Effect of Stabilization of Crude Whale Oil with Tertiary Butylhydroquinone and Other Antioxidants upon Keeping Quality of Resultant Deodorized Oil. A Feasibility Study[1]

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ABSTRACT

Crude whale oil was stored under accelerated conditions for 146 days alone and in the presence of added antioxidants: 0.02% butylated hydroxyanisole, 3,5-di-t-butyl-4-hydroxyanisole, propyl gallate, tertiary butylhydroquinone, TBHQ + 0.01% citric acid, and 0.01% citric acid. Inverse relationships were noted between peroxide values and oxidative stabilities and also between secondary oxidation products, measured by anisidine value, and oxidative stabilities at termination of the storage of antioxidant-treated crudes. Tertiary butylhydroquinone was most effective, followed by butylated hydroxyanisole,3,5-di-t-butyl-4-hydroxyanisole, and propyl gallate, in decreasing order, with respect to retardment of oxidative deterioration of stored crude whale oil. All antioxidant-treated crudes were alkali refined and steam deodorized. Stability times of deodorized oils from crudes treated with butylated hydroxyanisole,3,5-di-t-butyl-4-hydroxyanisole, propyl gallate and citric acid ranged from 13.5-18 days at 30 C. Deodorized oils from tertiary butylhydroquinone-and tertiary butylhydroquinone-citric acid-treated crudes gave much longer stability times against oxidative deterioration at 30 C, viz. 49.5 and 56 days, respectively. The major factor that contributed to the improvement in oxidative stability and caused continued effectiveness of tertiary butylhydroquinone even after deodorization was the carry-through of the antioxidant and its oxidation products from the crude into the deodorized oil. If tertiary butylhydroquinone-stabilized crude oils are deodorized, the residual antioxidant and its oxidation products should be determined quantitatively by adequate analytical methods and be included as part of the food-approved antioxidants in processed edible oils.

INTRODUCTION

Oxidative deterioration of oils, fats, and fat containing foods is one of the main problems in the food industry.

Extensive research work by American and Swedish investigators (1-5) indicated that the autoxidation of oils in the crude phase is harmful to both the flavor and oxidative stabilities after their processing for edible purposes. A parallel relationship has been identified between levels of hydroperoxides in crudes and the resultant occurrence of end products of oxidation in deodorized oils. The oxidative degradation compounds are derived from degradation of hydroperoxides and generally are termed secondary oxidation products. They occur in crude, refined, bleached, and deodorized oils and are composed of volatile and nonvolatile carbonyl compounds (6). The former are responsible for off-flavors in autoxidized oils. The latter are present at a much higher concentration than the former and are composed of high mol wt compounds. It has been reported (7) that the unsaturated nonvolatile carbonyl compounds autoxidize by the same basic mechanisms as the parent fatty acids; hence, they are precursors of volatile, flavorful carbonyls. In addition, it has been shown (8, 9) that nonvolatile carbonyls have a prooxidant effect proportional to their concentration in deodorized oils. The secondary oxidation products are determined in oils and fats by the benzidine or anisidine method outlined by Holm, et al., (4,5) or the dimer method described by Baumann, et al. (2).

Sherwin and Luckadoo (10, 11) observed a need to protect crude unsaturated oils from oxidative degradation during storage. These investigators successfully stabilized crude vegetable oils with tertiary butylhydroquinone (TBHQ) and propyl gallate (PG) during storage under accelerated conditions. Oxidation reactions were followed by peroxide measurements. In addition, the deodorized oils prepared from antioxidant-treated stored crudes had better oxidative stability than untreated crudes, especially in the case of TBHQ. Chemical examination of deodorized oils indicated that no antioxidants had been carried through. These investigators gave no explanation for the improvement in oxidative stability of deodorized oils prepared from TBHQ-treated crudes (10,11).

In the present investigation, the oxidative deterioration of crude whale oil was studied during storage without antioxidants and in the presence of TBHQ, PG, butylated hydroxyanisole (BHA) and 3,5-di-t-butyl-4-hydroxyanisole (Di-BHA). TBHQ is used as a food additive only in the U.S.; PG and BHA are food-approved antioxidants in Canada, U.S., and several other countries; Di-BHA is a developmental antioxidant. Special attention was given to the effect of these antioxidants upon the level of secondary oxidation products in stored crude oils and upon these same oils after laboratory deodorization. Careful consideration was given to various factors that contributed to the improvement in stability of deodorized whale oil from TBHQ-treated crude.

EXPERIMENTAL PROCEDURES

Fresh crude whale oil from regular production stocks of Karl Karlsen Co., Blandford, Nova Scotia, was used. The oil was a blend produced from fin whales (*Balaenoptera physalus*) taken off Nova Scotia. The oil had an iodine value of 113, a free fatty acid content of 0.6% (as oleic), and the peroxide and anisidine values (PV, AV) were 1.38 and 4.89, respectively.

Seven 1500 g oil lots were placed in dry, clean transparent glass (1 gal) jars, each fitted with a screw cap.

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TABLE I

Oxidative Stabilities of Whale Oils[a]

Antioxidant added to crude oil (percent)[b]	Stability of Crude Oil		Stability of oil deodorized after storage[d]
	Unstored[c]	After 146 storage days[c]	
None (unstored)[e]	---[f]	---	16.0
None (control)	8.0	2.0	9.5
0.02 BHA	12.0	13.0	18.0
0.02 PG	16.0	3.0	16.0
0.02 Di-BHA	16.5	9.0	17.0
0.02 TBHQ	39.0	18.0	49.5
0.02 TBHQ + 0.01 citric acid	41.0	15.0	56.0
0.01 Citric acid	9.0	2.0	13.5

[a]Time in days required for 10 g oil to increase 50 mg in wt.

[b]BHA = butylated hydroxyanisole, PG = propyl gallate, Di-BHA = 3,5-di-t-butyl-4-hydroxyanisole, and TBHQ = tertiary butylhydroquinone.

[c]Determined at 40 C.

[d]Determined at 30 C.

[e]The only sample that was not stored but was directly refined and deodorized.

[f]Undetermined.

The antioxidants used were TBHQ, PG, BHA, and Di-BHA. A refined grade of TBHQ (Eastman Chemical Products, Kingsport, Tenn.) and Di-BHA (ICI America, Stamford, Conn.) were used. The remaining antioxidants were food grade available commercially. Sufficient antioxidant dissolved in ethyl alcohol was added to the oil to furnish a concentration of 0.02%. The contents were shaken well and the solvent was evaporated completely from the oil. In addition, citric acid at the 0.01% level was added to whale oil, with and without TBHQ. A control sample of whale oil without added antioxidants also was stored. All samples were stored in closed containers kept at 40 C and subjected to illumination of cool-white fluorescent tubes at an intensity of 80 footcandles. The crude, stored oils were transferred after 113 days to a 60 C dark incubator. The oxidation reaction was accelerated further after 27 more days by replacing the head space gas of each stored sample with an atmosphere of oxygen (12). When the storage period amounted to 146 days, the crude oil (control) reached a satisfactory degree of rancidity (PV: 38.7). Therefore, the storage test for all the crude oils was terminated.

The progress of the oxidative deterioration of the oils during storage was followed by measuring at regular intervals changes in PV and AV levels. The former was determined by iodometric method described by Cocks, et al. (13). The latter was developed by Holm (personal communication). The AV ($E^{1\%,100}_{350\ nm}$), which measures the α-β unsaturated aldehydes in oils, was determined by reacting p-anisidine with the oil (0.5-4g) in hexane. The resultant color was measured at 350 nm (4, 5).

Oxidative stability was measured by wt gain of oil kept in air (14). Before and after storage, 10 g samples of all examined oils were weighed accurately in petridishes (10 cm) and placed overnight at 30-35 C under vacuum to remove traces of moisture. After cooling in a dessicator, the samples were reweighed and placed in a constant temperature incubator at 40 C. Unless otherwise specified, the oxidative stability tests were conducted in the dark. The samples were weighed daily. Time in days required for 10 g oil to increase 50 mg in wt was taken as the index for stability.

Alkali refining of the crude oils was conducted by adding, dropwise, a calculated amount of 0.1 N NaOH (10% excess) to 500 g oil dissolved in petroleum ether, bp 43 C (1:2). The ethereal solution was washed with distilled water until neutral to litmus. The solvent free refined oils were deodorized directly. Ca. 450 g oil was stripped for 3 hr with steam under vacuum (2-4 mm Hg) at 155-160 C in an all glass laboratory deodorizer (15). After deodorization the oil was cooled quickly to room temperature, and the vacuum was broken with nitrogen gas. Unstored crude oil kept under nitrogen in a freezer also was refined and deodorized.

Bleaching was not conducted to avoid introducing a factor that might have influenced the comparative effect of added antioxidants upon the level of secondary oxidation products and oxidative stability behavior of whale oil, a major objective in the present investigation. Batch bleaching with acid activated clays tends to increase, in varying proportions, the level of secondary oxidation products (4) and to influence the oxidative stability of oils (16, 17). In addition bleaching does not influence the concentration of natural antioxidants in oils (18, 19).

Residual TBHQ and PG in deodorized oils were determined quantitatively by standard colorimetric procedures (20, 21). The estimation of BHA was carried out by a method of the Association of Offical Analytical Chemists (22).

The oxidative stabilities of all eight freshly deodorized oils were established at 30 C. In addition, the rate of increase in AV of the eight oils was followed by placing a second series of these oils under the same conditions as the oxidative stability group. A sample of each oil (10 g) was placed in a petri dish (10 cm) and incubated at 30 C. The AV was determined after 13 and 20 days. Furthermore, the PV was assessed after 14 days on these same samples.

Deodorized whale oils prepared from stored antioxidant-treated crudes were stabilized by addition of TBHQ and the oxidative stability behaivor was evaluated at 40 C.

Oxidation of TBHQ was conducted by dissolving the antioxidant (0.5 g) in benzene (20 ml) and refluxing for 20 hr in presence of cupric palmitate while constantly bubbling oxygen. The benzene solution was evaporated. The oxidation products were extracted from the residue with ethanol and obtained after distillation of the solvent.

RESULTS AND DISCUSSION

Effect of Added Antioxidants upon Oxidative Stability of Crude Whale Oil during Storage

Antioxidants added to crude whale oil retarded oxidative deterioration during storage by controlling the progressive buildup of peroxides and secondary oxidation products. Inverse relationships were noted between PV and oxidative stability and also between AV and oxidative stability at termination of storage of antioxidant-treated crudes. The effectiveness of the antioxidants, in decreasing

order, was TBHQ, BHA, Di-BHA, and PG, with respect to retardment of oxidative deterioration of stored crude whale oil (Table I and Fig. 1). This superiority of TBHQ over BHA and PG agrees with the findings of Sherwin and Luckadoo (10, 11).

BHA should be considered superior to PG with respect to improving the oxidative stability of crude whale oil during storage (Table I). BHA and PG had similar effect upon the buildup of PV and AV (Fig. 1). However, the oxidative stability time of the BHA-treated stored oil was substantially superior to that of PG.

The synergistic effect of citric acid (23, 24) upon the oxidative stability of the unstored oil was rather small in presence of TBHQ and became negative as a result of storage. It is not possible to explain this phenomenon. Addition of citric acid alone to crude whale oil did not improve the oxidative stability; however, increases in PV and AV were controlled slightly during storage (Table I and Fig. 1). This might be due to the fact that naturally occurring trace metals in whale oil are not readily available for chelation prior to deodorization or heat treatment (25, 26).

Discoloration parallel to the extent of oxidative deterioration was noted in the stored crude oils.

Oxidative Stability of Deodorized Whale Oils Prepared from Untreated and Antioxidant-Treated Stored Crudes

Improvement in oxidative stability of deodorized whale oils obtained by processing antioxidant–treated stored crudes was noted at 40 C (Table IV and unpublished results). However, it was considered essential to establish again the oxidative stability of the eight deodorized oils at 30 C to obtain more pronounced differences (Table I). Stability times of deodorized oils from crudes treated with BHA, Di-BHA, PG, and citric acid ranged from 13.5-18 days at 30 C. Deodorized oils from TBHQ-and TBHQ-citric acid treated crudes gave much longer stability times against oxidative deterioration at 30 C, viz, 49.5 and 56 stability days, respectively (Fig. 2). Two factors contributed simultaneously to the extended induction period and caused the continued effectiveness of TBHQ even after deodorization: the antioxidative effect of the oxidation products of TBHQ and the relatively low concentration of substances reacting with anisidine. This latter effect was due to the protection of the antioxidants during crude storage, especially in the case of TBHQ, which resulted in the slowest rate of increase in AV (Table II). The former factor was more influential than the latter. The antioxidant action of TBHQ and its oxidation products kept the level of AV from increasing throughout the storage period and in the deodorized oil.

The AV of all stored oils decreased after deodorization, due to the disappearance of volatile carbonyls under conditions of deodorization. A similar observation was noted by Holm, et al. (4). The percentage loss of volatile carbonyls immediately after deodorization, as related to total carbonyls in the corresponding stored crude oils just before deodorization, was highest in the control and citric acid–treated samples and amounted to 35.6 and 40.5, respectively. The lowest percentage loss resulted from deodorization of TBHQ-citric acid and TBHQ-treated oils and amounted to 7.2 and 11.1, respectively (Table II and Fig. 1). The oils darkened slightly during the deodorization process, possibly because they were unbleached. Maximum darkening occurred with PG–treated oil, as a result of interaction between PG and iron present in the oil (27).

The level of secondary fatty oxidation products influenced the rate of oxidative deterioration of untreated deodorized whale oil. Substances responsible for the difference of 49.3 in the AV in deodorized whale oils prepared from unstored and stored untreated crudes decreased the stability by 6.5 days and also caused an eightfold increase in both PV and AV levels during incubation for 14 days at

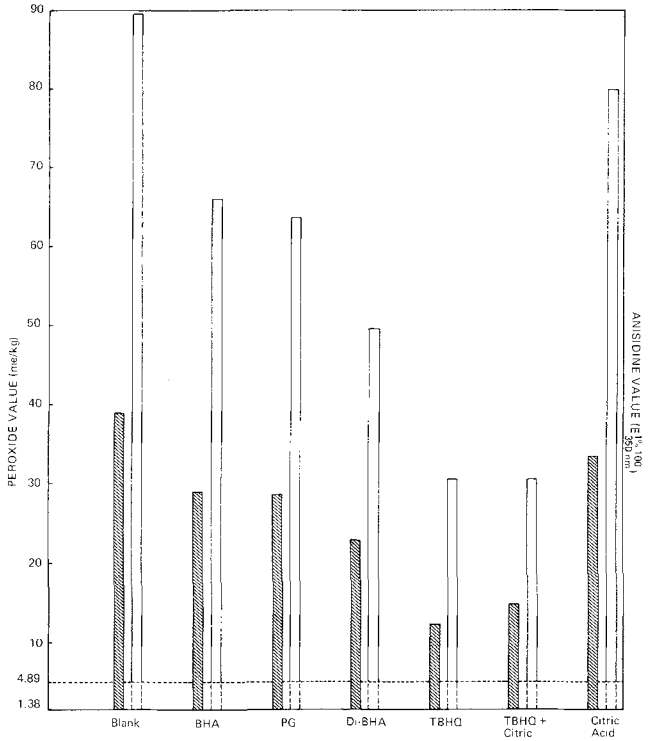

FIG. 1. Peroxide and anisidine values of crude whale oil stored for 146 days with antioxidants (0.02%) and citric acid (0.01%). BHA = butylated hydroxyanisole, PG = propyl gallate, and TBHQ = tertiary butylhydroquinone ▩ peroxide value (PV) □ anisidine value (AV).

30 C (Tables I, II). Other investigators (2, 8, 9) reached similar conclusions.

Surprisingly, the AV of the freshly deodorized oil prepared from TBHQ–treated crude increased only from 27.1 to 30.8 during incubation for 20 days at 30 C. During the same period the AV of the deodorized, untreated, and unstored crude oil increased from 8.3 to >350. The rates of increase in wt gain of the oils and accumulation of peroxides paralleled the differences in AV levels (Table II). Similar conclusions were reported by Sherwin and Luckadoo (10, 11) who measured the improvement in oxidative stability, under accelerated active oxygen method (AOM) conditions, of refined, bleached, and deodorized cottonseed, soybean, safflower, and sunflower seed oils, prepared from the corresponding TBHQ-treated stored crudes. It was obvious that the relatively low level of secondary fatty oxidation products was not the only factor responsible for the noticeable improvement in the oxidative stability of freshly deodorized, TBHQ-treated crude oil. Other constituents present in the deodorized oil as a result of treatment with TBHQ in the crude state were mainly responsible for the remarkable improvement in the oxidative stability and kept the AV level from increasing during an incubation period of 20 days at 30 C.

Three factors may be considered for the 40 day extension (Table I) in stability of deodorized whale oil, prepared from TBHQ-treated stored crude when compared to the unprotected control. These are described below.

There appeared to be a 5 day increase in oxidative stability due to the residual 0.002% TBHQ determined analytically to be present (Table III). When this level of TBHQ was added to deodorized control whale oil, oxidative stability at 30 C increased by 5 days.

The substances responsible for the 30.5 unit difference in AV between stored-untreated and TBHQ-treated freshly deodorized oils may be considered equivalent to an increase of 6.5 stability days. This was derived by analogy: the 49.3 unit difference in the AV of unstored and stored untreated

TABLE II

Effect of Incubation Period upon Changes of Anisidine and Peroxide Values of Freshly Deodorized Whale Oil at 30 C

Antioxidant added to crude oil (percent)[a]	Duration (days) 0 Anisidine value 1% .100 $E_{350\ nm}$	13 Anisidine value 1% .100 $E_{350\ nm}$	13 Wt gain mg/10 g	14 Peroxide value me/kg	14 Wt gain mg/10 g	20 Anisidine value 1% .100 $E_{350\ nm}$	20 Wt gain mg/10 g
None (unstored)[b]	8.30	22.0	15.2	60.3	24.6	>350	257.6
None (control)	57.6	180.	214.8	480	247.8	>350	368.6
0.02 BHA	51.2	54.0	14.5	34.9	17.1	134	177.3
0.02 PG	36.9	47.2	11.6	19.9	18.7	304	198.4
0.02 Di-BHA	39.4	43.6	9.8	25.6	12.6	281	212.0
0.02 TBHQ	27.1	26.1	2.7	11.2	2.7	30.8	6.2
0.02 TBHQ + 0.01 Citric acid	28.2	27.6	2.4	8.70	2.4	29.5	5.3
0.01 Citric acid	47.4	69.6	63.7	94.2	95.5	>350	262.2

[a]See Table I for definitions of abbreviations.

[b]The only sample that was not stored but was directly refined and deodorized.

deodorized oils amounted to a 6.5 day increase in the stability of the oil. It was, therefore, assumed that it would require ca. 6.5 days for the AV of the TBHQ-treated oil to reach the level of the AV of the stored untreated oil if TBHQ and its oxidation products could be removed from the oil (Tables I, II).

TBHQ oxidation products remaining in the deodorized oil must account for the remainder of the increased stability period, i.e. for 28.5 of the 40 days.

Oxidation products of TBHQ present in the deodorized oil prepared from TBHQ-treated stored crude were detected. The ethanolic extract of the deodorized oil (20) was subjected to thin layer chromatographic analysis as described by Argrett, et al. (28). Three separated components were visualized by spraying with molybdophosphoric acid and leucomethylene blue (29) but not by ferric chloride-dipyridyl reagent (30). The three spots had Rf values equal to those of three out of five reference spots detected by chromatographic and colorimetric analysis of TBHQ oxidation products prepared by catalytic oxidation of the antioxidant in benzene.

The autoxidation of unsaturated oils proceeds through a free radical chain reaction and antioxidants are themselves oxidized while performing their chain interference role. Bolland and ten Have (31) studied the kinetics of autoxidation of ethyl linoleate in the presence of hydroquinone. They concluded that the resulting hydroquinone oxidation product, i.e. p-benzoquinone, has an antioxidative effect. It also was proven that hydroquinone interrups the autoxidation chain reaction of ethyl linoleate by interaction only with the peroxidic radicals. Several investigators (17, 32-35) have outlined the completely reversible oxidation-reduction of hydroquinone-benzoquinone systems and the role of the corresponding intermediate semiquinones. Conversely, the completely reversible oxidation-reduction reaction system does not take place in the case of BHA and Di-BHA. These two antioxidants terminate chain reactions by interaction mainly with peroxidic radicals, and irreversible stable oxidation products ultimately are formed (33, 36, 37). Uri (38) has explained the effect of chemical structure of antioxidants as related to mechanisms of antioxidation.

The present results indicate that at least part of the TBHQ and its oxidation products remained in the oil during deodorization. TBHQ oxidation products continued to protect the deodorized oil from oxidative deterioration and contributed in part to the remarkable improvement in oxidative stability at 30 C as indicated by a lengthy induction period (Fig. 2).

The concentrations of phenolic antioxidants added to crude oils and the resulting oxidation products of these antioxidants are decreased by steam deodorization and, to a lesser extent, by alkali refining. However, industrial steam deodorization operating conditions are not standardized. The time, temperature, and stripping steam flow of the deodorization process vary widely among processing plants. Also, these conditions are altered depending upon the chemical characteristics of the oil (17, 39, 40). Accordingly, the concentration of residual antioxidants in an oil would vary considerably depending upon deodorization conditions. Therefore, it is essential to detect and determine residual antioxidants present after processing of antioxidant-treated crudes.

To avoid potential public health hazard in the U.S. and elsewhere, treatments of stored crude oils with TBHQ, as described by Sherwin and Luckadoo (9, 10), should be declared. Also the oxidation products of this antioxidant remaining in the oil after refining, bleaching, and deodoriza-

TABLE III

Concentration of Residual Antioxidants in Freshly Deodorized Whale Oil

Antioxidant added to crude oil before storage (percent)[a]	Antioxidant concentration in deodorized oil (percent)
0.02 BHA	<0.0005
0.02 PG	<0.0001
0.02 Di-BHA	---[b]
0.02 TBHQ	0.002
0.02 TBHQ + 0.01 citric acid	0.002

[a]See Table I for definitions of abbreviations.

[b]Undetermined.

TABLE IV

Effect of Added TBHQ upon Oxidative Stability of Deodorized Whale Oil Prepared from Antioxidant-Treated Crudes

Antioxidant added to crude oil before storage (percent)[a]	Stability of deodorized oil[b] No TBHQ added	TBHQ added (percent)	
None (control)	2	0.02	13
0.02 BHA	3	0.02	16
0.02 PG	3	0.02	7
0.02 Di-BHA	3.5	0.02	14
0.02 TBHQ	9.5	0.018	22
0.02 TBHQ + 0.01 citric acid	10	0.018	22
0.01 Citric acid	2	0.02	10.5

[a]See Table I for definitions of abbreviations.

[b]Time in days required for 10 g oil to increase 50 mg in wt and was determined at 40 C with illumination by fluorescent light at an intensity of 60 footcandles.

tion should be determined quantitatively. These, together with the residual antioxidant, should be accounted for as part of the maximum permissible level (0.02%) of food-approved antioxidants in processed edible oils and fat containing foods, as outlined by U.S. Government regulations for food additives. Obviously, the oxidation products of TBHQ are reduced simultaneously to TBHQ during catalytic hydrogenation of deodorized oil.

Effect of TBHQ Added to Deodorized Whale Oil Prepared from Antioxidant-Treated Crudes

Oil treated with TBHQ in the crude state responded better to further addition of TBHQ after deodorization (Table IV). This is due to the additive antioxidative effect of the added TBHQ and the residual oxidation products of TBHQ present in the oil as a result of treatment of the crude with TBHQ prior to storage.

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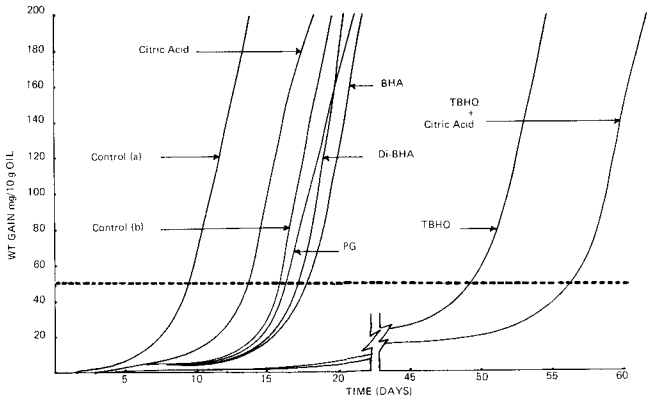

FIG. 2. Stability of freshly deodorized whale oils prepared from stored antioxidant-treated crudes at 30 C without illumination. (A) Control prepared from stored crude oil. (B) Control prepared from unstored crude oil. BHA = butylated hydroxyanisole, PG = propyl gallate, TBHQ = tertiary butylhydroquinone, and Di-BHA = 3,5-di-t-butyl-4-hydroxyanisole.

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