Oxidative Deterioration of Partially Processed Soybean Oil

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Abstract

The oxidative stability of partially processed soybean oil has been investigated in laboratory- and plant-scale tests. Oxidation, as measured by peroxide formation, has been related to storage time and temperature, and availability of oxygen. The effects of this oxidation on finished product quality have been measured.

Soybean oil stores best as crude oil. After refining and bleaching, the oil is more susceptible to oxidation than at other stages in processing. Increase in peroxide content is both time and temperature dependent. Substantial improvement in product quality can be obtained by minimizing exposure to oxygen.

Introduction

UNTIL RECENTLY, little has been reported in the literature concerning the oxidative stability of soybean oil stored under commercial conditions. Bailey (1) stated that prolonged storage of oil is undesirable because of the oxidative deterioration that occurs. However, he also stated (2) that vegetable oils high in tocopherol content can be stored in large tanks for extended periods without serious deterioration.

Evans et al., (3) showed that oxidation prior to deodorization is detrimental to the flavor and oxidative stability of soybean oil. Bubbling air through refined soybean oil at 60C resulted in faster flavor score decrease after deodorization than in an untreated control. The control had a peroxide value of 8.3 prior to deodorization. The test samples were oxidized to peroxide values of 22–110.

More recently, Baumann reported (4,5) on a 4-year ambient temperature storage of crude and refined soybean oils in drums. Although he showed that peroxides develop faster in refined than in crude oil, he indicated (4) that soybean oil could be stored for extended periods before it would fail to meet specifications under the Trading Rules of the National Soybean Processors' Association. It was concluded (5) that refined soybean oil could be stored for 3 to 4 years in commercial field tanks and still produce salad-grade deodorized oil with normal aging characteristics.

This paper reports on a laboratory study of the relative oxidation rates of soybean oil stored at several stages of processing. These results are related to commercial conditions by an extended storage test of refined oil in large field tanks.

Experimental Procedures and Data

A fresh nondegummed crude soybean oil was refined, bleached, and hydrogenated in a pilot plant under typical commercial conditions. The crude, the refined and bleached, and the refined, bleached, and hydrogenated oils were stored at 70F, 100F, and 120F in closed one quart, 50 lb, and 55 gal containers. Periodically samples were withdrawn for peroxide value analysis (6).

In an attempt to relate the laboratory results to commercial practice a lot of 1,500,000 lbs of refined bleached soybean oil was also put through a storage test. After thoroughly mixing the freshly processed oil in a nitrogen blanketed tank, half of it was moved to an air-blanketed tank. The two half-filled tanks of oil, one exposed to air, the other protected with a nitrogen atmosphere, were stored under ambient conditions for 5 months. Samples of the oils were then hydrogenated and deodorized in the laboratory for flavor stability determination. Flavor studies were also made on plant-made shortening produced from the two oils. The organoleptic procedures used were similar to those reported by Moser et al. (7).

Laboratory Studies

The effect of processing stage on the rate of oxidative deterioration of soybean oil is shown in Fig. 1. Data from the smallest size containers are depicted to emphasize relative differences. Refined and bleached oil is much more prone to develop peroxides than crude oil. Partially hydrogenated soybean oil is intermediate in deterioration rate.

The reason for the differences between the crude oil and the refined, bleached oil is unknown. Baumann's results (4) indicated that degummed crude oil oxidizes more rapidly than nondegummed crude oil. It could be speculated that the phospholipids in crude oil provide an antioxidant function above and beyond that of the tocopherols. Unlike the tocopherols, phospholipids are partially removed by degumming and essentially completely removed by refining. Partially hydrogenated oil would be expected to be more resistant to oxidation than unhydrogenated oil because of its reduced degree of fatty acid unsaturation. It is still somewhat surprising that the hydrogenated oil oxidizes more rapidly than the crude oil.

The rate of oxidation of soybean oil is dependent on temperature, as shown in Fig. 2. At 70F peroxides develop very slowly in refined, bleached oil. The rate of peroxide formation increases rapidly as the temperature is raised to 100F and 120F. Evidently, oxygen will diffuse into and react with the oil faster at the higher temperatures. The oxidation rate approximately doubles with each 20F temperature increase.

As with all results reported in this paper, it should be stressed that these data were obtained on particular lots of soybean oil. Although the relative effects would not be expected to change, the absolute values could differ widely depending on the oil and processing conditions used.

Oxidation of soybean oil is not only a function of temperature and time, but it is also dependent upon the amount of oxygen to which the oil is exposed. Fig. 3 indicates how the size of the container is a factor in oxidation. As the container gets larger, its surface-to-volume ratio and oxidation rate are decreased. Apparently, the rate of diffusion of oxygen across the air-oil interface limits oxidation rate. Thus, with less surface area per pound of oil, the overall peroxide development is slower. This is generally the case with larger containers. Extrapolation of laboratory data to a 30 ft diameter field tank holding 1,000,000 lbs of refined, bleached soybean oil would predict a 3.5 peroxide value after 5 weeks at 120F. The validity of this extrapolation very likely breaks down before the peroxide value reaches zero.

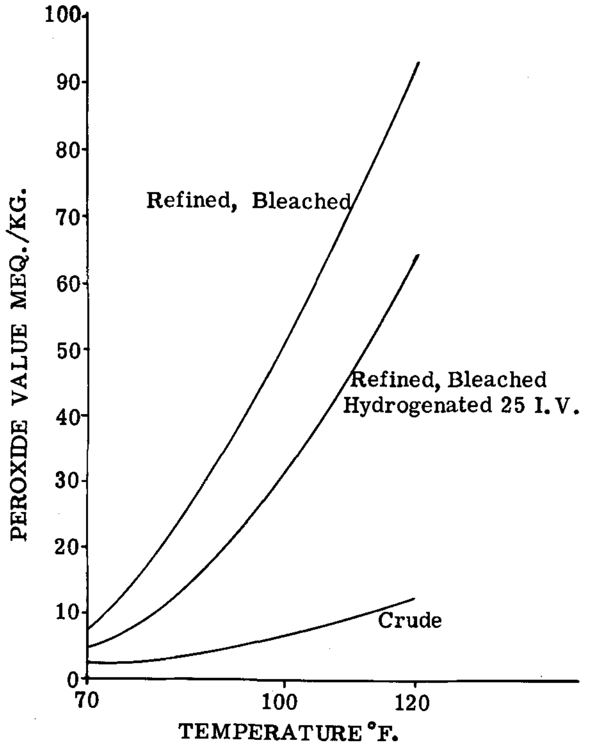

FIG. 1. Effect of processing on oxidative deterioration of soybean oil. Oil stored 7 weeks at temperature in 1 qt. containers.

Laboratory conditions are seldom, if ever, duplicated in commercial field tank storage. Under constant temperature conditions in the laboratory there is little or no movement of oil due to temperature gradients. However, under the continually changing ambient conditions of day and night to which a field tank is exposed, sizeable temperature gradients develop and considerable internal movement of oil results. This would be expected to significantly increase the quantity of oil available at the surface and to accelerate oxygen diffusion. Oxidation rate in field tanks would therefore be somewhat faster than under similar temperatures in the laboratory.

Plant Studies

Storage conditions for the nitrogen blanketed and the air exposed oils are summarized in Table I. The 5-month test was run at Long Beach, California beginning in midsummer. Thus, the oils were exposed to the highest temperatures during the early months of storage. For the last half of the test the bulk oil temperatures were below 75F. The oxygen content of the nitrogen-blanketed tank varied 1% around the average of 1.4%. The fastest peroxide buildup occurred during the first half of the storage time. By compensating for temperature and time effects, the peroxide value of the air-exposed oil agreed quite well with the prediction of tank storage in Fig. 3.

Laboratory deodorization of the two oils after 5 months of tank storage provided samples for accelerated aging study of flavor stability. Fig. 4 summarizes the first of these results. Even though there was only a 3.5 peroxide value difference between the two oils after 5 months of storage, there was a consistent and significant difference in their flavor stabilities. After 7 days at 140F, the flavors differed by 1½ grades. In this system of flavor evaluation, a good quality soybean oil should not

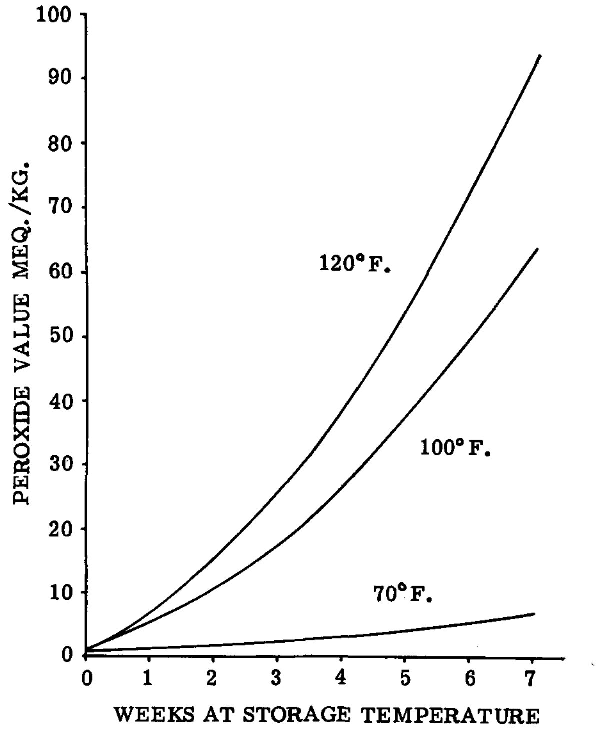

FIG. 2. Effect of storage temperature on deterioration of refined, bleached soybean oil. Oil stored in 1 qt. containers.

score below a grade of 5 in 7 days of accelerated aging. The oil stored under air was considered to have unsatisfactory stability even though its fresh flavor was acceptable.

Part of the stored oils were also hydrogenated prior to deodorization. The flavor stability of these oils is shown in Fig. 5. Here too, there is a significant difference in stability, in favor of the low peroxide value, nitrogen-blanketed oil. The air exposed sample scored well below the grade of 6 which

TABLE I

Conditions for Plant Storage Test on Refined, Bleached Soybean Oil

	Nitrogen	Air
Oil Temperature—Range	60F–93F	64F–87F
—Ave.	74.9F	75.0F
Average O_2 Content of Tank Headspace	1.4%	21%
Peroxide Value—initial	1.0	1.0
—final	1.5	5.0

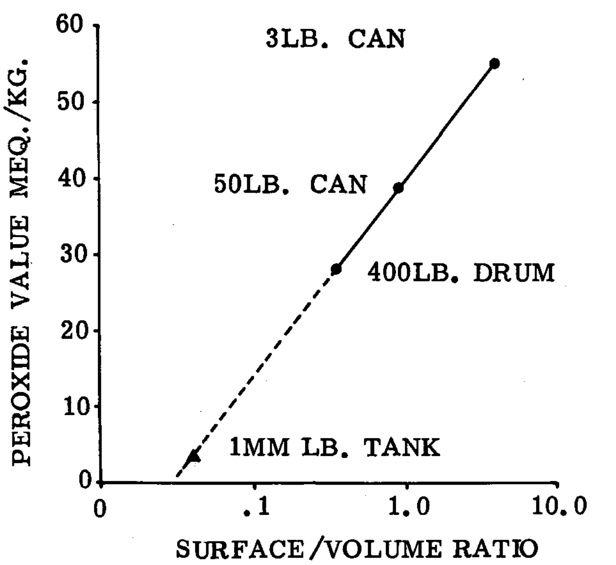

FIG. 3. Effect of storage container size on oxidative deterioration of refined, bleached soybean oil. Oil stored in full containers—5 weeks at 120F.

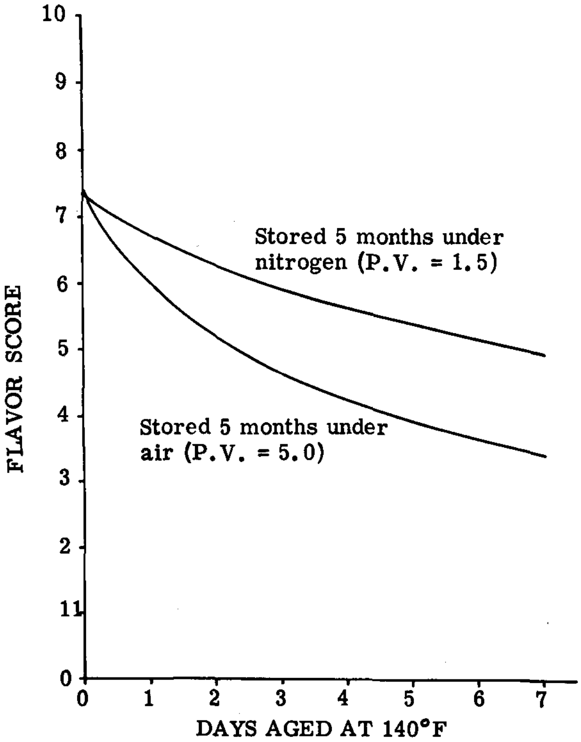

FIG. 4. Effect of air vs. nitrogen storage of refined, bleached soybean oil on flavor stability. Each oil deodorized in laboratory after storage.

is the expected minimum for high quality hydrogenated soybean oil.

These results were confirmed in a third test in which the stability was compared when using the two oils as components of plant-processed hydrogenated shortening. The test oils comprised about 80% of the shortening compositions. Data shown in Fig. 6 again indicate that the nitrogen blanketed oil was more stable than its air exposed counterpart. In each flavor evaluation, the fresh flavors

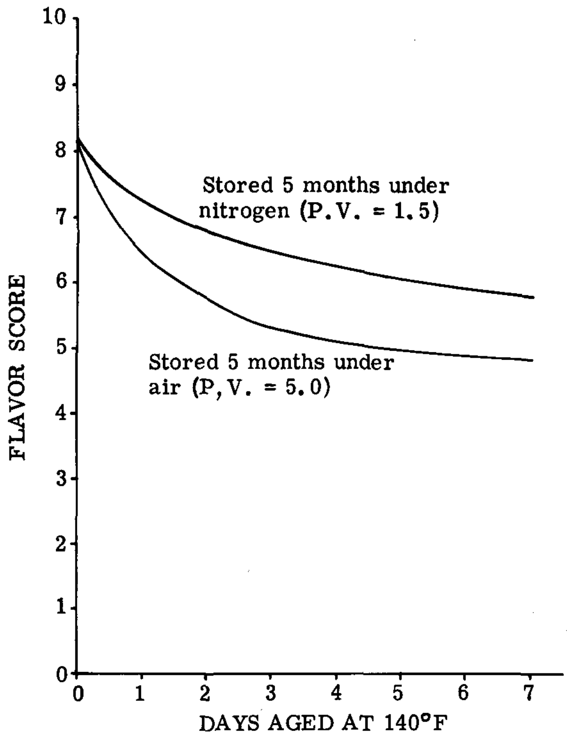

FIG. 5. Effect of air vs. nitrogen storage of refined bleached soybean oil on flavor stability. Each oil hydrogenated to 75 I.V. and deodorized in laboratory after storage.

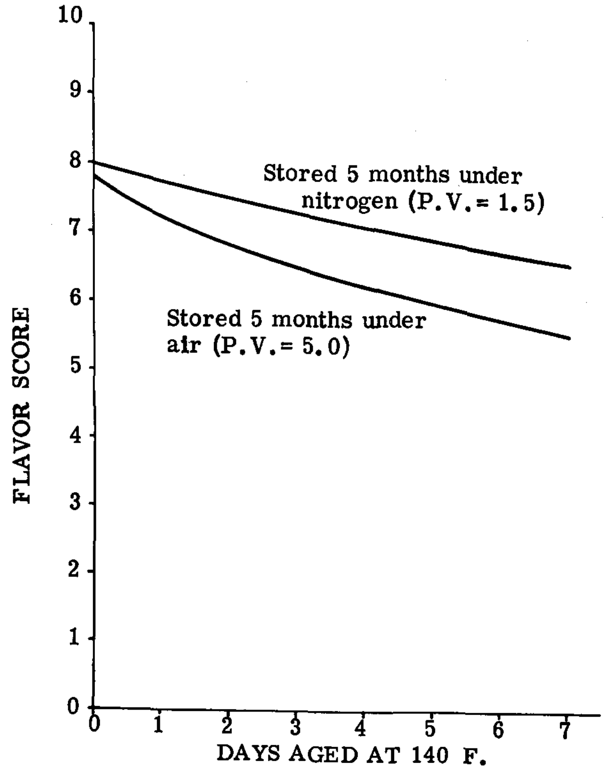

FIG. 6. Effect of air vs. nitrogen storage of refined, bleached soybean oil on flavor stability of plant processed hydrogenated shortening.

of the air exposed and nitrogen-blanketed oils were essentially equal. Thus, it is possible to achieve good fresh product quality when mild in-process oxidation occurs. However, the loss of aged stability cannot necessarily be recovered.

Discussion

The results of these studies indicate that soybean oil stores best as a clean-dry crude oil. Refined and bleached oil is the most susceptible to oxidation. It follows that storage of refined and bleached oil should be minimized and where there is an option, the oil should be stored as crude.

Nitrogen blanketing is an effective means of protecting partially processed soybean oil. Peroxide development, and the flavor instability which it causes, can be virtually eliminated by keeping oxygen away from the oil.

The diffusion of oxygen across an air-oil interface is time, temperature, and surface area dependent. By minimizing storage time, keeping the oil cool, and filling the tanks completely, oxidation can be markedly reduced. Oil in storage under air should not be mechanically agitated.

It may be concluded that relatively low levels of oxidation of soybean oil prior to deodorization can significantly impair the oxidative stability of the finished oil. Highest quality products require absolute minimization of such in-process oil degradation.

REFERENCES

1. Swern, D., "Bailey's Industrial Oil and Fat Products," 3rd ed., Interscience, New York, 1964, 613.
2. Ibid., 632.
3. Evans, C. D., E. N. Frankel, Patricia M. Cooney, and Helen A. Moser, JAOCS *37*, 452–456 (1960).
4. Baumann, L. A., "Predicting Quality of Stored Soybean Oil," U.S. Dept. Agr., Marketing Research Report No. 795, Sept. 1967.
5. Baumann, L. A., D. G. McConnell, Helen A. Moser, and C. D. Evans, JAOCS *44*, 663–667 (1967).
6. Official and Tentative Methods of the American Oil Chemists' Society, 1964–1965. Peroxide Value, Cd 8–53.
7. Moser, Helen A., H. J. Dutton, C. D. Evans, and J. C. Cowan, Food Technology *4*, 105–109 (1950).

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