculated iodine value (IV) was 127.4.

Oil Processing

Data relating to processing of salad oils (A-L) are given in Table I.

Degumming

The crude oil was degummed by weight with 2% water, 0.25% acetic (9) anhydride, or 0.1% phosphoric acid (10) according to the following procedure. Oil (900 g) was heated to 60 C under nitrogen and transferred to a Waring Blender. The degumming agent was added and the mixture stirred for 3 min. When either acetic anhydride or phosphoric acid was the degumming agent, 2% water (by weight of the oil) was added and the mixture blended for another 3 min. Degummed oils were recovered by centriguation and decantation.

Alkali Refining

Degummed oils were refined with either 9.5 (14° Bé) or 14.4% (20° Bé) sodium hydroxide at excesses of 0.1 and 0.5%. Degummed oil (700 g) was placed in the food blender with the required amount of alkali, and the mixture was stirred for 10 min. The refined oils were washed with 180 ml water and recovered by centrifugation and decantation.

Bleaching and Deodorization

The degummed, refined, water-washed oils were vacuum dried, bleached under vacuum with 0.5% by weight activated clay (Filtrol Corporation, Vernon, CA), and deodorized 3 hr at 210 C (11).

Unless otherwise noted, all oils were treated with 0.01% citric acid on the cooling side of deodorization.

Nondegummed Oils

Crude oil (10 kg) was refined with 1 kg of 10.5% sodium hydroxide, washed with 20% water, vacuum dried, and

---

[1] Presented at AOCS Meeting, Philadelphia, September 1974.

[2] Biometrician, North Central Region, ARS, USDA, Stationed at the Northern Center.

TABLE I

Processing, Oxidative Stability, and Metal Contents of Salad Oils from Crude Oil from Field- and Storage-Damaged Soybeans

Oil	Degumming agent	Method[a]	Alkali Refining		Bleaching with activated earth, %	Deodorization (3 hr) temperature, C	Active oxygen method peroxide value, 8 hr	Iron content, ppm	Phosphorus content ppm
			Alkali, %	Excess, %					
A	Water	Single	9.5	0.1	1/2	210	5.1	0.15	2.4
B	Water	Single	9.5	0.5	1/2	210	5.8	0.09	2.7
C	Water	Single	14.4	0.1	1/2	210	3.7	0.17	2.2
D	Water	Single	14.4	0.5	1/2	210	4.3	0.14	1.3
E	Phospboric acid	Single	9.5	0.1	1/2	210	2.9	0.15	2.4
F	Phosphoric acid	Single	9.5	0.5	1/2	210	3.5	0.11	2.7
G	Phosphoric acid	Single	14.4	0.1	1/2	210	3.5	0.13	2.7
H	Phosphoric acid	Single	14.4	0.5	1/2	210	3.6	0.13	2.9
I	Acetic anhydride	Single	9.5	0.1	1/2	210	2.4	0.13	1.5
J	Acetic anhydride	Single	9.5	0.5	1/2	210	3.1	0.13	0.6
K	Acetic anhydride	Single	14.4	0.1	1/2	210	3.1	0.13	1.1
L	Acetic anhydride	Single	14.4	0.5	1/2	210	3.3	0.12	0.9
Special Processing									
M	Phosphoric acid	Double	9.5	0.1	1/2	210	4.2	0.12	1.0
N	Phosphoric acid	Double	9.5	0.3	1/2	210	4.6	0.15	0.6
O	None	Single	9.5	0.1	1	210	2.0	0.10	2.1
P	None	Single	9.5	0.1	1	230	5.1	0.10	2.1
Q	None	Single	9.5	0.1	1	260	5.5	0.10	2.1
R	Water	Single	9.5	0.1	1/2	260[b]	5.8	0.19	2.1
S	Water	Single	9.5	0.1	1/2	260	4.8	0.19	5.5
T	Acetic anhydride	Single[c]	9.5	0.1	1/2	260	5.4	0.19	3.4
U	Acetic anhydride	Single	9.5	0.1	1/2[d]	260	7.9	0.16	3.0
V	Acetic anhydride	Double	9.5	0.1	1/2	260	7.8	0.14	2.2
W	Acetic anhydride	Double	9.5	0.1	1/2[d]	260	10.6	0.14	2.1
X	Phosphoric acid	Single	9.5	0.1	1/2	260	2.2	0.16	5.4
Y	Phosphoric acid	Double	9.5	0.1	1/2	260	3.0	0.12	6.4
Z	Water	Double	9.5	0.1	1/2	260	5.2	0.16	0.4

[a] Second refining made with 17.9% alkali, 0.1% excess.

[b] Deodorized 1 hr.

[c] Parent oil from which hydrogenated oils were prepared.

[d] Bleaching agent was activated carbon.

bleached with 0.5% activated clay in pilot-plant equipment (Table I, oils 0-Q). Deodorizations were carried out for 3 hr at 210, 230, and 260 C (11).

Specially Processed Oils

Crude oil was degummed with the appropriate reagent as described previously. Single refined oils were prepared with 9.5% alkali and 0.1% excess. Double refined oils were given an additional refining with 17.9% (24° Bé) alkali and 0.1% excess. The refined, washed, and dried oils (Table I, oils M-Z) were vacuum bleached with either 0.5% activated clay or activated carbon (Darco G-60, ICI America, Wilmington, DE). Deodorizations were carried for 3 hr at 260 C unless otherwise noted (Table I).

Hydrogenated and Hydrogenated-Winterized Oils

Crude oil (ca. 900 g) was charged into the food blender and refined with 90 g of 9.5% aqueous sodium hydroxide. After removal of the soapstock by centrifugation, the oil was recovered by decantation, washed with 180 ml water, dried under vacuum, and bleached with 0.5% activated clay.

Bleached oil (2000 g) was hydrogenated at 175 C (10 psi) in a 1-gal converter in the presence of 0.1% Girdler G-15 nickel catalyst. After removal of the catalyst by vacuum filtration, the oil was post-bleached (1% activated clay) under vacuum. Winterization for 3 days at 34 F yielded 73% liquid oil. Composition by GLC showed Pal 10.1, St 5.5, Ol 53.3, Lo 29.6, and Ln 1.5. Calculated IV was 101.0. The hydrogenated-winterized oil was deodorized 3 hr at 210 C.

Hydrogenated soybean oils (HSBO) (nonwinterized) were prepared from the crude oil by acetic anhydride degumming, single alkali refining, water washing, and bleaching with 0.5% activated clay as described previously. The degummed, refined and bleached oil (ca. 1100 g) was hydrogenated in a 2-liter stirred autoclave at 150 C (60 psi) with 0.2% Girdler G-15 nickel catalyst. After hydrogenation, the oils were filtered under vacuum to remove the catalyst and vacuum bleached with 1% super filtrol. Two hydrogenated oils were prepared: IV's 111.0 and 93.4. Their respective compositions by GLC were Pal 10.6, St 6.6, Ol 39.8, Lo 39.9, and Ln 3.0; Pal 11.0, St 7.4, Ol 56.9, Lo 22.8, and Ln 2.4. Deodorizations were conducted 3 hr at 260 C.

Control Oils.

The control soybean oils (processed from sound beans) used in some of the flavor evaluations were single lots obtained from commercial oil processors or purchased in local retail markets.

Oil Evaluations and Analyses

Flavor evaluations were conducted according to methods described by Moser et al. (12). Flavor data were supplied by a 20-member taste panel with two samples usually evaluated per panel session. Accelerated storage tests, peroxide values (PV), active oxygen method (AOM), and GLC analyses were carried out as described previously (13). Iron, phosphorous, and free fatty acids analyses were conducted according to established procedures (8,14).

RESULTS

Qualtiy of Conventionally Processed Oils

Small lots of the crude soybean oil from damaged beans were processed by treatments believed to be comparable to those in the commercial production of salad oils. Flavor evaluations of these oils are summarized in Table II.

Oils A-L (Table II) represent oils degummed with water,

TABLE II

Quality of Salad Oils from Damaged Soubeans: Effects of Degumming Agents, Alkali Strengths and Excesses and Single vs. Double Refining at Low Deodorization (210 C) Temperatures

Oil[a]	Initial flavor score and sig[b]	Predominant flavors
	Water Degummed, Single Refined	
A	4.7 (0.2)	Rancid, buttery, rubbery
B	4.7 (0.1) +	Rancid, buttery, grassy
C	4.8 (0.3)	Rancid, painty, grassy
D	5.0 (-) +	Rancid, grassy
	Phosphoric Acid Degummed, Single Refined	
E	4.9 (0.2)	Rancid, grassy, rubbery
F	4.5 (0.3) +	Rancid, grassy
G	4.8 (0.2)	Rancid, grassy
H	5.1 (0.2) +	Rancid, grassy
	Acetic Anhydride Degummed, Single Refined	
I	5.7 (0.4)	Rancid, buttery
J	5.7 (0.3) +	Rancid, buttery
K	5.7 (0.3)	Rancid, grassy
L	5.2 (0.3) +	Rancid, rubbery
	Acetic Anhydride vs. Water and Phosphoric Acid Degumming	
J	5.3 (0.2)	Grassy, rancid, beany
B	4.5 (0.3) *	Rancid, grassy, beany
J	5.5 (0.3)	Rancid, buttery, rubbery
F	5.4 (0.2) +	Rancid, rubbery, buttery
F	4.9 (0.1)	Rancid, grassy, buttery
B	5.4 (0.2) +	Rancid, grassy, buttery
	Phosphoric Acid Degummed, Single vs. Double Refining	
E	5.2 (0.1)	Rancid, grassy, beany
M	5.9 (0.1) *	Rancid, grassy, beany
F	5.1 (0.5)	Rancid, grassy, rubbery
N	6.2 (0.2) **	Grassy, buttery, beany

[a] See Table I.

[b] Values in parentheses are peroxide values at the time of tasting; in all tables + denotes no statistical sig, * sig at 95% level, ** sig at 99% level.

TABLE III

Effect of Deodorization Temperature and Time on Quality of Crude Oil from Damaged Soybeans

	Flavor scores and sig[a]		
	Deodorization for 3 hr[b]		
Days storage, 60 C	210 C	230 C	260 C
0	5.7 (0.5) **	6.7 (0.5)	
0		6.1 (0.5) **	6.8 (0.7)
0	5.1 (N.D.)	**	6.7 (N.D.)
Predominant flavors	Rubbery Rancid Grassy	Buttery Grassy Rancid	Buttery Beany Nutty
4	5.3 (2.0) +	5.6 (1.9)	
4		5.7 (N.D.) +	5.6 (N.D.)
4	5.2 (1.7)	+	5.7 (1.4)
	Deodorization time 260 C[c]		Commercial control from normal beans
	1 hr	3 hr	
0	7.8 (0.3) +	7.5 (0.2)	
0		6.7 (0.1) +	7.1 (0.1)
0	6.5 (0.1)	**	7.7 (0.0)
Predominant flavors	Buttery	Buttery Beany	Buttery Beany
4		5.3 (1.1) **	6.0 (1.5)
4	5.8 (1.0)	**	6.8 (1.6)
4	5.4 (1.1) +	5.9 (1.2)	

[a] See footnote b, Table II; N.D. = not determined.

[b] Oils O, P, and Q, Table I.

[c] Oils R and S, Table I.

phosphoric acid and acetic anhdyride, but each was given single alkali refinings at two alkali strengths and two excesses. For each degumming agent, the alkali strength or excess has no perceptible effect on initial oil quality. In subsequent tests, except where double refining was conducted, oils were refined with 9.5% alkali and 0.1% excess.

High-quality soybean salad oils, when processed from crude oils from normal beans, have bland, mildly beany, buttery or nutty flavors and will receive flavor scores in the 7-8 range on a 10-point (1 = bad, 10 = excellent) scoring scale. A flavor score of 6 is generally considered the breakpoint between satisfactory and unsatisfactory oils.

As shown in Table II, none of the 12 (A-L) oils would be considered acceptable as salad oils since no processing treatment produced an oil scoring 6.0 or better in flavor tests. In contrast to the bland, buttery, or beany flavors of high-quality salad oils, the damaged samples were described as rancid, grassy, painty, and rubbery. Because of their poor initial flavor scores, accelerated storage tests were not conducted on these samples. Although oil degummed with acetic anhydride failed to score 6.0 or above in organoleptic tests, their mean flavor scores are somewhat higher than oils degummed with either water or phosphoric acid.

Direct comparison of water, phosphoric acid and acetic anhydride degummed oils showed that acetic anhydride was significantly better than water but equal to phosphoric acid. Water and phosphoric acid degummed oils were not scored significantly different.

Phosphoric acid pretreatment and double refining of crude oil reportedly produce a salad oil of superior flavor and oxidative stability (15). Accordingly, we compared phosphoric acid degummed oils given single and double reginings. Although of borderline quality, double-refined oils scored significantly higher in flavor tests. Initial scores increased from about 5 to 6.

On the basis of data given in Table II, it became apparent that ordinary laboratory processing would not produce an oil scoring much above 6 in flavor tests and that other methods would be required to improve initial quality.

Deodorization Temperature and Time vs. Oil Quality

For many years it has been our standard practice to deodorize soybean oil for 3 hr at 210 C under a vacuum of less than 1 mm Hg. As discussed previously (Table II), these conditions failed to produce an oil scoring 6 or better in flavor tests. Increasing the deodorization temperature (oils O-Q not degummed) from 210 to 230 C improved initial flavor scores significantly (Table III). Similarly, oil deodorized at 260 C received a significantly higher flavor score than oil deodorized at 230 C. By increasing the deodorization temperature from 210 to 260 C, the initial score was raised from about 5.5 to 6.8. In comparison to water and phosphoric acid degummed oils (Table II), this increase amounts to about two flavor score units. Further evidence of the improvement in initial quality is noted by the changes in flavor descriptions with increasing deodorization temperature. The undesirable rubbery, rancid, and grassy flavors predominant in the 210 C oil are replaced by the more desirable buttery, beany, and nutty flavors at the 260 C deodorization temperature.

Accelerated storage tests indicated that the oils deteriorated to the same degree regardless of deodorization temperature. The slight differences favoring oils deodorized at 230 C and 260 C are not statistically significant.

The quality of soybean oil is related not only to deodorization temperature but to time as well. Generally, when temperatures are high, deodorization time should be short and, when temperatures are low, vice versa, to achieve the best balance between both initial quality and keeping properties (16). Accordingly, we undertook some evaluations of damaged samples (oils R and S, water degummed) deodorized at 260 C for 1 hr and for 3 hr (Table III). Throughout this study we observed that the taste panel scored damaged samples given different processing treatments higher, compared against each other, then against undamaged controls. To serve as an internal control, the better quality oils from damaged beans were compared against a single lot of high quality commercial soybean salad oil. Initially, the 1- and 3-hr oils scored high and were equal with no significant differences evident; the 3-hr oil was not significantly lower than the undamaged control. However, the 1-hr oil scored significantly lower than the undamaged control. After 4 days storage at 60 C, both oils from damaged beans had deteriorated to the same degree but had inferior keeping properties compared to the control. Previous work (13) has shown that the flavor deterioration of unhydrogenated soybean salad oil occurring during 4 days storage at 60 C is equal to about 3 months storage at room temperature.

Quality of Specially Processed Oils

Flavor evaluations of single-refined, acetic anhydride degummed oils and double-refined, phosphoric acid degummed oils (Table II) had indicated slight improvements in initial quality at low (210 C) deodorization temperatures. Deodorization evaluations (Table III) showed that temperature is a key factor in improving damaged oil quality. Our previous report (7) demonstrated that carbon treatment and rededorization significantly improved the initial flavor score of a salad oil commercially processed from damaged beans. On the basis of these observations, we

TABLE IV

Quality of Acetic Anhydride Degummed Oil: Comparison of Single and Double Refining and Activated Earth vs. Carbon Bleaches at High (260 C) Deodorization Temperature

Days storage, 60 C	Flavor scores and sig[a]				Commercial control from normal beans
	Activated earth		Carbon		
			Single refined[b]		
0	6.8 (0.3)		*		7.7 (0.2)
0			5.7 (0.2)	**	7.3 (0.2)
0	7.7 (0.1)	*	7.3 (0.0)		
4	6.0 (1.2)		+.		6.5 (1.1)
4	6.2 (0.7)	**	5.2 (0.7)		
4			5.1 (1.1)	**	7.0 (1.0)
			Double refined[c]		
0	6.7 (0.3)		*		7.6 (0.1)
0			6.4 (0.3)	**	7.6 (0.1)
0	6.5 (0.4)	+	6.2 (0.3)		
4	5.3 (1.4)		+		5.8 (1.4)
4			4.7 (1.5)	*	5.6 (1.3)
4	6.3 (1.7)	*	5.7 (1.9)		

[a] See footnote b, Table II.

[b] Oils T and U, Table I.

[c] Oils V and W, Table I.

TABLE V

Quality of Phosphoric Acid and Water Degummed Oil: Effect of Double Refining at High (260 C) Deodorization Temperature

Days storage, 60 C	Flavor scores and sig[a]				Commercial control from normal beans
	Single refined		Double refined		
			Phosphoric Acid Degummed		
0	7.2 (0.0)		+		7.7 (0.1)
0			6.5 (0.0)	+	7.1 (0.2)
0	7.2 (0.0)	+	6.8 (0.0)		
4	5.8 (0.7)		+		6.0 (1.0)
4			5.1 (0.8)	+	5.4 (1.0)
4	6.7 (0.7)	*	5.6 (0.8)		
			Water Degummed[c]		
0	6.7 (0.1)		+		7.1 (0.1)
0			6.4 (0.0)	*	7.4 (0.1)
0	6.8 (0.0)	+	7.3 (0.0)		
4	5.3 (1.1)		*		6.0 (1.5)
4			6.0 (1.1)	+	6.2 (1.1)
4	6.2 (1.2)	+	5.9 (1.2)		

[a] See footnote b, Table II.

[b] Oils X and Y, Table I.

[c] Oils S and Z, Table I.

TABLE VI

Quality of Oil from Damaged Soybeans: Effect of Hydrogenation and Hydrogenation-Winterization

Days storage, 60 C	Flavor scores and sig[a]					Commercial[b] HWSBO (IV 112) (sound beans)
	HWSBO (IV 101)	HSBO (IV 111)		HSBO (IV 93)		
0	6.9 (0.2)		+			7.2 (0.1)
0		8.0 (0.1)	+			7.6 (0.1)
0				7.5 (0.0)	*	6.8 (0.1)
4	5.0 (2.0)		*			6.1 (1.1)
4		4.9 (1.0)	**			6.9 (0.7)
4				5.1 (1.5)	**	6.9 (0.4)
AOM 8 hr PV[b]	5.5	3.2		3.2		1.3

[a] See footnote b, Table II. HWSBO = hydrogenated winterized soybean oil; only HWSBO contained citric acid; HSBO = hydrogenated soybean oil; both HWSBO and HSBO contained 0.076% Tenox 6-antioxidant. IV = iodine value. PV = peroxide value.

[b] Contained butylated hydroxy anisole, butylated hydroxy toluene and methyl silicone.

TABLE VII

Mean Flavor Scores Compared by Degumming Agent and Deodorization Temperature

Degumming agent	Mean flavor scores and sig[a]: Deodorization temperature 210 C[b]	260 C[c]
Water	4.80	7.17
Acetic anhydride	5.59	7.11
Phosphoric acid	4.82	7.16
Mean	5.07	7.14

[a] LSD (least significant difference) between degumming methods = 0.45 flavor score unit. LSD between deodorization temperatures = 0.78 flavor score unit. Mean at 210 C based on four flavor scores; at 260 C, on two.

[b] Oils A-L, Table I.

[c] Oils S, T and X, Table I.

conducted some evaluations to determine the effects of various degumming agents, double alkali refinings, and carbon bleaches at high deodorization temperatures.

Acetic anhydride degumming: Flavor evaluations of acetic anhydride degummed oils single refined are compared by bleaching agents (carbon vs. activated clay) at high (260 C) temperature in Table IV. Flavor evaluations for double refined oils, otherwise identically processed, also appear in Table IV. Included for comparison are evaluations made against the undamaged control.

In direct comparison (Single refined oil) carbon bleached oils were scored significantly lower than the activated clay sample both initially and after 4 days storage. Comparisons made against the undamaged control showed that single refined, activated earth bleached oil scored significantly lower initially but not after accelerated storage. In initial and accelerated storage tests, the carbon bleached oil was scored significantly lower than the undamaged control.

Flavor evaluations of double refined oils bleached with either agent are similar to those for single refined oils. Apparently in processing acetic anhydride degummed oil, carbon bleaching is inferior to activated clay bleaching at high deodorization temperatures. Because of inferior keeping properties of carbon bleached oil, further studies with carbon bleaches were not made in conjunction with water and phosphoric acid processed oils.

Phosphoric acid and water degumming: Evaluations of water and phosphoric acid degummed oils compared by refining methods (single vs. double) are given in Table V, including evaluations made against the undamaged control. Direct comparison of phosphoric acid degummed oil failed to demonstrate any significant improvement by double refining either initially or in accelerated storage tests. Results were similar with water degummed oils otherwise identically processed.

Hydrogenation and hydrogenation-winterization: Since much of the soybean oil produced in the United States is processed into margarine, shortening, and hydrogenated-winterized cooking and salad oils, we conducted some experiments to determine the effects of hydrogenation and hydrogenation-winterization on the quality of oil from damaged beans (Table VI).

Initially, both the hydrogenated-winterized soybean oil (HWSBO) and the hydrogenated soybean oil (HSBO) were scored equal to or significantly higher than commercial (sound beans) HWSBO, but all damaged samples had inferior keeping properties compared to the commercial HWSBO. We have repeatedly observed that even with undamaged beans, laboratory oil processing is apt to produce HWSBO with inferior keeping properties (17). Although extensive tests were not conducted to determine the effects of various degumming agents and single vs. double refining, the data given in Table VI suggest that hydrogenation or hydrogenation-winterization may provide a suitable outlet for oil from damaged beans over a wide range of iodine values, i.e. 93-111.

Statistical Treatment of Taste Panel Scores

The number of flavor evaluations required to determine the effects of individual processing variables (degumming agents, alkali strengths and excess, bleach types and concentrations, deodorization times and temperatures) is so great that this approach is prohibitive. Instead, taste panel data were treated statistically to analyze further the effects of processing variables on flavor. A three-way analysis of variance showed that in refining, alkali concentration or percentage excess of alkali had no significant effect on oil quality, but that the degumming agent had a significant effect at low deodorization temperatures (Table I, oils A-L). At high deodorization temperatures (260 C), bleach type was a highly significant source of variation, but none of the other processing variables were significant (Table I, oils T-Z).

Although there were no direct comparisons of oils deodorized at 210 and 260 C, deodorization temperature had a highly significant effect on initial quality as shown in Table VII where the mean flavor scores of single refined activated clay bleached oils are compared by degumming methods. Since alkali concentration or percentage excess of alkali had no significant effect on initial flavor, any differences in the alkali-refining steps were ignored.

Within degumming agents, the least significant difference (LSD) is 0.45 flavor score units, whereas the LSD between temperatures is 0.78. When the difference between means exceeds the LSD values, the difference is statistically significant. The difference between oils deodorized at 260 and 210 C amounts to about two flavor score units and clearly shows that deodorization temperature is the most important factor affecting the initial quality of oils from damaged beans.

Our previous report (7) implicated high-molecular-weight carbonyl compounds as a factor in the poor quality of oil from damaged beans. Commercial and laboratory processed oils showed little or no reduction in anisidine value after deodorization. The marked improvement in flavor offered by high temperature might logically be expected to result in lower anisidine values. Indeed, oils deodorized at 260 C showed substantial decreases in anisidine reactive materials, whereas those deodorized at 210 C showed little or no reduction. A statistically significant correlation was observed between flavor scores and the percent reduction in anisidine value by deodorization. Thus the marked improvement afforded by high temperature deodorization can be attributed to more efficient removal of flavor-bearing materials (18).

Phosphorus and Iron Contents

When we were presented with the problem, many oil processors felt that a high phosphorus content caused the poor flavor in oil from damaged beans. Following his tour of the industry after World War II, Goss (19) reported this same view had been held by German oil processors who felt that citric acid improved soybean oil stability through "inactivation" of lecithin. Subsequently, Dutton et al. (20,21) showed that, instead, citric acid functions solely as a metal scavenger.

On the one hand Mattikow (22) stated that the phosphorus content of refined oil should not exceed 0.5 ppm. On the other hand, Beal et al. (23) demonstrated that deodorized soybean oil exhibits optimum stability over a range of 2-20 ppm phosphorus.

In Table I are presented phosphorous contents of deodorized salad oils processed from the crude oil we studied. All of our processing treatments removed phosphorus to low levels ranging from about 0.5 to 6 ppm. The low correlation coefficient (0.28) between initial flavor scores and phosphorus content is not statistically significant. Most phosphorous values fall within the optimum range reported earlier (23). Although nonhydratable phosphatides may contribute to high refinery losses, we find no evidence implicating phosphorus in the poor flavor of oil from damaged beans. However, it must be emphasized that vigorous contact was maintained between oil and degumming agents and alkali in our laboratory and pilot-plant refining studies.

Our previous reports (7,8) indicated that high iron contents of the crude oil contributed at least in part to the poor quality of finished salad oils. The iron contents of commercially processed oils from damaged beans and from separate plants ranged from 0.1 to 0.7 ppm, but these oils still had poor falvor and oxidative stability despite the wide range of iron. Apparently iron is difficult to remove from oil, or some processors do not use metal inactivators during deodorization. In our experience, soybean oil deodorized in the presence of 0.3 ppm or greater of iron is likely to be of poor quality even if treated with citric acid. On the one hand, where processing does not remove iron to low levels (0.1-0.2 ppm), poor quality oils are likely. On the other hand, where processing removes iron to sufficiently low levels, metal inactivators become important. Effects of citric acid on the flavor and oxidative stability of a salad oil (oil S, Table I, 0.19 ppm iron) from damaged beans are illustrated (Table VIII). Evaluations of freshly deodorized oils showed a slight, but not significant, lowering of the initial falvor score of the noncitrated sample. However, after accelerated storage at 60 C, the noncitrated sample was scored about 4 units lower than the citrated control and had deteriorated to such an extent that the panel scored the citrated sample higher after 4 days storage than it did initially. Further evidence of the deleterious effect of iron on the noncitrated sample can be seen in the increased storage and markedly higher 8 hr AOM peroxide values.

TABLE VIII

Effect of Citric Acid on Flavor and Oxidative Stability on Oil[a] from Damaged Soybeans

	Flavor scores and sig[b]		
Storage days, 60 C	Citrated		Noncitrated
0	6.5 (0.1)	+	6.2 (0.2)
4	6.9 (0.6)	**	3.1 (5.3)
AOM 8 hr PV	4.8		84.9
Iron content, ppm	0.19		0.19

[a] Oil S, Table I

[b] See footnote b, Table II.

Although all processing treatments reduced the iron content to low levels (Table I), these results emphasize the importance of using citric acid in processing of oils, particularly those from damaged beans.

DISCUSSION

Poor flavor is just one of the problems encountered in processing of oil from field- or storage-damaged beans. Private reports from industry and our own experiences have shown that crude oil from severely damaged beans is difficult to degum because of the presence of nonhydratable phosphatides. In view of the high refinery losses encountered during processing of damaged bean oil, phosphoric acid or acetic anhydride would probably be superior to water as a degumming agent. Although no attempts were made to determine actual refining losses in the small-scale studies reported here, we did observe that phosphoric acid and acetic anhydride gave a cleaner separation of gums compared to water. Both Sullivan (10) and Braae (15) have shown that phosphoric acid pretreatment decreases refinery losses.

It should also be pointed out that finished salad oils processed from damaged beans are somewhat darker than those from sound beans. For example, the sound control oil had a Gardner color of 2, whereas salad oils (O-Z) from damaged beans had Gardner colors from 5 to 6. The lightest colors were observed in phosphoric acid degummed oils. Although the color difference is slight, this would favor phosphoric acid degumming in processing of oil from damaged beans.

With other factors being equal, our results clearly show that deodorization temperature is the most important factor influencing the quality of salad oils from damaged soybeans. Modern commercial deodorizers, as reviewed by Bailey (18), vary considerably with respect to operating temperature and oil residence time. For example, a continuous deodorizer may operate from 232 to 246 C with an oil residence time of only 20 min while another may operate at about the same temperature but with an oil residence time of 54 min (18). It is difficult to translate results obtained in a small-scale laboratory-batch deodorizer with what may be expected in commercial operations. However, it would seem advisable for oil processors to deodorize soybean salad oils at maximum temperature or to increase the residence time of the oil in the deodorizer, or both.

ACKNOWLEDGMENT

G.W. Nofsinger conducted the refining studies; R.L. Reichert and J.P. Friedrich conducted the hydrogenations. B.K. Boundy assisted in the flavor evlautions.

REFERENCES

1. Sanders, J.H., Oil Soap 21:357 (1944).
2. Hutchins, R.P., Ibid. 22:165 (1945).
3. Krober, O.A., and F.I. Collins, JAOCS 25:296 (1948).
4. Anon., Soybean Dig. 32:7 (1971).
5. Anon., Ibid. 33:26 (1972).
6. Robertson, J.A., W.H. Morrison III, and D. Burdick, JAOCS 50:443 (1973).
7. List, G.R., C.D. Evans, W.F. Kwolek, K. Warner, B.K. Boundy, and J.C. Cowan, Ibid. 51:17 (1974).
8. Evans, C.D., G.R. List, R.E. Beal, and L.T. Black, Ibid. 51:444 (1974).
9. Hayes, L., and H. Wolff, Ibid. 33:440 (1956).
10. Sullivan, F.E., U.S. Patent 2,702,813 (1955).
11. Schwab, A.W., and H.J. Dutton, JAOCS 25:57 (1948).
12. Moser, H.A., H.J. Dutton, C.D. Evans, and J.C. Cowan, Food Technol. 4:105 (1950).
13. Evans, C.D., G.R. List, H.A. Moser, and J.C. Cowan, JAOCS 50:218 (1973).
14. List, G.R., C.D. Evans, and W.F. Kwolek, Ibid 48:438 (1971).
15. Braae, B., Chem. Ind. 1152 (1958).
16. Moser, H.A., P.M. Cooney, C.D. Evans, and J.C. Cowan, JAOCS 43:632 (1966).
17. McConnell, D.G., C.D. Evans, and J.C. Cowan, Ibid. 42:738 (1965).
18. Bailey, A.E., "Industrial Oil and Fat Products," 3rd Edition, Edited by D. Swern, John Wiley & Sons, New York, pp. 911, 923-927, 1964.
19. Goss, W.H., "The German Oilseed Industry," Hobart Publishing Co., Washington, DC, pp. 10, 11, (1947).
20. Dutton, H.J., H.A. Moser, and J.C. Cowan, JAOCS 24:261 (1947).
21. Dutton, H.J., A.W. Schwab, H.A. Moser, and J.C. Cowan, Ibid. 26:441 (1949).
22. Mattikow, M., Ibid. 25:200 (1948).
23. Beal, R.E., E.B. Lancaster, and O.L. Brekke, Ibid. 33:619 (1956).

[Received June 1, 1976]