Long Term Storage of Soybean and Cottonseed Salad Oils[1]

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ABSTRACT

Commercially prepared and packaged soybean and cottonseed salad oils from several different processors were evaluated periodically during storage for 12 months. Partially hydrogenated and winterized soybean oils, as well as unhydrogenated soybean salad oils, were stored in bottles and cans at 78 and 100 F. Control samples of all oils were held at 0 F during the entire test. Some lots in bottles and cans were packaged under nitrogen to improve storage stability. Agreement was good between organoleptic and oxidative evaluation of aged oils. After 26 weeks of storage at 100 F, the flavor of partially hydrogenated-winterized oils packaged under nitrogen showed a minimum loss. These same oils did not exhibit much, if any, reduction in their oxidative stability as indicated by storage peroxide values (active oxygen method). Soybean oil not protected with nitrogen demonstrated progressive flavor deterioration at 100 F. After 10 weeks of storage, the deterioration became marked and the flavor score was below 5. From limited observations, bottled oils appear to have a better stability than oils packaged in screw-cap tin cans. Hydrogenated oils packaged under nitrogen in cans had good oxidative stability, but some lowering of the flavor score was observed. Nonhydrogenated soybean oils packaged in tin cans not under nitrogen exhibited the most rapid flavor deterioration of all lots of oil investigated.

INTRODUCTION

The storage stability of salad and cooking oils for long periods concerns a number of governmental agencies, commercial users and producers, as well as the individual consumer. Public reaction usually occurs only when rancid or oily flavors lower the quality of food purchased.

Although unhydrogenated soybean salad oil is a major ingredient in salad dressings and mayonnaise (1,2), only hydrogenated soybean oil in shortening has found acceptance by the Defense Supply Agencies (3). Federal specifications for military purchases of vegetable salad oil were confined to type B oils. This limitation permitted only cottonseed or corn oils or mixtures thereof with a maximum of 0.5% linolenate (3).

At the request of the U.S. Army Natick Laboratories, we undertook cooperative studies to determine if commercially marketed soybean oil specially processed (hydrogenated-winterized) would meet the Defense Department's needs. We knew that oils produced industrially would meet their requirements except for the low linolenate content of 0.5%. After consultation with Natick, it was established that the major requirements any oil should meet were an acceptable flavor score and good oxidative stability in the original package after 6 months at 100 F. Accordingly we undertook a 12 month storage investigation of some commercially available vegetable salad oils, particularly those made with soybean oil.

MATERIALS AND METHODS

Evaluations were made on 11 lots of commercially processed salad oils, 8 soybean and 3 cottonseed. Each lot consisted of 20-40 individual cans of salad oil. Since tests were on these commercial materials, a single lot of oil packaged under various conditions was not available for evaluation. The samples are believed to represent the soybean and cottonseed salad oils available to domestic consumers. Oils purchased on the open market were packaged in both screw-capped bottles and cans. Both "specially processed" (hydrogenated-winterized) soybean oil and unhydrogenated oil containing 7-8% linolenic acid were bought. Oils purchased were packaged in both clear and brown bottles, but a study of clear vs. brown glass was not made. All samples were stored in the dark. Flavor evaluations were conducted by a 20 member taste panel using procedures described previously (4). Fatty acid analyses were determined by gas liquid chromatography (GLC) on a DEGS column at 190 C after transesterification with methanol and a sodium methoxide catalyst. Peroxide values were run on aged samples according to Wheeler's procedure (5) and after 8 hr under conditions of active oxygen method (AOM) (6).

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TABLE I

Composition of Salad Oils

Oil[a]	Calculated iodine value	Fatty acid, % (GLC)[b]					Headspace gas
		Pal	St	Ol	Lo	Ln	
Soybean							
1-B[c]	135.4	9.2	4.7	24.0	54.2	8.0	Nitrogen (2.4% O_2)
2-BH[c]	116.3	10.0	6.1	38.4	41.3	4.1	Air
3-BH[c]	115.2	9.9	6.2	38.8	40.6	4.4	Air
4-BH[c]	110.7	8.4	5.3	48.0	34.8	3.5	Nitrogen (0.0% O_2)
5-BH	111.5	10.2	5.7	43.2	37.0	3.9	Nitrogen (2.1% O_2)
6-C	135.6	10.0	4.9	23.8	53.4	8.7	Air
7-C[c]	138.1	10.3	4.5	20.4	55.2	9.6	Air
8-CH[c]	109.6	8.4	5.6	48.3	34.4	3.3	Nitrogen (0.0% O_2)
Cottonseed							
9-B	114.1	22.5	2.6	18.3	56.8	---	Nitrogen (0.0% O_2)
10-B	113.9	19.1	2.9	20.1	55.8	---	Air
11-C	116.4	20.4	2.6	16.7	59.5	---	Air

[a]B = bottle; C = can; and H = hydrogenated-winterized oil.

[b]GLC = gas liquid chromatography; Pal = palmitic; St = stearic; Ol = oleic; Lo = linoleate; and Ln = linolenate.

[c]Label indicated sample contained a mixture of antioxidants.

TABLE II

Evaluation of Salad Oils

Oil[a]	Initial flavor score	Oils aged 4 days at 60 C: Flavor score	PV[b]	AOM[b] PV after 8 hr
Soybean				
1-B	7.0	5.3	0.6	2.3
2-BH	8.6	6.8	0.4	1.3
3-BH	7.5	6.3	0.2	3.1
4-BH	7.6	6.9	1.4	2.2
5-BH	7.8	5.6	0.3	1.0
6-C	8.1	6.2	1.0	6.5
7-C	6.1	5.8	1.4	11.1
8-CH	7.9	7.5	0.5	1.3
Cottonseed				
9-B	7.9	5.9	1.5	17.9
10-B	7.3	5.7	1.1	15.9
11-C	6.6	5.9	10.9	31.7

[a]Same individual description as in Table I.
[b]PV = peroxide values; AOM = active oxygen method.

Composition of the salad oils, their packing conditions and the presence or absence of added antioxidants are given in Table I. Samples 1-B, 6-C and 7-C of unmodified soybean oil were manufactured by three different companies. Samples of hydrogenated-winterized soybean oils, packaged both in bottles and cans, came from four different sources. Some were packaged in air and some under nitrogen. Sample 5-BH was packaged under nitrogen without added stabilizers. All other hydrogenated-winterized oils were protected with multicomponent stabilizers. According to the labels, the cottonseed salad oils did not contain additives.

As shown in Table I, little difference exists in the composition of the hydrogenated-winterized oils prepared by the various processors. Iodine values vary from ca. 110 to 116; apparent linoleate levels, from 34 to 41%; and apparent linolenate values, from 3.3 to 4.4%. Because of the similarity, any differences in quality of the oils must arise from factors other than these minor differences in composition.

Headspace gas analysis of the samples was conducted by the method of Evans and Selke (7). As indicated in Table I, samples 4-BH, 8-CH and 9-B were packaged under pure nitrogen. Samples 1-B and 5-BH were partially protected by nitrogen, but oxygen was not completely eliminated from the headspace gas. All other samples packaged in air contained various levels of oxygen. Complete uptake (loss) of oxygen from the headspace had been observed by Evans and Selke (7) within 3 weeks of storage at 100 F for corn salad oil, and similar losses could be expected for other less stable oils.

For a 4 day storage test by a taste panel, samples were poured in air from the original container into 8 oz bottles (two-thirds full) and loosely stoppered with cellophane-covered corks. Samples were then stored in the dark in a forced-draft oven at 60 C for 4 days.

For long term storage tests, samples were kept in their original containers and no bottle or can was opened until the time of evaluation. When the bottles were placed in storage, all caps were checked and any bottles with loose caps discarded. Samples were stored in a 100 F ± 1 F forced-draft oven. Other samples were stored in the dark at room temperature (78 F). An equal number of control samples were frozen at -20 F, and all taste evaluations were made between the aged sample and the control sample. Fourteen evaluations were made during 1 year of storage for the 100 F samples and six evaluations were made for the 78 F samples. The 78 F samples were also evaluated after 2 years of storage. To avoid extensive tabulations, most data are presented in the form of graphs showing the loss of flavor with time for the various conditions of packaging and storage.

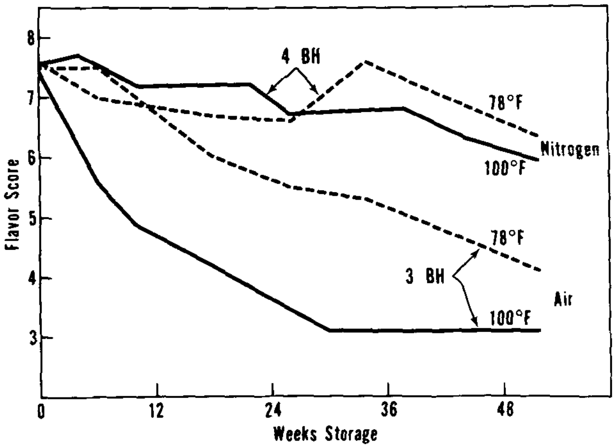

FIG. 1. Effect of nitrogen packaging (sample 4-BH) contrasted with air (3-BH) on flavor scores of hydrogenated-winterized soybean oils stored in bottles for 1 year at 78 and 100 F.

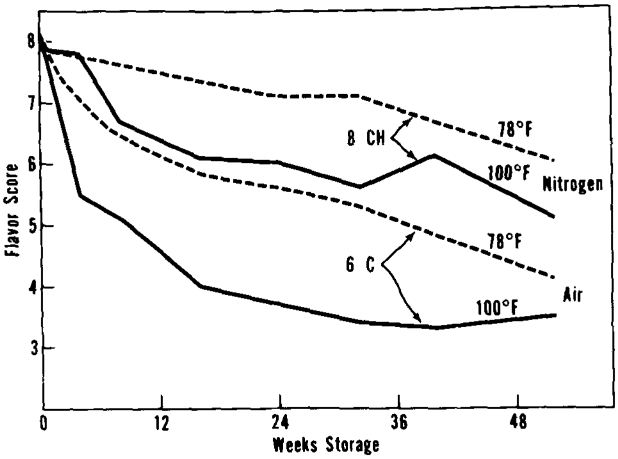

FIG. 2. Flavor loss of soybean oils stored in cans (C) at two temperatures. Sample (8-CH) hydrogenated-winterized oil in gallon tins under nitrogen; (6-C) nonhydrogenated oil in gallon tins packaged under air.

RESULTS AND DISCUSSION

Soybean Oil Stability

Flavor and oxidative stability, as measured by our usual short term storage and AOM tests, are given in Table II. All soybean samples scored high in initial flavor except for 7-C. The oxidative stability of 7-C was also the lowest as determined by peroxide values in the AOM test and again after portions of the original 7-C had been aged in air at 60 C for 4 days. We learned that sample 7-C came from oil that had been bulk shipped before being packaged in small containers. Usually peroxide values at the time of tasting need to be 0.5 or less if unhydrogenated oil is to have a high flavor score (8). All three unhydrogenated oils were above this value and were generally scored lower than the hydrogenated-winterized samples. The peroxide value after 8 hr under AOM conditions for hydrogenated-winterized soybean oils usually will be between 1 and 4, and all our samples fell within these limits. For unhydrogenated oils, 8 hr AOM peroxide values below 10 usually result when stabilizers are present. The peroxide values for sample 7-C indicate poor stability, and the long term storage test on this oil confirmed such an assessment.

Initial flavor scores of all hydrogenated oils (Table II) were high, and the samples aged 4 days at 60 C were relatively high except for the sample 5-BH that did not

TABLE III

Periodic Evaluation of Hydrogenated-Winterized Soybean Oil Stored for 1 Year Under Nitrogen and Under Air

Weeks[a] at 100 F	Flavor score	Peroxide value	After storage AOM-8 hr PV	Flavor descriptions
Sample 4-BH under nitrogen				
0	7.6	0.0	2.2	Buttery
2	7.5	0.0	0.8	Buttery
4	7.7	0.0	1.0	Buttery
10	7.2	0.0	1.3	Butter grassy
14	6.4	0.0	1.1	Buttery grassy
18	7.4	0.0	1.4	Buttery grassy
26	6.7	0.0	2.0	Buttery grassy
34	6.8	0.0	1.6	Buttery
38	6.8	0.0	1.5	Buttery grassy
44	6.3	0.0	1.2	Buttery grassy
52	5.9	0.0	1.4	Buttery grassy
Sample 3-BH under air				
0	7.5	0.3	3.1	Buttery grassy
2	6.9	0.8	4.7	Buttery grassy
4	5.8	1.1	6.7	Rancid grassy
10	4.9	2.9	7.1	Rancid grassy
14	3.7	3.3	12.4	Rancid grassy
18	4.2	4.8	15.4	Rancid painty
26	3.4	6.3	19.9	Rancid painty
34	3.3	5.8	20.3	Rancid painty
38	—	4.9	16.3	Not tasted
44	—	6.2	15.7	Not tasted
52	3.1	6.1	16.7	Painty, rancid, melony

[a]Storage in original containers as packaged in the processor's plant.

contain antioxidants. A high quality oil is illustrated by sample 4-BH, which had high initial and aged flavor scores and low peroxide values after 4 days at 60 C and after 8 hr under AOM conditions.

The flavor results after long term storage for hydrogenated-winterized soybean oils stored under nitrogen and under air for a year are shown in Table III. The composition of both oils is about the same, and both had the protection of added antioxidants. The retention of a relatively high flavor score for 26 weeks and the absence of peroxide development for the nitrogen-protected sample indicate excellent stability. The loss of flavor for the oils packed under air (scores below 5) and the increase in peroxide value to ca. 3 in 10 weeks provide convincing data favoring nitrogen packing. In 4 weeks, the flavor score of air-packed samples dropped below 6, whereas 52 weeks were required for the nitrogen-packed oil to reach this same level.

The value of nitrogen protection for salad oils cannot be overstated. The constant increase in peroxides in storage tests at 100 F under air indicates the poor efficiency of stabilizers for soybean oil under these conditions. Flavor descriptions of the aged oils are given in column 5 of Table III. The initial flavors are buttery, but as the oils age, grassy and beany flavors develop. When the oils become oxidized further, descriptions of rancid, painty and melony are indicated by the taste panel. Responses are listed in the order of their predominance. Rancid responses in soybean oil develop around a peroxide level of 1.0 and at higher peroxide levels become submerged by the more repulsive painty and melony flavors. For hydrogenated soybean oil, such as sample 3-BH, the painty responses predominated at a peroxide level of 6, but for unhydrogenated oil, sample 7-C, they occur at peroxide levels as low as 1.5.

AOM PV values (Table III) were determined on the respective samples of oils after each sample had been stored for a specified time. The air-stored samples show a constant increase in AOM peroxides (loss of stability) up to 34 weeks of storage, at which time peroxide development leveled off. Salad oils stored under 100% nitrogen had no increase in AOM peroxides. This low and constant level of peroxide formation indicates little, if any, oxidative deterioration of the oil during 1 year of storage.

In Figure 1 the loss of flavor score is depicted over a

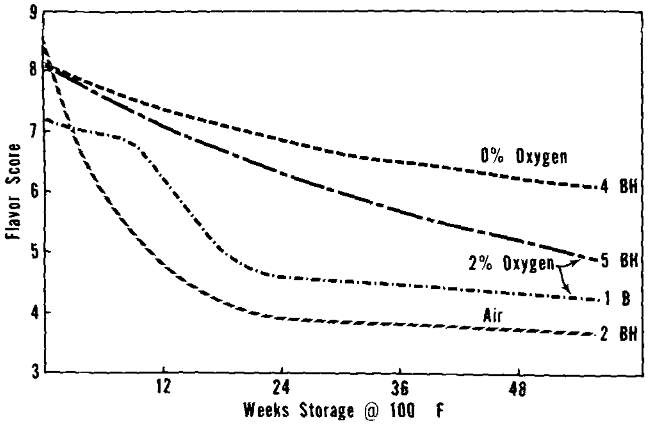

FIG. 3. Flavor loss of soybean oils stored in bottles under different oxygen levels in the headspace gas. Samples (4-BH, 5-BH and 2-BH) hydrogenated-winterized oils; (1-B) a nonhydrogenated oil.

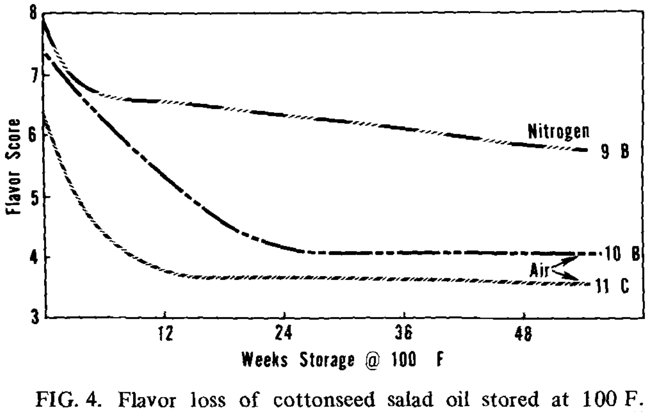

FIG. 4. Flavor loss of cottonseed salad oil stored at 100 F. Sample (9-B) oil bottled and stored under nitrogen; (10-B) oil bottled in air; (11-C) oil packaged in quart tins in air.

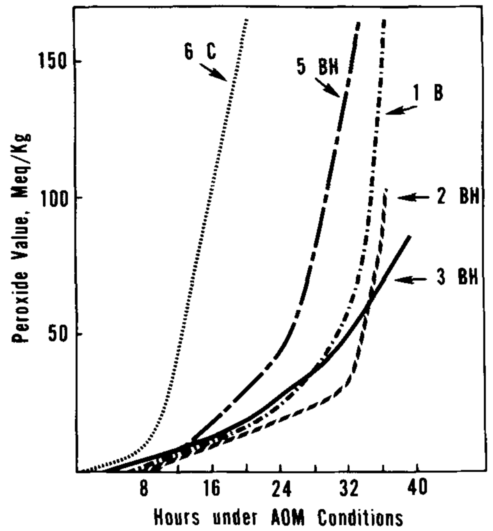

FIG. 5. Oxidative stability-peroxide curves of soybean oils developed by aeration under active oxygen method (AOM) conditions. See Table I for sample identifications.

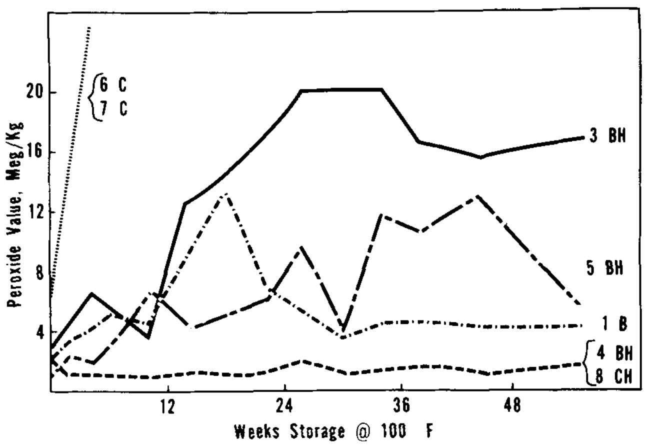

FIG. 6. Peroxide development in oils upon aeration for 8 hr under AOM conditions after the oils had been previously stored at 100 F for the indicated periods. See Table I for sample identification.

year for hydrogenated-winterized soybean oils stored under nitrogen and air at 78 and 100 F. During storage in air, the loss of flavor score is rapid at both temperatures. The effect of temperature is pronounced. At room temperature, flavor scores remain high for ca. 40 weeks. When the temperature is raised to 100 F, flavor scores of the oil drop rapidly to below 5 in 10 weeks. These same samples stored at 0 F (controls) had no change in flavor score; the nitrogen-protected samples ranged from 7.1 to 8.0 (average 7.5) and the air-packaged samples, from 7.5 to 8.2 (average 7.9).

Since the air-packaged samples were not protected with antioxidants or metal chelates, the series of curves in Figure 1 contrasts the extremes of a fully protected oil with an oil bottled under air. Hydrogenation alone, without added antioxidants, metal inactivating agents and nitrogen protection, is not sufficient to ensure good, long shelf life for hydrogenated-winterized soybean oils, particularly at elevated temperatures. The improvement in flavor stability, obtained by hydrogenation of soybean oil to iodine values of 112-115, is shown by comparing the air-packaged hydrogenated samples (Fig. 1) with the air-packaged nonhydrogenated oils (Fig. 2). Little improvement was found at 100 F, but appreciable improvement was evident at 78 F during the early part of the storage.

The storage stability of two types of soybean oils packaged in screw-cap tin cans is shown in Figure 2. Oil sample 8-CH (hydrogenated), which contains added antioxidants and is fully protected by nitrogen, shows acceptable storage stability although it has less stability than the same type of oil packaged in bottles (Fig. 1). The top curve in Figure 2 indicates that oils packaged in screw-cap cans and protected by nitrogen are equivalent in quality, for at least a year, to oils packaged in bottles under nitrogen if the storage temperature is no higher than 78 F. At higher storage temperatures cans appear somewhat less desirable than bottles, but this may have been related to differences in the closures used. Sample 3-BH is hydrogenated soybean salad oil unprotected by added antioxidants or nitrogen packaging. Its shelf life, as evaluated by flavor scores after storage at 100 F, is ca. 10 weeks. The two bottom curves in both Figure 1 (hydrogenated oil) and Figure 2 (unhydrogenated) are similar and show an immediate, rapid loss of flavor score on extended storage. After ca. 20 weeks of storage at 100 F, flavor scores drop below 4.0.

The effects of three different levels of oxygen on the flavor scores of soybean oils stored at 100 F are plotted in Figure 3. The positions of curves 4-BH, 5-BH and 2-BH for hydrogenated-winterized soybean oil correspond to the oxygen content of the headspace gas. Curve 1-B is for nonhydrogenated soybean oil protected by antioxidants, but with incomplete nitrogen protection. A score of 5 is reached after the unhydrogenated oil had been stored for 18 weeks. Stability of the partially nitrogen-protected unhydrogenated oil at 8-10 weeks is greater than that of an air-packaged sample of hydrogenated oil (curve 2-BH). After several months of storage a drop in flavor score occurs for both hydrogenated and nonhydrogenated oils, unless they are protected by nitrogen. The improvement in storage life effected by 100% nitrogen (0% oxygen) over 2% oxygen is obvious and supplements flavor data discussed previously. These curves suggest that storage under 1% oxygen would be superior to storage under 2%.

Cottonseed Oil Stability

The differences in flavor stability between nitrogen-protected and -unprotected cottonseed oil are as great as those for hydrogenated-winterized soybean oil. Figure 4 depicts a year's storage in bottles of cottonseed oil when protected and unprotected with nitrogen, curves 9-B and 10-B, as well as an unprotected sample stored in a screw-cap metal can, curve 11-C. As with soybean oil, a decrease in flavor score occurs in the unprotected oil after several weeks of storage. The drop in flavor score was more rapid for the sample packaged in a metallic can. Since the initial flavor score of this oil was not so high as the other two, some deterioration probably occurred in this oil before its storage at 100 F. The flavor score of the nitrogen-protected cottonseed oil showed a small but consistent drop with length of storage.

Flavor descriptions of the cottonseed oil during storage varied at the beginning from buttery with a few rancid and nutty responses to the year's storage sample of rancid and a few buttery responses. From experience with taste panel operation, the description of rancidity in most cases, where the oil is scored as good, is a matter of staleness and not true rancidity, as would be experienced with low scoring oils (scores of 4.0 and lower). In our experience, flavor scores are much more reliable than flavor descriptions.

The flavor scores of aged cottonseed oils seem to level off at a score of ca. 4; this is about a unit higher than the aged scores of soybean oil. The painty, rancid responses of soybean oil are more objectionable than the plain rancidity of oleic-linoleic acid fats.

The PV of the cottonseed samples protected by nitrogen was zero at all tastings through the year of storage and this again would indicate that rancidity is not a correct description term. The bottle sample (10-B), packaged in air, showed a slow increase in peroxides throughout the year from 0.0 to 2.7 meq. The oil sample packaged in the metal cans (11-C) had high peroxides (2.0 me) at the time it was placed in storage, and the peroxide level slowly increased to 3.8 meq after 30 weeks. After reaching a maximum, the peroxide value then slowly dropped to the initial level at the end of the year.

The AOM 8 hr PV determined on oil samples after the two storage periods (Fig. 4) showed the same general trend as peroxides measured at each taste evaluation period. Samples protected with nitrogen showed no increase in AOM peroxides (15.0 meq) even after a year's storage. Samples packaged in air gave increasing AOM values of 15.0 to 32.0 after 30 weeks where the values plateaued for the rest of the storage period. Samples packaged in air in metal cans gave erratic AOM values, which varied from 28 to 51, and such results are interpreted as can-to-can effects of metal contamination on oxidation. Conditions of storage that favor peroxide development will produce oils of very poor AOM stability. Any peroxides developed under storage will act autocatalytically on the oil when it is exposed to AOM conditions, and high peroxide levels will be developed on short aeration times. If peroxides are not developed in the oil during storage, AOM values will not change regardless of the length of storage.

Oxidative Stability of Stored Soybean Oils

The oxidative stability of fats and oils is most easily ascertained by running an AOM peroxide development curve until the sample shows the typical induction or breakpoint. Figure 5 contains a set of five curves showing typical data for soybean oil. Curve 6-C is for unstabilized, nonhydrogenated soybean oil and curve 1-B is for stabilized nonhydrogenated soybean oil. Curve 5-BH is for unstabilized hydrogenated-winterized soybean salad oil, and curves 2-BH and 3-BH are for stabilized hydrogenated-winterized oils. The effects of both hydrogenation and stabilization are apparent from these curves. The inability of antioxidants to improve the flavor stability of nonhydrogenated soybean oil, although they improve oxidative stability, may account for their limited use in some packaged oils.

Figure 6 shows the results of AOM PV run on seven different soybean oils after samples had undergone storage at 100 F for various lengths of time. The samples with the poorest stability are the nonhydrogenated unprotected oils packaged in cans (samples 6-C and 7-C). Initial AOM 8 hr peroxide values of 6.5 and 11 for samples 6-C and 7-C increased within 4 weeks of storage at 100 F to levels of 32 and 40.5, respectively. A sample of oil (1-B) protected by antioxidants and under partial nitrogen (98%) gave values only slightly higher than the original level of 2.3. The one erratic value at 18 weeks for this sample indicates bottle-to-bottle variation. This bottle probably had a poor seal with air leakage into the headspace. Individual bottles could not be checked for headspace gas before storage because then the seal would be broken, and after long storage oxygen analysis would not indicate true initial values (7).

Storage in metal cans can be adequate to maintain quality stability if the oils are protected with nitrogen. Sample 8-CH shows the stability results of antioxidant and nitrogen-protected oil sealed in a screw-cap can. In this particular sample, no individual cans showed AOM values significantly different after storage from the initial value of the sample. A can of this oil (8-CH) stored for 2 years at room temperature had no increase in AOM value and received a flavor score of 5.4. The sample after 2 years of storage showed no peroxides and was described as grassy and buttery.

Indications are that any level of oxygen contamination in the headspace gas is detrimental to flavor, and the best possible storage system is to exclude oxygen completely from packaged salad oils. Oils do decrease in flavor score when stored under nitrogen for long periods at elevated temperatures. This loss of freshness has been described by our taste panel as an increase in rancidity and grassiness. The various degrees of staleness are hard to describe in appropriate words. Because our experience has been with oils that have been oxidized, our descriptive terms basically concern oxidative deterioration. Panel members continue to use oxidative descriptive terms to denote oil flavor changes even though the change may be nonoxidative in character. The origin or character of compounds resulting from nonoxidative flavor deterioration of edible oils is unknown, and their isolation and study will not be easy. Speculation about the reason for loss in flavor score with oils packed in 99+% nitrogen suggests that our methods of analysis for oxidation or oxidative products need to be improved.

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