# An Evaluation of the Oxidative and Flavor Stability of Stored Soybean Oils

L. A. BAUMANN, Market Quality Research Division,[1] Washington, D. C.
D. G. McCONNELL, HELEN A. MOSER and C. D. EVANS,
Northern Regional Research Laboratory,[2] Peoria, Illinois

## Abstract

Results of 4-year storage tests are reported for crude and refined soybean oils held in 50-gal drums under conditions simulating field tank operations. Once-refined oils stored in filled drums without breathers showed lower peroxide values and lower dimer contents than oil stored in full drums with breathers. Refined oils in half-filled drums exhibited higher storage temperatures and, consequently, higher peroxide values and dimer contents than any other storage condition. Nondegummed and degummed crude oils held in drum storage had lower peroxide values and lower dimer contents than refined oils stored under similar conditions. Relationships are significant not only between storage peroxide values and dimer contents, but also each of these with flavor scores. Evidently, stored crude or stored refined soybean oils with peroxide values under 60 could be deodorized to produce salad-grade oils with initial flavor quality equal to that of oils processed from stocks having considerably lower initial peroxide values. The relative rate of peroxide increase for field tank storage can be estimated from linear regression analysis on data from storage of soybean oil in drums. Once-refined soybean oil held under large field tank storage conditions would not be expected to reach peroxide levels of 60 until after 3–4 years, even in warm areas.

## Introduction

Little is known about oxidative stability of soybean oils that have been stored under commercial conditions for more than a few months. Long-time storage (up to 4 years) of crude, degummed crude and once-refined soybean oils in large field tanks could affect their oxidative and flavor stability. An experimentally controlled study of stored oils in a number of field tanks for several years would be too expensive. Although storage of oils in 50-gal drums has provided data to arrive at changes in quality characteristics for evaluating the oils for trading purposes, no data are available concerning the oxidative and flavor stability of field tank-stored oils.

In the early 1950's, the Commodity Credit Corporation held large quantities of refined cottonseed oil for periods up to 4 years at several different locations. Tests made on these oils showed decreases in oxidative stability (increase in peroxides) to be significantly related to the time and temperature of storage (1).

Studies in the mid-sixties show that after 4 years, peroxide values of once-refined soybean oils stored in drums (2) were similar to those of refined cottonseed oils stored in drums. In field tanks, peroxide values were much less for the same storage period.

When a refined soybean oil is autoxidized at 60C in the presence of oxygen, there are significant relationships between peroxide value before deodorization and dimer content after deodorization (4). Dimer content varied little compared to flavor scores for freshly refined soybean oils evaluated immediately after deodorization. The relationship between the dimer content and flavor score becomes significant for oils aged 4 days at 60C after deodorization.

Fourteen samplings of crude, degummed crude and once-refined soybean oils were taken from each of 36 drums for tests and evaluation during the 4 years of the overall study (2). Results reported here are for samples taken at the end of each year of storage for flavor and oxidative tests.

## Experimental

After the first year of storage, samples were taken annually from 6 drums of once-refined soybean oil of the same initial lot, from 2 drums of the same lot of nondegummed crude soybean oil and from 2 drums of the same lot of degummed crude oil. The samples at the three processing stages were not identical initially; however, they were milled at the same location from soybeans grown in Illinois.

The 2 crude oil drums and 2 drums of the refined oils, designated "control" drums, were painted aluminum and were provided with breathers to simulate usual conditions of field tank storage. Two drums of the refined oils were stored under the same conditions as the control drums, except that the drums were only half-filled. Oil in the half-filled drums showed a greater range of temperatures during storage than did the controls. Two drums of refined oil, stored under the same conditions as the controls, were designated "no-breather" drums, and were kept tightly closed except when opened for sampling. All drums were stored outdoors and exposed to atmospheric conditions at Beltsville, Md.

The refined oils were tested for peroxide value as stored and after deodorization. Peroxide values of deodorized oils were also obtained after aging at 60C for 4 days, and after 8 hr under AOM conditions. Dimer content and flavor scores were determined after deodorization. An additional lot of freshly refined and bleached oil was held at −18C (−17.8C) during the 3-year period between tests. For flavor comparisons, samples of this lot of oil were deodorized at the same time and under the same conditions as oils from outdoor storage.

Peroxide values are reported for the crude oils as stored and after refining and bleaching. Dimer contents were determined on the crude oils after storage and after the crude oils were refined, bleached and deodorized.

## Results and Discussion

The peroxide values and dimer contents of the stored −18C oil used in taste panel evaluations and of

[1] ARS, USDA.
[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

TABLE I
Oxidative Stabilities of Freshly Refined Soybean Oil Stored at −18C and Refined Soybean Oil Stored Outdoors

| Years in storage | Stored at −18C[a] | Stored outdoors[b] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Control drums[c] | | | Half-filled drums[d] | | No-breather drums[e] | |
| | | 130 | 132 | 118[f] | 122 | 131 | 118[g] | 127 |
| | | Dimer content in percent after deodorization | | | | | | |
| 1 | ...... | 1.6 | 1.7 | .... | 2.2 | 2.2 | 1.5 | 1.2 |
| 2 | ...... | 1.5[h] | 2.1[h] | .... | 3.2 | 2.9 | 1.7 | 2.6[h] |
| 2 | ...... | 1.4[h] | 2.8[h] | .... | .... | .... | .... | 2.9[h] |
| 3 | ...... | 3.6 | 3.9 | 2.8[h] | 4.5 | 4.9 | ... | 1.7[h] |
| 3 | ...... | .... | .... | 3.3[h] | .... | .... | ... | 2.4[h] |
| 4 | ...... | 4.0 | 3.8 | 3.6 | 5.9 | 5.6 | ... | 2.4 |
| | | Peroxide value[i] in meq/kg before deodorization | | | | | | |
| 1 | ...... | 35 | 36 | .... | 54 | 48 | 31 | 26 |
| 2 | ...... | 87 | 75 | .... | 126 | 123 | 58 | 49 |
| 3 | ...... | 111 | 104 | 103 | 175 | 180 | .... | 42 |
| 4 | ...... | 139 | 138 | 133 | 207 | 200 | .... | 47 |
| | | Peroxide value[i] in meq/kg after deodorization—0 days | | | | | | |
| 1 | 0.19 | 0.24 | 0.28 | ...... | 0.22 | 0.29 | 0.24 | 0.24 |
| 2 | 0.30 | 0.19 | 0.39 | ...... | 0.19 | 0.24 | 0.23 | 0.24 |
| 3 | 0.46 | 0.34 | 0.54 | 0.65 | 0.77 | 0.44 | ...... | 0.93 |
| 4 | 0.47 | 0.58 | 0.78 | 1.71 | 1.62 | 0.74 | ...... | 1.03 |
| | | Peroxide value[i] in meq/kg after deodorization—held 4 days—60C | | | | | | |
| 1 | 6.90 | 2.16 | 4.82 | ...... | 4.25 | 4.38 | 2.98 | 4.20 |
| 2 | 8.22 | 7.32 | 6.52 | ...... | 7.20 | 6.27 | 8.35 | 7.67 |
| 3 | 5.20 | 2.09 | 1.34 | 2.21 | 1.16 | 1.20 | ...... | 1.16 |
| 4 | 3.94 | 0.34 | 0.46 | 0.34 | 0.63 | 1.41 | ...... | 2.16 |
| | | Peroxide value[i] in meq/kg after deodorization—AOM 8 hr[j] | | | | | | |
| 1 | 53.3 | 17.2 | 23.8 | ...... | 28.8 | 29.6 | 15.7 | 22.2 |
| 2 | 43.0 | 50.2 | 43.5 | ...... | 41.7 | 48.5 | 38.2 | 33.1 |
| 3 | 43.4 | 48.7 | 54.6 | 62.2 | 155.3 | 139.3 | ...... | 75.4 |
| 4 | 35.3 | 107.6 | 57.5 | 56.8 | 137.8 | 129.3 | ...... | 37.0 |

[a] Held at −18C between sampling for tests.
[b] Stored outdoors and exposed to atmospheric conditions at Beltsville, Md.
[c] Painted aluminum and provided with breathers to simulate usual conditions of field tank storage.
[d] Same as footnote c except only half-filled.
[e] Same as footnote c except with no breathers and opened only for sampling.
[f] At the time of sampling at the end of the second year, a breather was inadvertently placed on drum 118, so it was considered a "control" for the rest of the storage period.
[g] According to Reference 4.
[h] Average of duplicate determinations used in following calculations.
[i] According to Reference 6, Cd 8–53.
[j] According to Reference 6, Cd 12–57.

the refined oil stored in drums are summarized in Table I.

An increase of both peroxide value and dimer content of all the soybean oils was evident during outdoor storage for 4 years. The faster rate of increase in the half-filled drums and the slower rate of increase in the no-breather drums, as compared to the control drums, reflects the effect of higher temperatures in the half-filled drums and the limited access to air in the no-breather drum. Peroxide values are quite similar to those found in the cottonseed oil study (1).

The accumulation of nonperoxidic oxidizing substances during extended drum storage of the oils was shown by the apparent increase in peroxide values determined on the oils after deodorization (0 days). When the drum-stored deodorized oils were again subjected to an aging (oxidation) condition, i.e., under air storage at 60C for 4 days and for some oils under AOM conditions for 8 hr, the presence of these oxidizing nonperoxidic substances will produce a nontypical autoxidation of the oil. These nonperoxidic substances accumulated sufficiently during 2 years of drum storage that they markedly affected further peroxide development in the oil.

All stored oils gave these atypical stability results (peroxide development at 60C for 4 days) especially after the third and fourth year of drum storage. This same phenomenon occurs during short-time autoxidation of refined oils at elevated temperatures (3). Although the test results varied rather widely, there apparently was no increase or decrease in peroxide value due to holding the stored −18C oil for 3 years during which it was used for comparison to the drum-stored oils.

There were significant relationships between dimer content of the drum-stored oils and peroxide value of the oils at the end of the drum-storage period. The dimer content of a deodorized soybean oil can be used to estimate the degree of oxidation that an oil has received before its deodorization (3,4). Correlations between dimer content and storage peroxide values are illustrated in Fig. 1 for the control, half-filled and no-breather drums.

Although there were insufficient observations to draw any reliable conclusions for the no-breather drums, apparently the rate of increase in peroxide value is less than for the control or half-filled drums. The lower rate indicates that limited access to air in the no-breather drums during storage affected both dimer content and peroxide value. There is no difference in the ratio of peroxide to dimer increase in the control and half-filled drums, and these data can be grouped as in Fig. 2. The relationship shown in Fig. 2 of dimer content to peroxide value is comparable to soybean oil autoxidated under laboratory conditions (4).

The present report gives b at 0.023, r at 0.938, $S_{yx}$ at $\pm 0.456$ and an initial dimer content of 0.70%. The earlier laboratory study (4) showed that the dimer content of freshly refined oils after deodorization varied from 1–3%. Although there were some differences in the initial dimer content of the drum-stored oil and that of laboratory-autoxidized oil, these differences could be accounted for by the different processing times of the two oils including the deodorization. The current study agrees with the earlier one in that peroxide values increased by about 40 meq/kg for each percent of dimer increase.

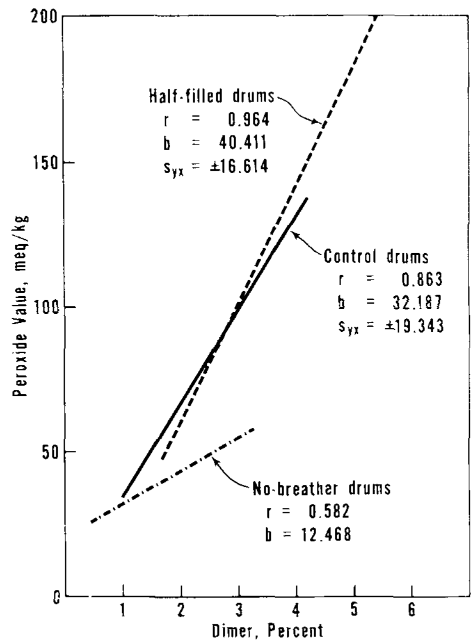


FIG. 1. Relationship of storage peroxide value of refined soybean oil stored in drums, under three different conditions, to dimer content after deodorization.

Dimer contents of the crude oils determined after storage, and on the same oils after refining, bleaching and deodorizing, together with peroxide values for the stored oils and the refined and bleached oils, are listed in Table II.

Crude oils did not increase in dimer and peroxide value as fast as the refined oils (Table I). The better oxidative and storage stability of crude soybean oil when compared to refined oil was confirmed by the more detailed storage study (2).

A slightly lower dimer content was observed after the crude oils were refined, bleached, and deodorized. A correlation coefficient of $r = 0.55$ was obtained between the stored peroxide values and the dimer contents of the crude oils. A higher correlation could not be expected between the dimer content and peroxide value after refining and bleaching because of partial decomposition and removal of some of the peroxides during these processing operations. Statistical tests of the regression coefficients showed no difference between the crude oil results and those reported in Fig. 2.

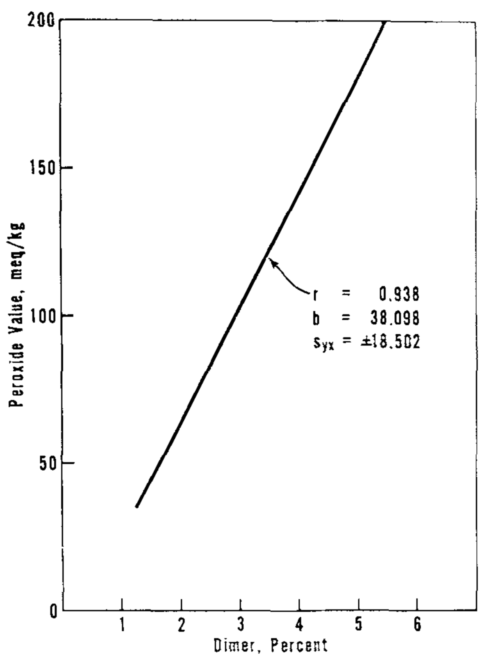


FIG. 2. Relationship of storage peroxide value of refined soybean oil, stored in filled and half-filled drums, to dimer content after deodorization.

TABLE II

Oxidative Stabilities of Crude Soybean Oils Stored in Drums[a]

| Years in storage | Nondegummed | | Degummed | |
|---|---|---|---|---|
| | 125 | 133 | 128 | 129 |
| | Dimer content[b] in percent as stored | | | |
| 1 | .... | .... | 1.4 | 1.9 |
| 2 | ... | .... | 1.2 | 1.2 |
| 3 | 1.3 | 1.1 | 2.2 | 1.8[c] |
| 3 | ... | .... | | 2.3[c] |
| 4 | 2.4 | 1.7 | 2.6 | 2.8 |
| | Peroxide value[d] in meq/kg as stored | | | |
| 1 | .... | .... | .... | .... |
| 2 | .... | .... | 0 | 0 |
| 3 | 40 | 34 | 67 | 77 |
| 4 | 86 | 75 | 86 | 94 |
| Dimer content[b] in percent, after refining, bleaching and deodorizing | | | | |
| 1 | 2.1[c] | 1.1[c] | 1.4 | 1.3 |
| 1 | 2.4[c] | 0.9[c] | | ... |
| 2 | 1.0 | 0.6 | 0.6[c] | 0.8 |
| 2 | .... | .... | 0.5[c] | .... |
| 3 | 1.6 | 0.9 | 2.2 | 1.2[c] |
| 3 | .... | .... | | 1.2[c] |
| 4 | 1.3 | 1.4 | 1.5 | 1.7 |
| | Peroxide value[d] in meq/kg after refining and bleaching | | | |
| 1 | .... | .... | ... | .... |
| 2 | 11 | 7 | 9 | 8 |
| 3 | 12 | 14 | 16 | 26 |
| 4 | 23 | 17 | 18 | 32 |

[a] All drums stored under "control conditions"—see footnote c in Table I.
[b] See footnote g in Table I.
[c] See footnote h in Table I.
[d] See footnote i in Table I.

#### Flavor Evaluation

The quality of the stored refined oils was determined by taste panel evaluation (5) after small lots of the oils were deodorized in the laboratory. Post refining or bleaching was not done before deodorization of the drum-stored oils. A refined, bleached soybean oil held in storage at −18C for the 3-year period was deodorized at the same time and was used as the oil for comparative purposes.

Flavor scores (Table III) for the drum-stored oils varied over the 4 years of the study primarily according to the condition of storage. Low initial flavor scores that occurred in the first and second years are obviously out of line with the rest of the data. A bias value of this extent must be considered as an error in handling or processing since later samples from the same drums were in agreement with the overall data. Flavor scores of duplicate drums also were in good agreement. The oil held at −18C for comparison to the drum-stored oils, had an average initial flavor score of 7.6 ± 0.4 and an average aged score after 4 days' storage at 60C of 4.9 ± 0.2. After 4 years of drum storage, only the no-breather drum No. 127 gave no statistically lower flavor score when evaluated immediately after deodorization. Oxidatively (Table I) this stored oil, No. 127, was equal to the oil held at −18C in the 4-day 60C flavor test and the AOM 8-hr oxidative test. The increased dimer content resulting from storage of sample No. 127 was apparently not sufficient to lower the stability and quality of the oil as measured by these tests. All other oils had a significant or highly significant drop in flavor and oxidative stability when compared to the −18C oil on the same day after deodorization. Oxidative stability and flavor of the half-filled drums were the poorest of all of the stored oils prior to the heat treatment of 4 days at 60C.

TABLE III
Flavor Scores of Freshly Refined Soybean Oil Stored at −18C and Refined Soybean Oil Stored Outdoors

| Years in storage | Stored at −18C[a] | Stored outdoors[b] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Control drums[c] | | | Half-filled drums[d] | | No-breather drums[e] | |
| | | 130 | 132 | 118[f] | 122 | 131 | 118[f] | 127 |
| | | Same day after deodorization (0 time) | | | | | | |
| 1 | 7.4 | 6.1 | 7.9 | .... | 6.4 | 3.2 | 7.2 | 8.2 |
| 2 | 7.2 | 4.1 | 6.7 | .... | 6.8 | 6.3 | 7.8 | 7.9 |
| 3 | 8.2 | 6.9 | 6.3 | 6.3 | 5.4 | 6.1 | .... | 6.2 |
| 4 | 7.5 | 6.2 | 6.2 | 6.2 | 4.5 | 6.0 | .... | 7.6 |
| | | After 4 days at 60C | | | | | | |
| 1 | 4.6 | 5.8 | 5.7 | .... | 5.6 | 2.7 | 5.8 | 6.3 |
| 2 | 4.8 | 4.7 | 4.8 | .... | 3.8 | 4.6 | 4.8 | 4.5 |
| 3 | 4.8 | 3.3 | 2.9 | 3.1 | 4.0 | 2.9 | .... | 3.4 |
| 4 | 5.3 | 3.7 | 3.6 | 3.4 | 4.5 | 4.5 | .... | 4.8 |

[a] Held at −18C between sampling for tests.
[b] Stored outdoors and exposed to atmospheric conditions at Beltsville, Md.
[c] Painted aluminum and provided with breathers to stimulate usual conditions of field tank storage.
[d] Same as footnote c except only half-filled.
[e] Same as footnote c except with no breathers and opened only for sampling.
[f] At the time of sampling at the end of the second year, a breather was inadvertently placed on drum 118, so it was considered a "control" for the rest of the storage period.

Oils processed by the addition of citric acid at the end of deodorization will usually exhibit a slightly better initial flavor score and a marked improved 4-day 60C storage flavor score. The −18C storage sample when processed with citric acid had a 4-day 60C storage flavor score 3 units higher than a non-citrated sample. Flavor improvement on the drum-stored oils could be expected through the use of citric acid.

There were significant relationships between dimer content and the 4-day 60C aged flavor score. This relation was also true for the storage peroxide value and the 4-day 60C aged flavor score. These relationships are not evident due to the wide variations in the flavor scores as shown in Table III after 4 days at 60C. These associations are shown in Fig. 3. The similarity of the two relationships is expected in view of the relationship of the peroxide value and dimer content previously discussed. An estimation of aged flavor score can be made from the storage peroxide value and by the more involved dimer determination, but it would require testing a greater number of oils to make a general statement for all soybean oils.

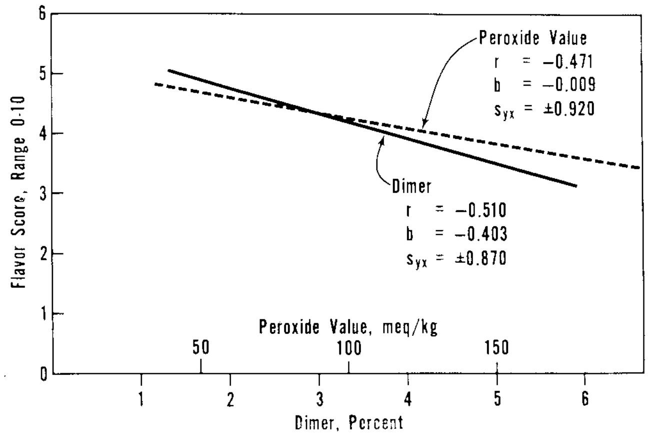


FIG. 3. Relationships of flavor score of stored, refined soybean oil, after deodorization and heat treatment of 4 days at 60C, to outdoor storage peroxide value and dimer content.

From the completed field tank study of an 8,000,000-lb lot of refined cottonseed oil, stored in one of the warmer areas of the country (2), it was estimated that the peroxide value would increase to about 60 after 3–4 years. Crude soybean oils stored under these same conditions can be expected to reach a peroxide value of about 40. From the data presented and the relationship shown between storage and flavor stability, it can be expected that average quality soybean oils stored in large field tanks with storage peroxide values under 60 would show normal change in flavor after deodorization and should compare favorably to fresh oils with lower peroxide values. Research on the nature and composition of initial oxidation products could reveal flavor constituents which survive deodorization and provide objective tests on oils to predict flavor stability more accurately.

A further study of the oxidative and flavor stability of deodorized oils in containers is now in progress.

REFERENCES

1. Baumann, L. A., Predicting Quality of Stored Cottonseed Oils, U. S. Dept. Agr., Marketing Research Report No. 523, February 1962.
2. Baumann, L. A., Predicting Quality of Stored Soybean Oils, U. S. Dept. Agr., Marketing Research Report No. 795, in press.
3. Evans, C. D., E. N. Frankel, Patricia M. Cooney and Helen Moser, JAOCS 37, 452–456 (1960).
4. Frankel, E. N., C. D. Evans, Helen A. Moser, D. G. McConnell and J. C. Cowan, Ibid. 38, 130–134 (1961).
5. Moser, Helen A., H. J. Dutton, C. D. Evans and J. C. Cowan, Food Technol. 4, 105–109 (1950).
6. Official and Tentative Methods of the American Oil Chemists' Society, 1964–1965, Chicago, Ill.

[Received May 31, 1967]

## • *Addendum*

JAOCS *44*, 341, 1967, James Hunter and C. Roland Eddy: "Dielectric Properties of Some Long-Chain Esters in the Solid State."

On page 341, Table I, under the heading "Compound" the second compound should read: Hexadecyl tetradecanoate; the third compound should read: Octadecyl tetradecanoate.