Antioxidants in Soya Oil

D.F. BUCK, Eastman Chemical Products, Inc., Kingsport, TN

ABSTRACT

Oxidation is a major problem associated with refining, storing and using soya oil. Phenolic antioxidants have been used for several decades to alleviate this problem. The mechanism of oxidation and the action of phenolic antioxidants in inhibiting oxidation in soya oil are reviewed. Specific antioxidant applications discussed are: treatment of crude soya oil with TBHQ antioxidant; TBHQ antioxidant treatment as an alternative to hydrogenation of soya oil; and usage of TBHQ antioxidant in soya oil used in frying system.

INTRODUCTION

Unsaturation and Oxidation in Soya Oil

Soya oil is the major edible oil produced in the world today. An important feature is its high percentage of unsaturated fatty acids. Approximately 85% of the fatty acids are oleic, linoleic, or linolenic. Soya oil's iodine value (IV), which is an indication of total chemical unsaturation, is high, generally in the range of 125-135 IV. Soya oil also contains the highest level of linolenic acid esters found in any of the major edible vegetable oils. The double bonds found in oleic, linoleic and linolenic acids are chemically reactive sites. These properties make soya oil very susceptible to oxidative rancidity.

Mechanism of Oxidation

Oxidation of soya oil occurs in a series of steps and is often called free-radical oxidation because the initiating step is the formation of a free radical on the fatty acid portion of the fat molecule (Fig. 1). This occurs when a hydrogen ion or proton is lost from the α-methylenic carbon in the fatty acid group (the α-methylenic carbon is the carbon adjacent to the double bond). This free radical is highly reactive and forms peroxides and hydroperoxides by reaction with atmospheric or dissolved oxygen. These free radicals also initiate further oxidation by propagating other free radicals. As a final or terminating step, the hydroperoxides split into smaller organic compounds such as aldehydes, ketones, alcohols and acids (1-6). These compounds give the rancid odor and flavor that characterize oxidized soya oil. Oxidative rancidity is a major problem associated with refining, storage, and usage of soya oil.

Phenolic Antioxidants and Antioxidant Mechanism

In the 1930s, researchers discovered a distinct relationship between the tocopherol (vitamin E) content of soya oil and its resistance to oxidative deterioration. Lecithin also was shown to have antioxidant properties. However, significant quantities of these natural antioxidants are removed from soya oil during processing and refining. Soya processors and users began to look for other means to increase the stability of soya oil and products containing it. During the 1940s and 1950s, several phenolic compounds were identified that would inhibit oxidation. During this period, the mechanism of their antioxidant action also was determined (Fig. 2). The phenolic structure of these compounds allows them to donate a proton to a fatty free radical, thereby regenerating the glyceride molecule and interrupting the free radical mechanism of oxidation. In doing this, the phenol derivatives themselves become free radicals. However, these free radicals can stabilize themselves through hybridization and do not promote or propagate further oxidation. As a result, phenolic derivatives (Fig. 3) such as BHA (2 and 3 tertiary butyl-4-methoxyphenol), BHT (2,6-ditertiary butyl-4-methoxyphenol), and gallic acid esters gained approval for food use as antioxidants. During the 1950s and early 1960s, BHA, BHT and propyl gallate met the needs of the fats and oils industry (7).

The increased use of polyunsaturated vegetable oils gave rise to the need for a more potent antioxidant. BHA and BHT are not very effective in soya oil (Figs. 4 and 5). Propyl gallate has good antioxidant properties in soya oil, but its usage is hindered by low oil solubility and a tendency to complex with metal ions to cause discoloration. In addition, the gallates are heat-sensitive and are rapidly lost from oil at high temperatures. These deficiencies triggered the development of TBHQ (tertiary-butylhydroquinone) (8,9). Under a food additive regulation issued by the U.S. government in 1972, TBHQ (Fig. 3) became legal as an additive in fats and oils. Laboratory tests and commercial experience have shown that TBHQ is the most effective antioxidant for highly unsaturated vegetable oils (10). In addition, this greater antioxidant performance can generally be achieved without the color, solubility and volatility problems associated with the use of other antioxidants. The ability of TBHQ to stabilize refined soya oil is well documented. Recent experiments have shown TBHQ

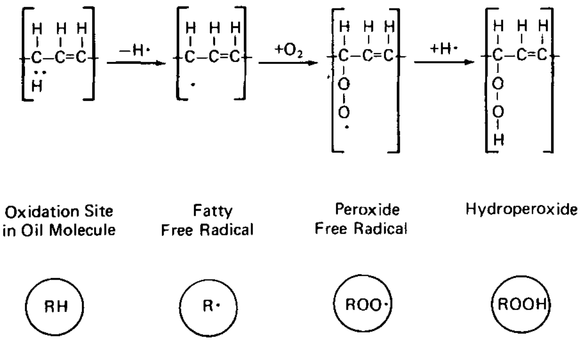


FIG. 1. Free radical oxidation of soya oil.

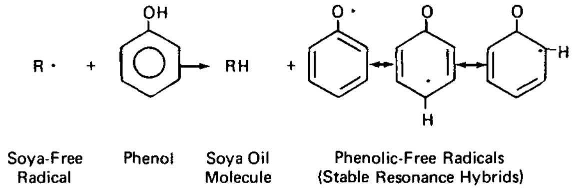


FIG. 2. Antioxidant mechanism of phenolic antioxidants in soya oil.

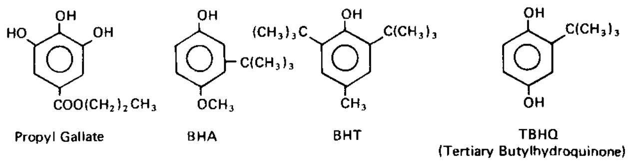


FIG. 3. Phenolic derivatives. Propyl gallate/BHA/BHT/TBHQ.

to be of substantial benefit in other facets of soya production and usage as well.

EXPERIMENTAL

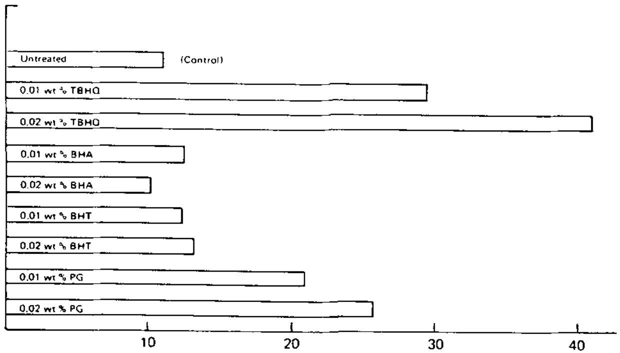
TBHQ in Crude Soya Oil

Crude soya oil contains substantial amounts of natural antioxidants such as tocopherols and phospholipids. Even though crude soya oil is very stable, the use of TBHQ can be beneficial (11). Laboratory studies have shown that the addition of 200 ppm (0.02%) TBHQ can double the AOM stability of crude soya oil (Fig. 6). Active oxygen method (AOM) is an accelerated stability test in which a fat or oil is held at 200 F (97.8 C) and exposed to a constant flow of air. The peroxides formed in the fat or oil during exposure to heat and air are measured periodically (12). The additional stability gained by adding TBHQ to crude soya oil could allow processors to store crude oil until market conditions become economically favorable. The production of soya oil often is secondarily important to the production of soya meal. Additional storage stability of crude soya oil could help the processor avoid oversupply conditions that now occur seasonally.

Studies with other crude oils have shown that TBHQ protects carotene against decomposition (Fig. 7) (13). Products of carotene decomposition form colored compounds during refining and bleaching. As a result, more bleaching clay is required to obtain refined oils of acceptable colors. Crude oils stabilized with TBHQ generally require less stringent conditions to bleach to acceptable colors (Fig. 8).

Evidence exists that TBHQ has a stabilizing effect on the tocopherol in soya oil. Laboratory-scale experiments have shown that the addition of TBHQ to crude soya oil significantly improves the tocopherol content of the deodorizer distillate. A commercial test designed to substantiate these results under plant-scale conditions is in progress. Initial results from this test are very promising.

Studies have shown that TBHQ is completely removed from crude soya during steam deodorization. The refined oil is free of antioxidant and can be labeled as such.



Peroxide value is defined as milliequivalent (meq) of peroxide per kilogram of fat.

FIG. 4. Effectiveness of antioxidants in refined soya oil.

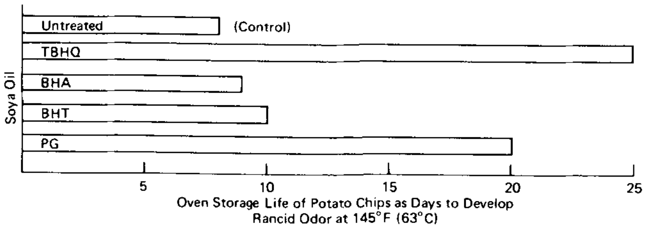


FIG. 5. Carry-through of stability into potato chips (crisps) deep fried in oil containing 0.02% antioxidant.

TBHQ As Alternative to Hydrogenation

One primary purpose of hydrogenating refined soya oil is to improve its oxidative stability by reducing the total unsaturation. Partial hydrogenation, however, has several disadvantages. Extra time, capacity and capital expense are required. The liquid properties of soya oil are lost if the oil is hydrogenated to an IV below 80. Hydrogenation of soya oil reduces its linoleic acid content, which is essential to the diet. An experiment was designed to determine if TBHQ could provide effective economical alternatives to the use of hydrogenation to achieve oxidative stability—both by the use of TBHQ in conjunction with lesser degrees of hydrogenation and by the use of TBHQ alone (14).

A series of soya oils variable in degree of hydrogenation were tested with and without TBHQ antioxidant. The oils were tested by two stability tests, AOM stability and Schaal oven stability. Regression equations were derived relating

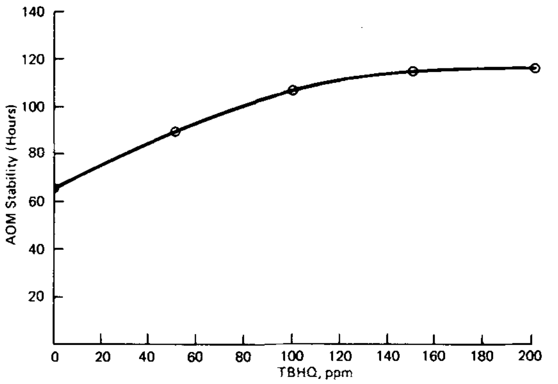


FIG. 6. Effect of TBHQ on the AOM stability of crude soya oil.

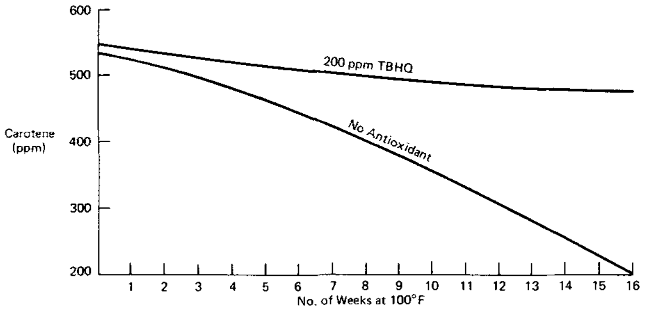


FIG. 7. Effect of TBHQ on the carotene content of crude palm oil.

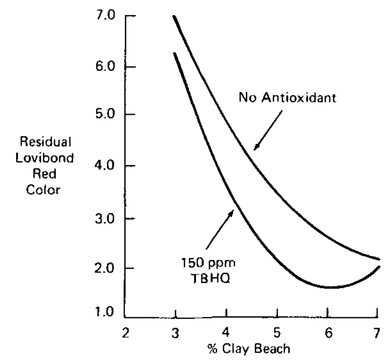


FIG. 8. Effect of TBHQ on bleachability of palm oil.

the IV and TBHQ content of the oil to each resource and contour graphs were obtained of oxidative stability as a function of the variables (Figs. 9 and 10). These plots illustrate that TBHQ is an effective supplement or alternative to hydrogenation. A cost analysis of comparative treatments provides considerable economic incentive for using TBHQ.

TBHQ in Frying Systems

Frying systems subject oils to some of the most rigorous processing conditions encountered. These conditions also place severe demands on antioxidants used to stabilize frying oils. Conditions of high temperature and steam distillation rapidly deplete antioxidants from frying systems. An experiment was designed to compare volatilities of BHA, BHT and TBHQ from soya oil at frying conditions. A series of tests was performed in which antioxidant-treated soya oil was subjected to frying temperatures (180 C). Another series of treated oils was heated to 180 C, and water was injected into the heated oil to effect steam distillation. The oils were sampled periodically, and the antioxidant contents of the soya oil were determined. Results from these tests indicated that BHA, BHT and TBHQ are volatilized at approximately the same rate (Fig. 11). Steam distillation did not significantly increase the rate of antioxidant loss at 180 C (Fig. 12). AOM

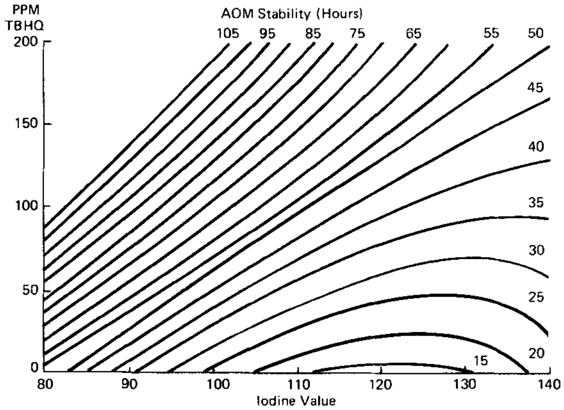


FIG. 9. Effect of TBHQ antioxidant treatment and hydrogenation on the oxidative stability (AOM) of soya oil.

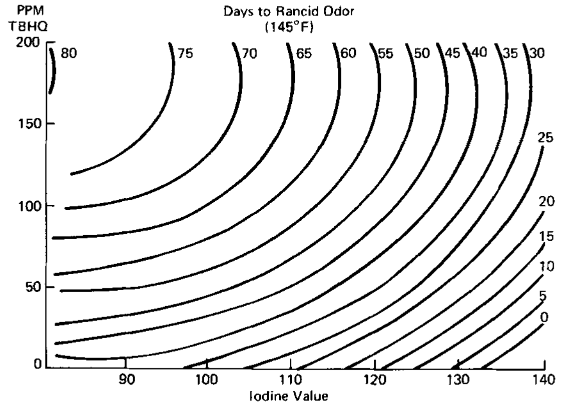


FIG. 10. Effect of TBHQ antioxidant treatment and hydrogenation on oxidative stability (Schaal oven stability) of soya oil.

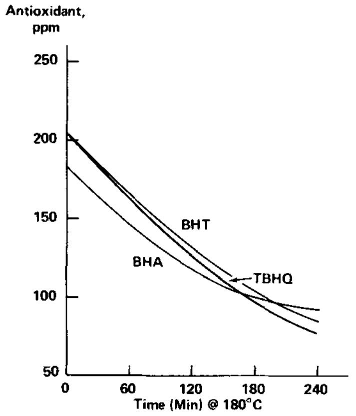


FIG. 11. Effect of heat on loss of antioxidants from soya oil at 180 C.

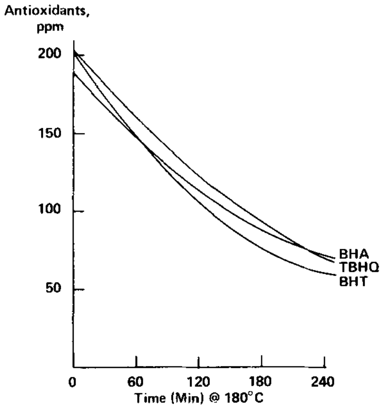


FIG. 12. Effect of heat and steam distillation on loss of antioxidants from soya oil at 180 C.

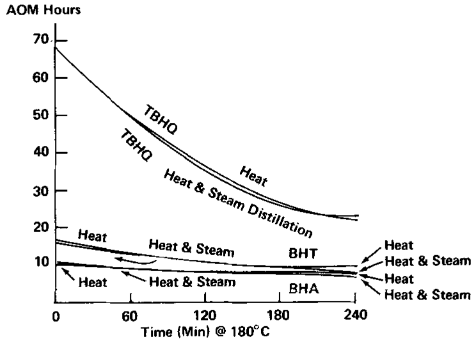


FIG. 13. Effect of heat and steam distillation on AOM stability of antioxidant-treated soya oil.

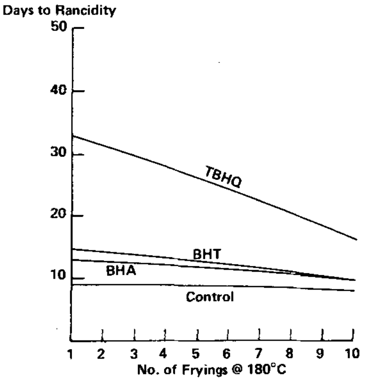


FIG. 14. Effect of antioxidant loss on Schaal oven stability of potato chips.

stability test on the soya oil showed that TBHQ provides maximal protection at frying conditions (Fig. 13). Actual frying tests preparing potato chips with soya oil as a frying medium illustrate the "carry-through" effectiveness of TBHQ into fried foods—even at relatively low concentrations (Fig. 14). The low effectiveness of BHA and BHT antioxidants also is illustrated.

REFERENCES

1. Lundberg, W.O., "Autoxidation and Antioxidants," Vol. I, Interscience Publishers, New York, NY, 1961.
2. Lundberg, W.O., Ibid., Vol. II, 1962.
3. "Bailey's Industrial Oil and Fat Products," 3rd Edition, edited by D. Swern, Interscience Publishers, New York, NY, 1964.
4. Schultz, H.W., E.A. Day and R.O. Sinnhuber, "Symposium on Foods: Lipids and Their Oxidation," The AVI Publishing Co., Westport. CT. 1962.
5. Weiss, T.J., "Food Oils and Their Uses," The AVI Publishing Co., Westport, CT, 1970.
6. Emanuel, N.M., and Yu N. Lyaskovshaya, "The Inhibition of Fat Oxidation Processes," Pergamon Press, New York, NY, 1967.
7. Sherwin, E.R., JAOCS, 53:430 (1976).
8. Thompson, J.W., and E.R. Sherwin, Ibid. 43:683 (1966).
9. Sherwin, E.R., and J.W. Thompson, Food Technol. 21:106 (1967).
10. "Effectiveness of TBHQ Antioxidant in Refined Vegetable Oils," Eastman Chemical Products, Inc., Publication no. 2F-204A, November 1974.
11. Sherwin, E.R., and B.M. Luckadoo, JAOCS 47:19 (1969).
12. "Official and Tentative Methods of the American Oil Chemists' Society," AOCS, Champaign, IL, 1971, Method Cd 12-57.
13. "A Study of the Stabilization of Whole-Crude, Once-Refined and Oxidized Crude Palm Oil with TBHQ Antioxidant," Eastman Chemical Products, Inc., Publication no. 2G-215B, February 1978.
14. "Alternatives in Processing Soybean Oil using TBHQ Antioxidant," Eastman Chemical Products, Inc., Publication no. 2G-207C, December 1978.

Metabolic Aspects of Positional Monounsaturated Fatty Acids Isomers

E.A. EMKEN, Northern Regional Research Center, Agricultural Research,
Science and Education Administration, U.S. Department of Agriculture, Peoria, IL 61604

ABSTRACT

Absorption and distribution of positional *cis* and *trans* octadecenoic acid isomers in lipids from rat, egg and human tissues are reviewed. Selected data on enzyme, single-cell, and whole-animal studies with positional octadecenoic acid isomers are summarized and compared.

INTRODUCTION

Partial hydrogenation of soya oil is used to increase the flavor and odor stability by reducing the level of polyunsaturated fatty acids and, in particular, the linolenic acid content. Hydrogenation or hardening also imparts desirable physical qualities useful in the formulation of margarines and shortenings. Soya oil products are highly palatable and are widely consumed in the U.S. In fact, it can be estimated that hydrogenated soya oil contributes ca. 22% of the visible and nonvisible fat consumed in the American diet. Table I illustrates the effect of various levels of partial hydrogenation on the composition of soya oil (1).

In addition to the changes in fatty acid composition, the structure of a portion of the unsaturated fatty acids is rearranged to form *cis* and *trans* positional isomers (2-4). The distribution of these positional isomers in the monounsaturated fraction from hydrogenated soya oil is illustrated in Figure 1 for a commercial nickel hydrogenated soya oil.

The contribution of positional isomers to the daily American diet is estimated in Table II (5) to be ca. 9 g, which is ca. 0.6 of a tablespoon. Thus, the individual monomer isomers contribute ca. 80 calories/day, which is not particularly significant. The nutritional and biological impact of these isomers in the human diet is difficult to assess. We do know that due to biohydrogenation, ruminant

TABLE I

Fatty Acid Composition (%) of Soybean Oil (SBO) and Partially Hydrogenated Soybean Oils (1)

Fatty acid[a]	SBO	HSBO-1[b]	HSBO-2[b]	HSBO-3[b]
16:0	11	11	11	11
18:0	4.1	4.3	7	10.5
c-18:1[c]	22	29	33	18
t-18:1[c]	–	12	12	51
9*c*,12*c*-18:2	54	31	22	–
9*c*,12*t*- and 9*t*,12*t*-18:2	–	4	6	–
9*t*,12*t*-18:2	–	–	–	–
9*c*,13*t*- and 8*t*,12*t*-18:2	–	2	4	9
Conjugated isomers	–	2	0.5	
18:3 (all isomers)	7.5	2.3	2.0	–
>20:0	1	1	1	1

[a] Abbreviations used: Geneva numbering system used for fatty acids, where the first number indicates the position of the double bond; the *c* or *t* following the first number indicates *cis* or *trans* configuration, if known; and the second number indicates number of carbons in the acyl chain, with the number following the colon designating the number of double bonds.

[b] HSBO = partially hydrogenated soybean oil.

[c] Includes positional octadecenoic acid isomers.