Effect of Antioxidants on Refined Palm Oil

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ABSTRACT

Alkali refined palm oil and hydrogenated cottonseed oil were stabilized with butylated hydroxytoluene, butylated hydroxyanisole, and tertiary butylhydroquinone. Under bulk storage temperatures significant reductions in the peroxide formation of palm oil were obtained only with tertiary butylhydroquinone. The reduction in peroxide formation with tertiary butylhydroquinone was much greater than anticipated from the active oxygen method results. The stability improvement of a snack product fried in palm oil stabilized with tertiary butylhydroquinone depended greatly on the frying conditions used. Under mild frying conditions tertiary butylhydroquinone had somewhat greater carry-through than butylated hydroxytoluene. Under more severe frying conditions tertiary butylhydroquinone provided less protection than butylated hydroxytoluene. Both palm oil and hydrogenated cottonseed oil stabilized with only butylated hydroanisole had higher active oxygen stabilities than the unstabilized controls; however, no reduction in peroxide formation of the butylated hydroxyanisole oils compared to the controls was found during storage of the oil or the snack product at 50-60 C.

INTRODUCTION

Peroxide values of palm oil samples received from suppliers for evaluation in food products varied from 1 to 8. Compared to other oils received for evaluation, the frequency of palm oil samples with high peroxide values was unusual. It was decided to check the deterioration of palm oil under bulk storage temperatures of 50-60 C. At the same time, the effect of various antioxidants including tertiary butylhydroquinone (TBHQ), which has been reported to have a higher potency (1), were evaluated.

EXPERIMENTAL PROCEDURES

Oil Storage Evaluations

Palm oil samples were obtained from different suppliers. All had been alkali refined, bleached, and steam deodorized. Free fatty acids in the oils were <0.05%, and the Lovibond color was <3.5 red. The unstabilized oils were treated with antioxidants within 1-2 weeks from the time of refining. Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) were added to the oils as 20% solutions in peanut oil, and TBHQ was added as a 20% solution in propylene glycol. The treated oils were held at 54-60 C for 24 hrs with occasional stirring to assure uniform dispersion of the antioxidants. The iodine value (IV) (2), initial peroxide value (3) and the active oxygen method (AOM) stability (4) then were determined. The levels of BHA and BHT were checked by the method of Schwecke and Nelson (5).

Sixteen oz glass jars (6 cm in diameter and 16 cm high) were filled two-thirds full with ca. 225 g oil. The jars, loosely capped, were stored at 54 C without agitation. At 2-week intervals a jar was removed from storage, the oil mixed, and the peroxide value determined. For each oil sample, enough jars were stored so that no jar, once removed from storage and the oil mixed, had to be reused.

Frying Experiments

Oil (2400g) was added to a home-type deep fat fryer. The oil was heated to 190 C, which required ca. 30 min. For the next 30 min the oil was kept hot without agitation, and the temperature adjusted to hold steady at 190 C. A 60 g batch of snack pellets, with a moisture of ca. 12% then was fried for 40 sec. The frying basket was removed from the oil and the excess oil allowed to drip back into the fryer for 20 sec. One batch was fried every 4 min. The first 5 batches were not saved for product evaluation. After 1 hr of frying, 600 g of fresh oil was added to replenish the oil in the fryer. The oil then was held at 190 C for 3 hr with slight agitation to simulate an interruption in a continuous frying operation. Intermittent frying deteriorates oil more severly than uninterrupted frying. A second 1 hr of frying was then carried out in the same manner as the first.

The products from the frying experiments were stored in 16 oz glass jars at 54 C. Initially and at weekly intervals, the peroxide value of the oil extracted from the product was determined. The following extraction procedure was used. After the product had cooled, it was crushed and

TABLE I

Active Oxygen Method (AOM) Stability of Oils Treated with Different Antioxidants

	Palm oil			Hydrogenated cottonseed oil	
Supplier	A	B	C	A	B
Iodine value	53.1	55.5	58.0	65.7	65.9
For oil storage	1	2	4	1	3
For product storage	-	6 & 7	-	-	5
Antioxidant added[a]	AOM stability (hr)				
None	45	40	40	95	80
BHA + BHT - 100 ppm each	60	55	55	130	120
BHA - 200 ppm	-	55	-	-	120
BHT - 200 ppm	-	60	-	-	120
TBHQ - 50 ppm	-	-	60	-	-
TBHQ - 100 ppm	100	90	85	200	160
TBHQ - 200 ppm	-	125	115	-	220

[a] BHA = butylated hydroxyanisole; BHT = butylated hydroxytoluene; TBHQ = tertiary butylhydroquinone.

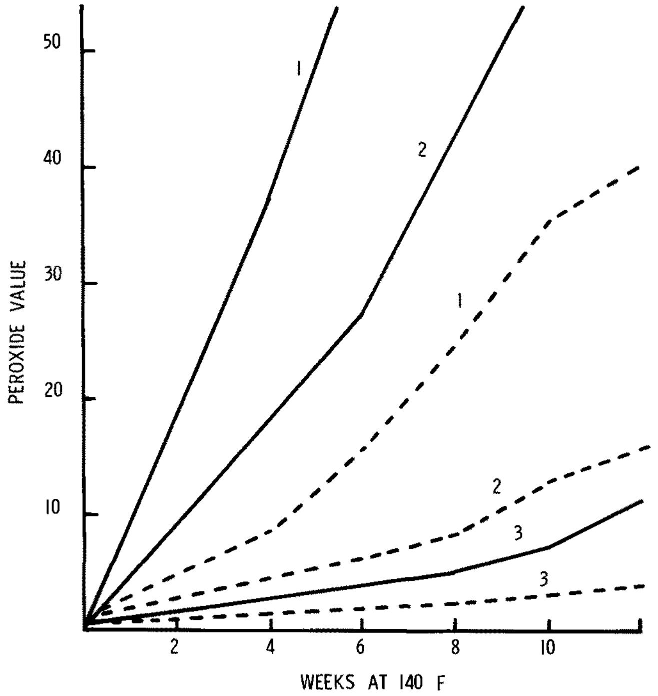

FIG. 1. Peroxide formation of stored palm oil (–) and hydrogenated cottonseed oil (---) treated with no antioxidants (1), with 100 ppm each of butylated hydroxyanisole and butylated hydroxytoluene (2), and with 100 ppm tertiary butylhydroquinone (3).

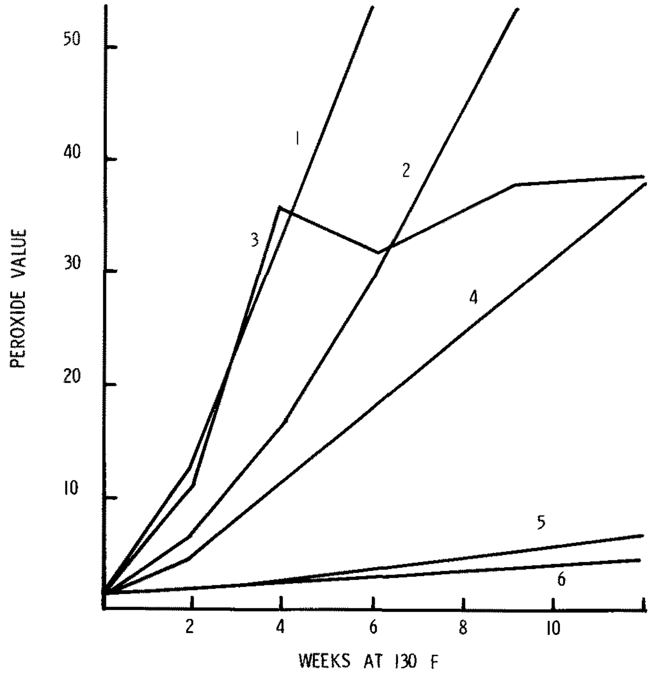

FIG. 2. Peroxide formation in stored palm oil containing no antioxidants (1), 81 ppm butylated hydroxyanisole (BHA) and 106 ppm butylated hydroxytoluene (BHT) (2), 190 ppm BHA (3), 229 ppm BHT (4), ca. 100 ppm tertiary butyl hydroquinone (TBHQ) (5), and ca. 200 ppm TBHQ (6).

mixed. Ten to 20 g of the sample and 150 ml of Skelly F were placed in a beaker and stirred intermittently for 9 min. The solvent then was filtered through Whatman No. 4 paper into a weighed flask. The solvent was stripped off in a vacuum evaporator using a 55 C water bath, and the oil in the flask was allowed to cool before the vacuum was broken. The extraction procedure was checked using oils with peroxide values ranging from 5 to 50. The peroxide values of the portion of these oils carried through the extraction and solvent evaporation procedure was within 5% of the peroxide value determined directly from these oils.

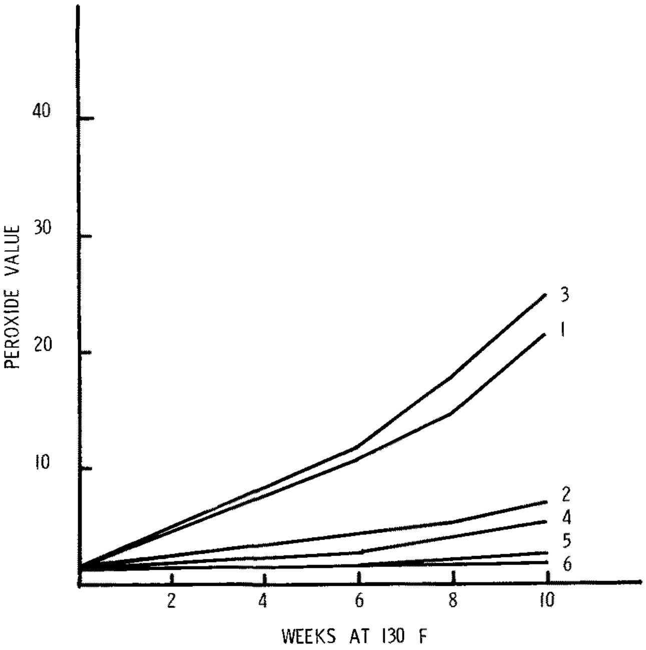

FIG. 3. Peroxide formation in stored hydrogenated cottonseed oil containing no antioxidants (1), 90 ppm butylated hydroxyanisole (BHA) and 97 ppm butylated hydroxyquinone (BHT) (2), 173 ppm BHA (3), 187 ppm BHT (4), ca. 100 ppm tertiary butylhydroquinone (TBHQ) (5), and ca. 200 ppm TBHQ (6).

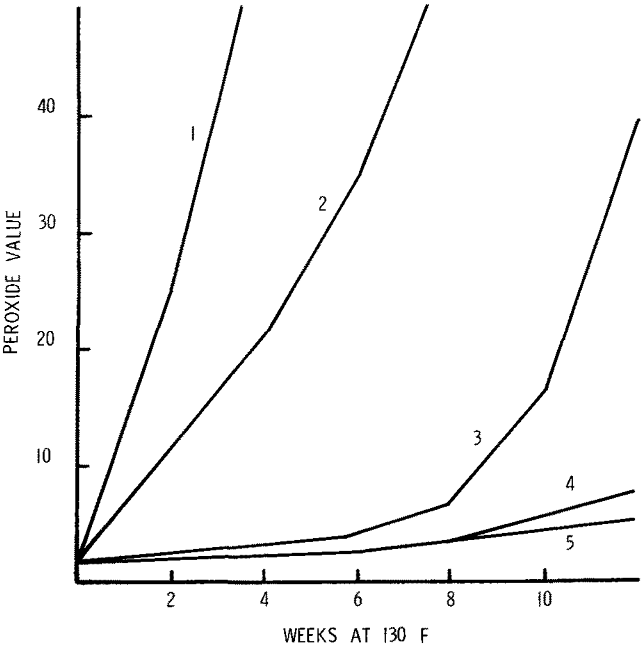

FIG. 4. Peroxide formation in stored palm oil containing no antioxidants (1), 98 ppm butylated hydroxyanisole (BHA) and 122 ppm butylated hydroxytoluene BHT (2), ca. 50 ppm tertiary butylhydroquinone (TBHQ) (3), ca. 100 ppm TBHQ (4), and ca. 200 ppm TBHQ (5).

RESULTS AND DISCUSSION

AOM stability results for three palm oil samples and two hydrogenated cottonseed oil samples are shown in Table I. The increase in the peroxide values of these oils at bulk storage temperatures are shown in Figures 1-4. Under the

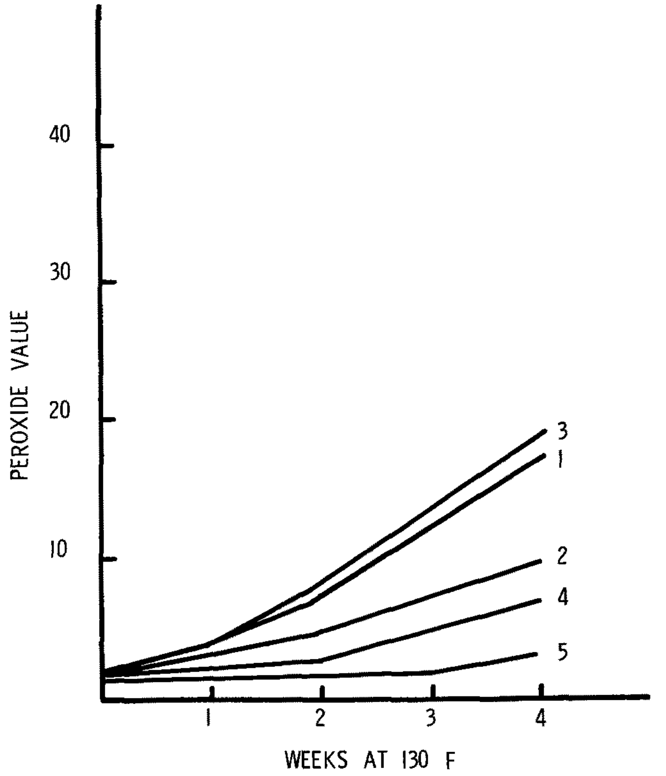

FIG. 5. Increase in peroxide value of a snack product fried under mild conditions in hydrogenated cottonseed oil stabilized with no antioxidants (1), 100 ppm butylated hydroxyanisole (BHA) and 110 ppm butylated hydroxytoluene (BHT) (2), 150 ppm BHA (3), 140 ppm BHT (4), and ca. 150 ppm tertiary butylhydroquinone (5).

latter conditions, the peroxide value of all three palm oil samples without antioxidants increased very rapidly. BHT reduced the rate of peroxide formation by a factor of ca. 1.5, which was consistent with the results of the AOM stability tests. On the other hand, TBHQ reduced the peroxide formation at 54 C much more effectively and to a greater extent than anticipated from the AOM results. BHA did not reduce the peroxide formation at 54 C in spite of the fact that the AOM stability of the samples with only BHA were higher than that of the unstabilized samples. From the results shown in Figure 2, it appears that BHA at levels of 150-200 ppm did not inhibit oxidation, but merely accelerated the decomposition of peroxides.

The increase in peroxide values of product collected during the first hr of frying in hydrogenated cottonseed oils is shown in Figure 5 and for palm oils in Figure 6. The rate of oxidation of the oil in the product was more rapid and the protection provided by the antioxidants less than that of the fresh oils stored at 54 C. Under these mild frying conditions, TBHQ had a somewhat greater carry through than the same level of BHT; however, the lower level of TBHQ did not. The results obtained for a snack fried in palm oils under more severe conditions are shown in Figure 7. The effectiveness of the antioxidants was even less, and the carry-through of TBHQ less than that of BHT.

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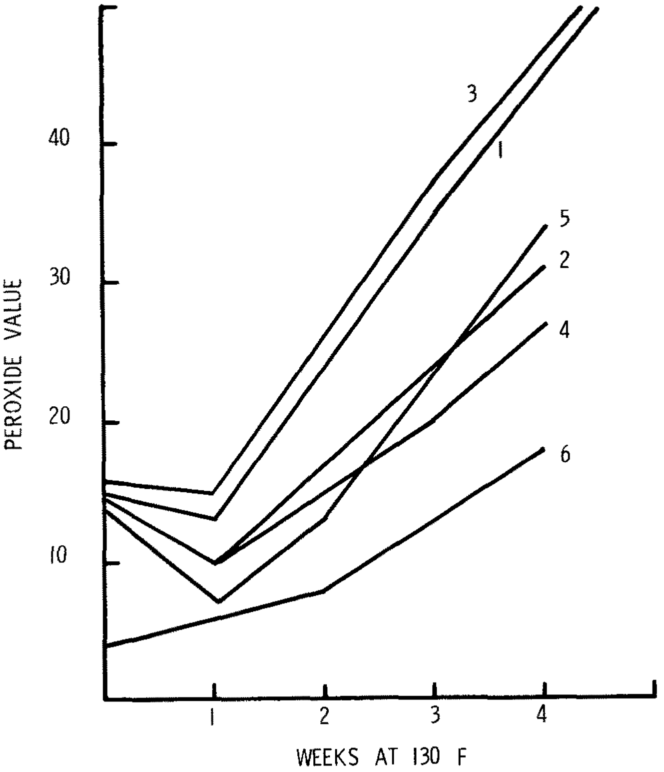

FIG. 6. Increase in peroxide value of a snack fried under mild conditions in palm oil stabilized with no antioxidants (1), 81 ppm butylated hydroxyanisole (BHA) and 106 ppm butylated hydroxytoluene (BHT) (2), 190 ppm BHA (3), 229 ppm BHT (4), ca. 100 ppm tertiary butylhydroquinone (TBHQ) (5), and ca. 200 ppm TBHQ (6).

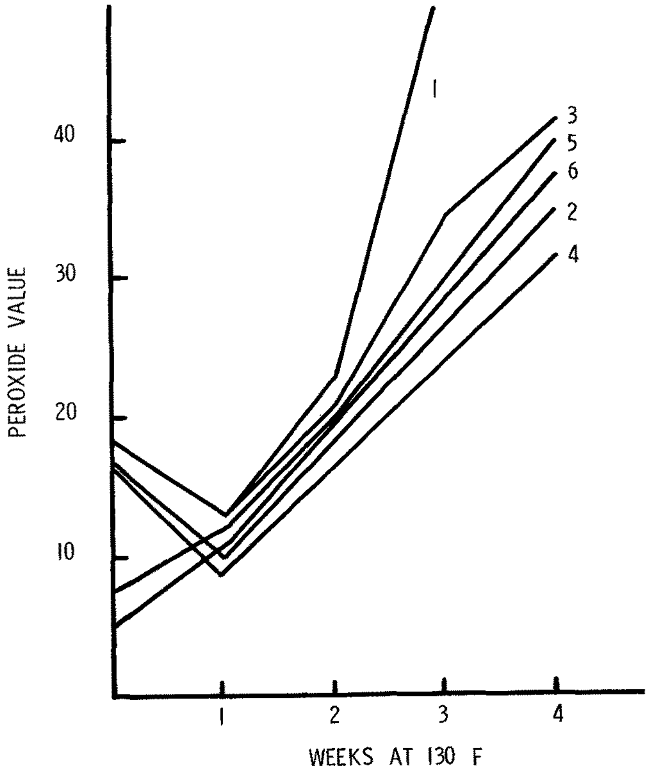

FIG. 7. Increase in peroxide value of snack fried under harsh conditions in palm oil stabilized with no antioxidants (1), 81 ppm butylated hydroxyanisole (BHA) and 106 ppm butylated hydroxytoluene (BHT) (2), 190 ppm BHA (3), 229 ppm BHT (4), ca. 100 ppm tertiary butylhydroquinone (TBHQ) (5), and ca. 200 ppm TBHQ (6).