Tertiary Butylhydroquinone as Antioxidant for Crude Sunflower Seed Oil[1]

B.M. LUCKADOO and **E.R. SHERWIN**, Eastman Chemical Products, Inc., Kingsport, Tennessee 37662

ABSTRACT

This study indicates that crude sunflower seed oil is very susceptible to oxidation; thus prolonged storage should be avoided. Protection of the crude oil with a potent antioxidant such as tertiary butylhydroquinone (TBHQ) would seem both practical and beneficial. Discoloration which develops in the crude oil with or without TBHQ can be removed by proper selection of bleaching materials. Additional benefits to be derived from using TBHQ should be investigated by using test methods designed to study subtle flavor qualities of deodorized oils.

INTRODUCTION

The world's supply of sunflower seed oil has increased more than 60% since 1961 to rank second only to that of soybean oil (1-4). Current United States interest in sunflower appears to have been stimulated partly by its success in Russia and the availability of the new and improved Russian varieties (1,4). Breeding sunflowers to improve yield and oil quality remains a primary research objective (5,6).

Major use of sunflower seed oil at the present time is in the manufacture of margarines, shortenings and salad oils. Acceptance for other food uses has not been widespread as it tends to polymerize under conditions such as those encountered in deep-fat frying. Additional applications may well develop for the newer high oil varieties of sunflower.

Many published articles have cited various oxidative changes occurring in crude vegetable oils during storage and some attempts have been made to relate these changes in crude oils to the quality of refined oils (7). While most of these earlier studies have been conducted with cottonseed and soybean oils, recent data have been reported on oxidative characteristics of crude and refined sunflower seed oils. Mikolajczak (8) found that crude sunflower seed oil oxidizes more readily than many refined oils and that significant differences in oxidation tendencies exist between U.S. and Russian varieties.

Since antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and propyl gallate have played vital roles in the marketing of other vegetable oils for food use, it would seem their use would be warranted in sunflower seed oil, a polyunsaturated oil. However, treatment of sunflower seed oil with antioxidants has not received much attention until recently. Sedlacek (9,10) and Schmidt-Hebbel et al. (11) have cited the favorable response of refined sunflower seed oil to treatments with BHA, BHT, propyl gallate and ascorbyl palmitate. Sherwin and Luckadoo (7) illustrated the inhibitory effects of three phenolic antioxidants (BHA, propyl gallate and tertiary butylhydroquinone) in a variety of crude vegetable oils including sunflower seed oil. This work further demonstrated that where oxidation occurs in crude vegetable oils during storage the adequacy of food-approved antioxidants BHA and propyl gallate may be questionable, but a developmental antioxidant tertiary butylhydroquinone (TBHQ) appeared to be quite effective. There was also evidence that TBHQ protection of crude safflower, soybean and cottonseed oils during storage resulted in improved oxidative stability characteristics of the refined oils.

An apparent anomaly in these findings was observed with refined sunflower seed oil. This oil not only had an apparent reduction in stability but was noticeably discolored. It thus became our objective to explore further the causes for this stability reduction. This is a report of our laboratory studies to determine if such instability and color problems were simply related to the laboratory techniques used in the earlier work, or if such problems can be anticipated under more normal handling conditions and will preclude use of TBHQ as an antioxidant in crude sunflower seed oil.

EXPERIMENTAL PROCEDURES

Crude sunflower seed oil was obtained from regular production stocks of a commercial supplier and to minimize oxidation prior to use the crude oil was packaged under nitrogen. The oil was a blend from two Russian varieties VNIIMK8931 and PEREDOVIK, with a fatty acid composition of 72% linoleic, 16.5% oleic, trace of linolenic, trace of myristic, 7.0% palmitic and 4.5% stearic acid. The oil had an iodine value of 137, a free fatty acid value of 0.45% (as oleic) and no detectable peroxides.

The antioxidant evaluated was a refined grade of TBHQ identical to that used in our preliminary program with crude vegetable oils (7). Where TBHQ was added to the crude or deodorized sunflower seed oil, such application was by direct addition at 140 F with adequate agitation to insure complete solution. (Deodorized refers to a finished, refined oil prepared from crude oil by the alkali refining, bleaching and steam deodorization methods described under experimental procedures.)

The active oxygen method (AOM) stability of the crude or deodorized oil, determined in accordance with AOCS Method Cd 12-57, was expressed as the number of hours required to reach a peroxide value of 70 meq/kg of oil.

Oven storage tests consisted of holding small samples (2

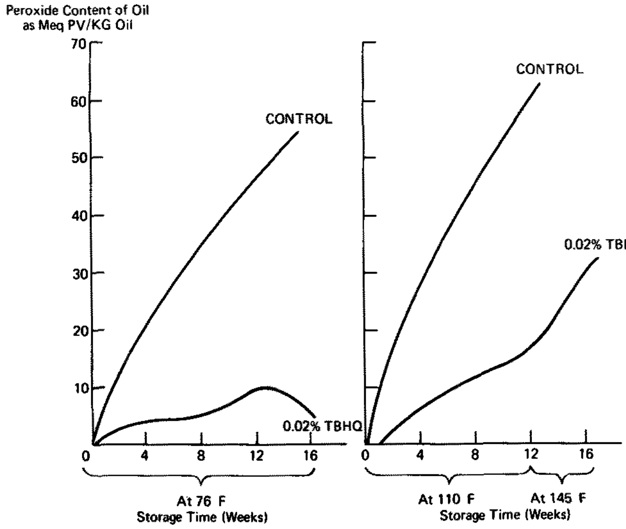

FIG. 1. Peroxide formation in crude sunflower seed oil during storage.

[1]Presented at the AOCS Meeting, Houston, May 1971.

TABLE I

Storage Tests With Crude Sunflower Seed Oil

Storage conditions	Initial antioxidant treatment	Stability evaluations: AOM, hr	Oven, days	Color ratings[a]: F.A.C.	Lovibond
Unstored	None	8	15	11	4.2R,25Y
	0.02% TBHQ	48	55	11	4.2R,25Y
76 F (4 mo)	None	2	16	11B	4.55R,25Y
	0.02% TBHQ	44	50	11B	6.54R,35Y
110-145 F (4 mo)	None	1	13	17	9.14R,50Y
	0.02% TBHQ	12	24	31	14.0R,70Y

[a]Deodorized oils had F.A.C. rating of 1 and Lovibond ratings of 1 red, 6 yellow.

oz each) of the oils in capped glass jars in a convection-type electrically heated oven at 145 F. The endpoint was the time when rancid odor was detected in the sample by a majority of the organoleptic panel members.

The crude oil was refined by adding cold caustic (16° Baumé + 0.2% excess NaOH) to the oil at 80 F and holding the mixture at this temperature for 20 min with moderate agitation. The agitation was decreased and the temperature rapidly raised to 150 F to break the emulsion and facilitate settling of the soapstock, which was allowed to settle for 1 hr. The refined oil was decanted from the soapstock and washed twice with 10% portions of water.

The refined oil was bleached by adding 2% diatomaceous earth and 0.5% fuller's earth to the oil at 200 F with agitation. The slurry was stirred for almost 10 min and vacuum filtered. The refined bleached oil was steam deodorized for 3 hr in a specially devised laboratory apparatus at 400 F and 2-4 mm pressure.

For long term storage the crude sunflower seed oil was stored in the dark in half gallon clear glass jars with screw caps, at temperatures cited in Figure 1 and Table I. The jars were kept tightly closed except when the stored oils were sampled to determine peroxide content by the same iodometric procedure employed in the AOM tests. Color evaluations were conducted by Lovibond and F.A.C. methods (12,13). TBHQ analyses were by a standard colorimetric procedure used in our laboratory (14) while metal analyses were conducted by atomic absorption spectrophotometry.

RESULTS

The effect of temperature on the rate of oxidative deterioration in crude sunflower seed oil is shown in Figure 1. As expected, peroxide development is more rapid at elevated temperatures. We confirmed our earlier work since TBHQ markedly inhibits peroxide buildup irrespective of storage conditions.

As shown in Table I the AOM and oven stabilities of unstored and stored crude oils are greatly enhanced by TBHQ treatment. Furthermore the presence of TBHQ in the crude oil during storage apparently provides a slight stability improvement in the deodorized oil and a more favorable response to further antioxidant treatment (Table II). F.A.C. and Lovibond color determinations (Table I) indicate that some discoloration develops in both control and TBHQ treated oils especially during high-temperature exposure. There was no carry-through of this color into the deodorized oil as observed in our initial work.

DISCUSSION

These stability studies indicate that TBHQ can be used to protect crude sunflower seed oil with success similar to that obtained with other crude vegetable oils. Discoloration can develop in stored sunflower seed oil to yield unacceptably dark crude and refined oils. The color can be removed efficiently with a bleaching system comprised of diatomaceous and fuller's earth. The effective use of fuller's earth as a bleaching agent for crude sunflower seed oil has recently been reported (15).

Color formation in crude sunflower seed oil is apparently caused by oxidation of natural oil components. Darkening of crude vegetable oils has been attributed to oxidation of proteins, pigments, carbohydrates (16,20) and phosphatides (17). Such reactions are catalyzed by heat (16), metal contamination (16,18) and even bleaching agents (15,19). Where TBHQ is present some destruction of the antioxidant also takes place. Phenolic antioxidants oxidize in the presence of heat and metals to form colored quinoid compounds (21). We found ca. 1.0 μg iron and 3.0 μg sodium/g of oil in the test sunflower seed oil. Popov and

TABLE II

Stability Studies With Deodorized Sunflower Seed Oil

Deodorized oil prepared from:	No antioxidant added[a]: AOM, hr	No antioxidant added[a]: Oven, days	0.02% TBHQ added: AOM, hr	0.02% TBHQ added: Oven, days
Unstored crude				
Without TBHQ	10	11	50	48
With 0.02% TBHQ	10	11	---	---
Crude stored at 76 F for 4 mo				
Without TBHQ	9	11	51	35
With 0.02% TBHQ	10	12	50	42
Crude stored at 110-145 F for 4 mo				
Without TBHQ	10	11	46	38
With 0.02% TBHQ	14	13	49	48

[a]Analyses indicated no antioxidant carried through from the TBHQ treated crude oils.

Stefanov (18) report that crude sunflower seed oil normally contains high levels of iron ranging from 0.42-2.13 μg/g.

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