TBHQ IN SUNFLOWER OIL.

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ABSTRACT

The sunflower is the second largest source of vegetable oil in the world today. Approximately 85 — 90% of the fatty acids in sunflower oil are oleic and linoleic acids. This high degree of chemical unsaturation makes sunflower oil rather susceptible to oxidation changes. Oxidative deterioration is a major problem associated with the refining, storage, and usage of sunflower oil. Laboratory and commercial experience during the last decade has shown Tertiary Butyl Hydroquinone (TBHQ) to be the most effective phenolic antioxidant for highly unsaturated vegetable oils. The objective of this study was to determine if TBHQ is effective in alleviating oxidative changes in sunflower oil during storage and usage. Specific topics include TBHQ in crude sunflower oil, TBHQ in refined sunflower oil and TBHQ in a frying system using sunflower oil as the frying medium. In all cases, TBHQ was effective in inhibiting oxidative changes. The experimental design used in these studies allowed the derivation of equations that predict the stability that can be achieved with the usage of TBHQ.

INTRODUCTION

Properties of Sunflower Oil — The sunflower is the second largest source of vegetable oil in the world today. Its usage in the United Stages has also increased dramatically during the last decade. Sunflower oil is derived primarily from unsaturated fatty acids. (Table 1) Approximately 85 — 90% of the fatty acids in sunflower oil are oleic and linoleic acids. This high degree of chemical unsaturation makes sunflower oil rather susceptible to free radical oxidation. The objective of this study was to determine if TBHQ antioxidant could alleviate problems resulting from oxidation of sunflower oil during storage and usage.

Table 1

TYPICAL PROPERTIES OF REFINED SUNFLOWER OIL

Fatty Acid Distribution

Acid	%
Palmitic	7
Stearic	5
Oleic	19
Linoleic	68
Linolenic	0.5
Iodine Value	122-139

Effectiveness of TBHQ in Vegetable Oils — TBHQ antioxidant is highly purified tertiary-butylhydroquinone. (Figure 1) Laboratory and commercial experience over the last decade has shown TBHQ to be the most effective phenolic antioxidant for highly unsaturated vegetable oils. AOM stability tests on soybean, cottonseed, safflower, palm, rapeseed, and sunflower oil illustrate the effectiveness of TBHQ in inhibiting oxidative changes in vegetable oils. (Table 2)

Figure 1.

TBHQ
(Tertiary-Butylhydroquinone) Antioxidant

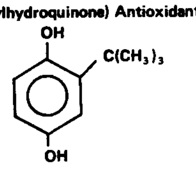
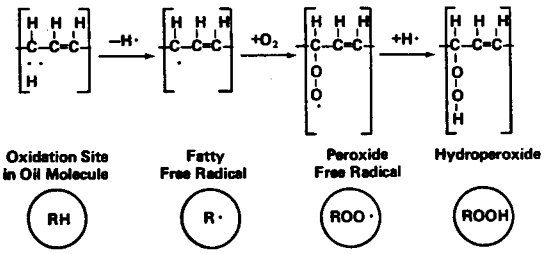


Table 2

EFFECTIVENESS OF TBHQ ANTIOXIDANT IN REFINED VEGETABLE OILS

Oil	Antioxidant Treatment, Wt %	AOM Stability (Hrs. to Reach PV of 70 meq/kg)
Soybean	None (Control)	8
	TBHQ (0.02)	41
Cottonseed	None (Control)	10
	TBHQ (0.02)	44
Safflower	None (Control)	6
	TBHQ (0.02)	40
Rapeseed	None (Control)	10
	TBHQ (0.02)	64
Sunflower	None (Control)	5
	TBHQ (0.02)	34

Figure 2. FREE RADICAL OXIDATION OF SUNFLOWER OIL



Mechanism of Free Radical Oxidation — To understand the role of TBHQ in preventing oxidation of sunflower oil, an understanding of the mechanism of free radical oxidation is required. (Figure 2) The oxidation of sunflower oil occurs in a series of steps and is often referred to as a free radical type of oxidation because the initiating step is the formation of a free radical on the fatty acid portion of the fat molecule. This occurs when a hydrogen ion is lost from the α-methylenic carbon in the fatty acid group. The α-methylenic carbon is the carbon ajacent to the double bond. (Figure 3) 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. (Figure 4) These compounds give the rancid odor and flavor that characterize oxidized sunflower oil. Oxidative randicity is a major problem associated with refining, storage, and uage of sunflower oil.

Figure 3

TRIGLYCERIDE MOLECULE WITH DOUBLE BOND

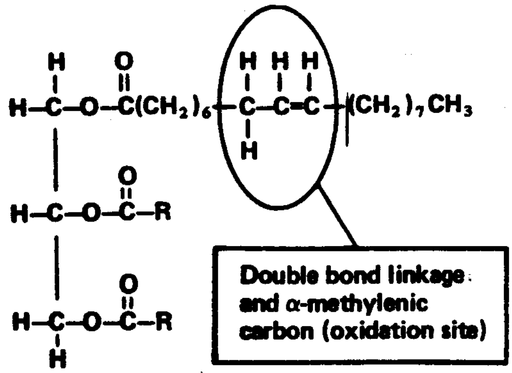
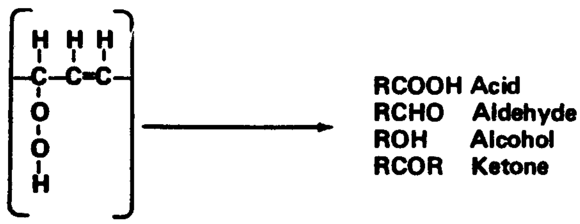


Figure 4

DECOMPOSITION OF HYDROPEROXIDE

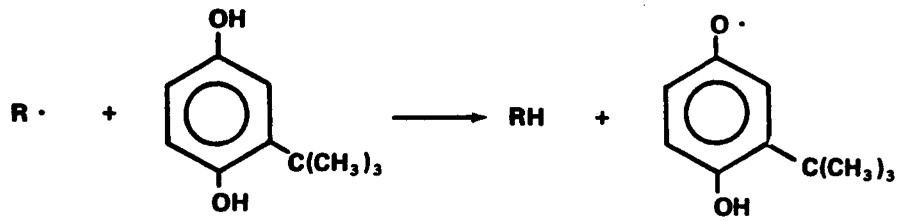


Hydroperoxide

Mechanism of Antioxidants — TBHQ inhibits oxidation by donating a hydrogen ion to a sunflower oil free radical, thereby regenerating the triglyceride molecule and interrupting the free radical mechanism of oxidation. (Figure 5) In doing this, TBHQ itself becomes a free radical; however, the TBHQ free radical can stabilize itself through hybridization and does not promote or propagate further oxidation (Figure 6)

Figure 5

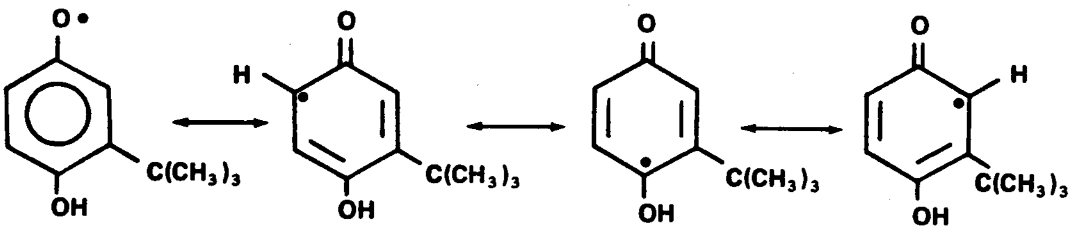
ANTIOXIDANT MECHANISM OF TBHQ ANTIOXIDANT IN SUNFLOWER OIL



Sunflower Oil Free Radical — TBHQ — Sunflower Oil Molecule

Figure 6

ANTIOXIDANT MECHANISM OF TBHQ ANTIOXIDANT IN SUNFLOWER OIL



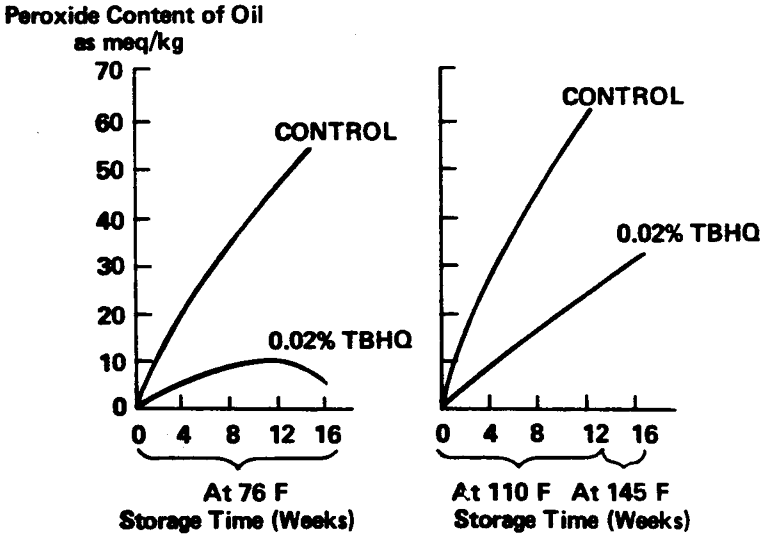
TBHQ Stable Resonance Hybrids

EXPERIMENTAL

TBHQ in Crude Sunflower Oil — Many crude vegetable oils contain significant amounts of natural antioxidants, such as tocopherols and lecithin, and are quite resistant to oxidation. However, crude sunflower oil is quite susceptible to oxidation. Laboratory studies have shown TBHQ can be beneficial in inhibiting oxidation in crude sunflower oil. The addition of 200 ppm TBHQ markedly inhibits the peroxide formation at various storage temperatures. (Figure 7) The AOM stability of crude sunflower oil is increased approximately 600% by the addition of TBHQ. Furthermore, refined oil derived from TBHQ-treated crude sunflower oil has better stability than oil derived from untreated crude sunflower oil.

Figure 7

EFFECTIVENESS OF TBHQ ANTIOXIDANT IN CRUDE SUNFLOWER OIL



TBHQ in Refined Sunflower Oil — Oxidative deterioration of refined sunflower oil during storage can be responsible for substantial economic losses. An experiment was designed to determine the effectiveness of TBHQ and citric acid in inhibiting oxidation in refined sunflower oil during prolonged storage. The experiment was based on response surface methodology that would determine optimum levels of TBHQ and citric acid and provide equations for predicting the stability gained from various combinations of antioxidant treatment. Test responses used to measure oxidative changes were AOM stability, Schaal oven stability, and storage stability at 115°F. The sunflower oil used in this experiment was northern sunflower oil obtained from a commercial supplier. The oil had an initial AOM stability of 5 hours and no detectable peroxides. Samples of the sunflower oil were treated with various levels of TBHQ and citric acid according to a central composite design. Equations for predicting test responses as a function of TBHQ concentration, citric acid concentration, and time were derived by computer. (Table 3). These equations can be used to predict the stability that can be obtained by treating sunflower oil with various levels of TBHQ. These equations were also used to plot response surface diagrams for each response. (Figures 8, 9 10) These response surfaces are contour plots. TBHQ concentration is shown on the x-axis and citric acid concentration on the y-axis. The curves indicate treatments that give equal test responses. Results of these tests indicate the effectiveness of TBHQ in inhibiting oxidative changes in refined sunflower oil during storage. Test results failed to show any optimum combinations of TBHQ and citric acid. Higher levels of TBHQ resulted in increased oxidative stability. Test results also indicated little, if any, synergistic effect from citric acid. These plots and equations can be valuable in assisting producers and users of sunflower oil in adding the correct level of TBHQ to obtain the stability they need.

REFINED SUNFLOWER OIL
B VALUES FOR DETERMINING EQUATIONS TO PREDICT RESPONSES

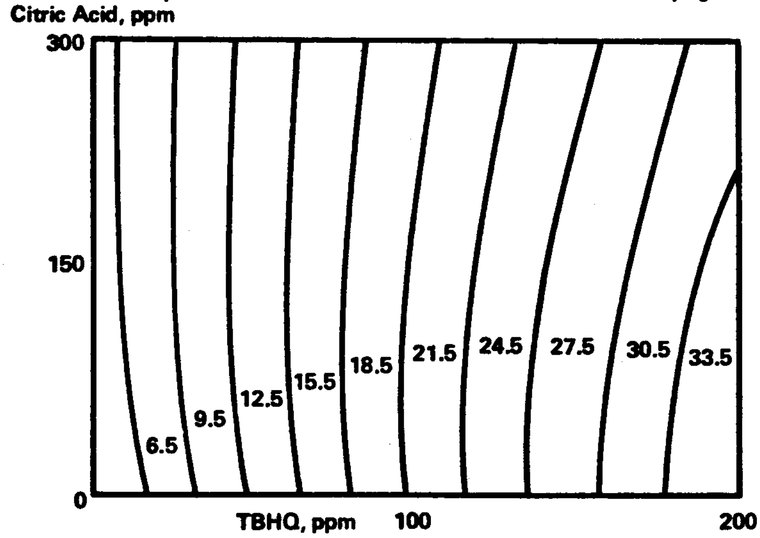
Table 3

	Schaal Oven Stability	AOM Stability	Storage Stability @ 115°F	Peroxide Value
TBHQ	0.17308	0.20403	1.02856	–2.04463
$TBHQ^2$	–	–0.0002	–0.00231	0.00734
CA	–	0.01371		–0.29395
CA^2	0.00014	–0.00002		0.00029
TM	–	–		–14.45767
TM^2	–	–		1.56835
CA TBHQ	–0.00061	–0.0001		–0.00259
CA TM	–	–		0.00266
TBHQ TM	–	–		–0.03733
K	4.86280	3.42344	13.31507	196.01150
R	0.7373	0.9968	0.9820	0.7914
F	8.41	438.03	299.57	23.18
Time	Days	Hours	Days	Days

EFFECT OF TBHQ AND CITRIC ACID CONCENTRATION ON THE AOM STABILITY OF REFINED SUNFLOWER OIL.

Response is Hours to Reach a Peroxide Value of 70 meq/kg

Figure 8



EFFECT OF TBHQ AND CITRIC ACID CONCENTRATION ON THE SCHAAL OVEN STABILITY OF REFINED SUNFLOWER OIL.

Response is Days @ 145°F to Reach Rancidity

Figure 9

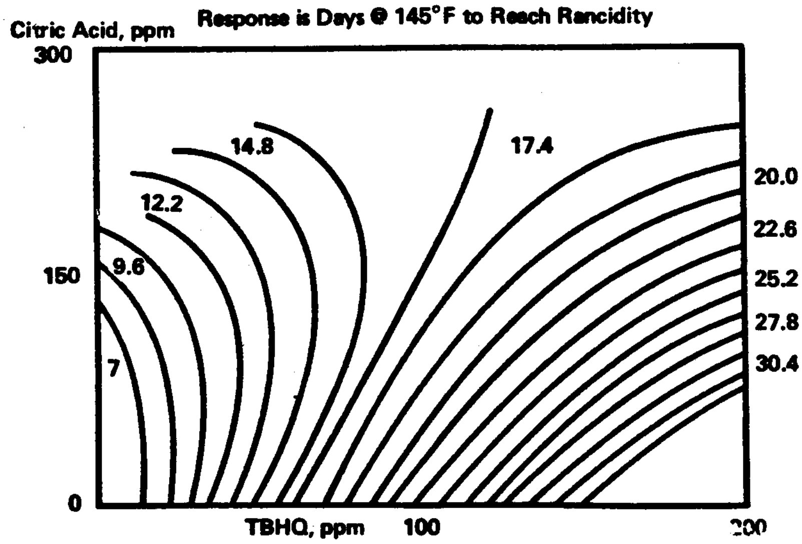
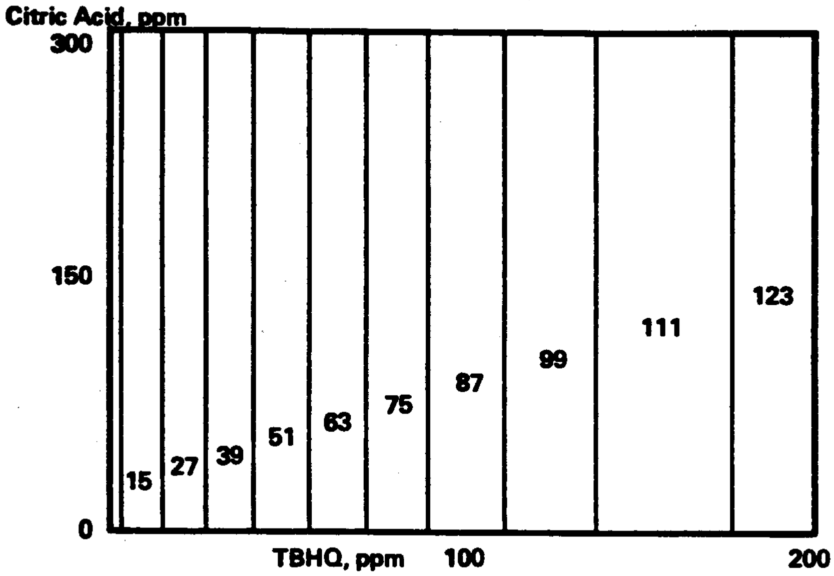


Figure 10

EFFECT OF TBHQ AND CITRIC ACID CONCENTRATION ON THE STORAGE STABILITY OF REFINED SUNFLOWER OIL @ 115°F.

Response is Days to Reach a Peroxide Value of 70 meq/kg



TBHQ in Sunflower Oil Frying Systems — The objective of this study was to evaluate the effectiveness of TBHQ in protecting frying systems using sunflower oil as the frying medium. In this experiment, the stability of potato chips fried in sunflower oil was used to measure the performance of TBHQ. Since previous work has shown high correlation between the Schaal oven stability of potato chips and the AOM stability of frying oil, the effectiveness of TBHQ in protecting the frying oil could also be measured. This study also included a comparison of the effectiveness of BHA and BHT antioxidants with TBHQ. Individual batches of refined sunflower oil were treated with 200 ppm TBHQ, BHA, and BHT, respectively. Ten potato chip fryings were performed in each batch of treated oil to determine "carry-through" effectiveness. The Schaal oven stability of the potato chips was determined according to standard laboratory procedures to measure the effectiveness of each antioxidant treatment. Test results indicated TBHQ was by far the most effective antioxidant. (Figure 11) BHA and BHT provide little, if any, protection to the frying system. The superior "carry-through" effectiveness of TBHQ was also demonstrated. Equations for predicting the Schaal oven stability of potato chips as a function of the number of fryings in sunflower oil were derived for each antioxidant. (Table 4)

Figure 11

EFFECT OF ANTIOXIDANTS ON THE SCHAAL OVEN STABILITY OF POTATO CHIPS FRIED IN REFINED SUNFLOWER OIL

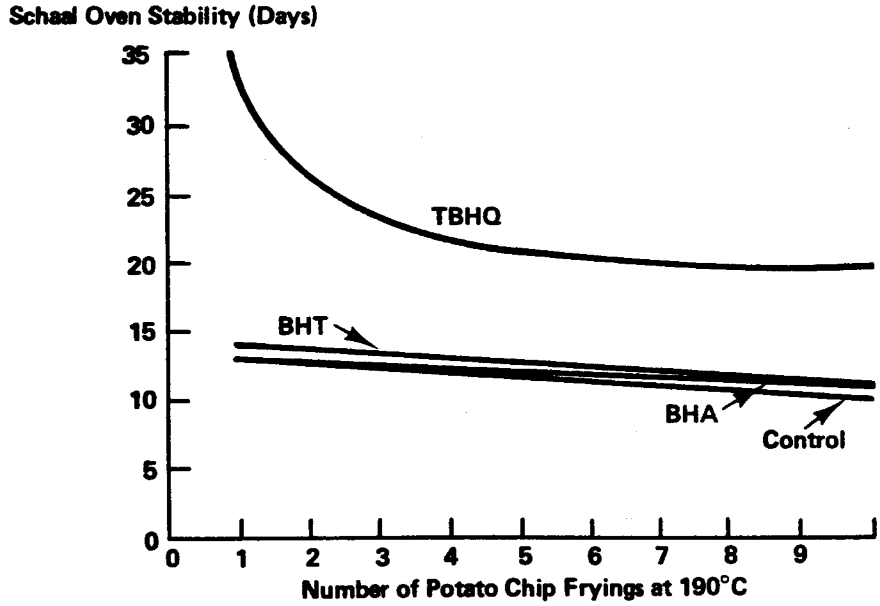


Table 4

EQUATIONS FOR PREDICTING SCHAAL OVEN STABILITY OF POTATO CHIPS AS A FUNCTION OF NUMBER OF FRYINGS IN REFINED SUNFLOWER OIL

Antioxidant	Initial Level (ppm)	Equation	R^2
Control	0	$y = 13.7333 - 0.4697x$	50.5
TBHQ	200	$y = 36.1083 - 4.4057x + 0.2746x^2$	86.2
BHA	200	$y = 13.0333 - 0.0970x$	38.8
BHT	200	$y = 13.8333 - 0.2788x$	74.6

y = Schaal Oven Stability (Days)
x = No. of Fryings @ 190°C

CONCLUSIONS

Test results indicated that TBHQ is effective in inhibiting oxidative changes in sunflower oil in various facets of production and usage. The superior benefits of TBHQ as compared to other phenolic antioxidants, such as BHA and BHT, were also demonstrated. The equations derived from these experimental data should be useful to processors and users of sunflower oil in predicting the stability that can be derived by using TBHQ anitoxidant.