ABSTRACT: Soybean oil, owing to its FA composition, is highly susceptible to deterioration by oxidation. The use of nitrogen gas permits the removal of dissolved oxygen and oxygen in the headspace of tanks and bottles. The objective of this work (an industrial trial) was to evaluate the shelf life of soybean oil packaged in polyethylene terephthalate (PET) bottles with different levels of oxygen in the headspace (<0.3, 5–6.5, 7–9, and >15%). The quality of the oil was evaluated during 6 mon. FFA and moisture increased and the smoke point decreased in all experimental conditions, even though the difference between the experiments was not significant. An increase was observed for peroxide value (PV), anisidine value (AV), and specific extinction, and higher increases in these parameters were observed in higher oxygen concentrations. After 180 d, the difference between the PV and AV was significant. According to sensory analysis, the shelf life of the oil increased from 60 to 90, 120, and 180 d as the initial concentration of oxygen was reduced from >15%, 7–9%, 5–6.5%, and 0–3%, respectively. The results demonstrated that shelf life of soybean oil packaged in PET bottles can be significantly increased by using nitrogen to reduce available oxygen in the headspace.

KEY WORDS: Oxidation, oxygen in headspace, PET, soybean oil, stability.

Because of its quality and low cost, soybean oil is the most important vegetable oil produced worldwide. Brazil produced more than 4.4 million tons and consumed approximately 2.4 million tons in 2005, the latter tonnage representing 95% of the total vegetable oils consumed (1). Because of its high content of PUFA, soybean oil is susceptible to oxidative rancidity, which can be caused by the reaction of atmospheric oxygen and/or the oxygen in the headspace of the plastic containers and/or the oxygen dissolved in the product with the unsaturated portion of the FA present in the oils and fats. The reaction is favored by high temperatures, the incidence of light, and the presence of pro-oxidant metals (2).

Soybean oil processing includes several stages, such as refining and packaging, that are designed to provide high-quality refined oil to the consumer. The package has a fundamental role in the control of interactions between the oil and the environment, protecting against oxidation and preserving product quality until the end of its useful life. Plastic, mainly PET (polyethylene terephthalate), has been dominating the Brazilian market in the last two decades. Although PET forms a good barrier to oxygen, its permeability to water vapor is relatively high, and the product contained therein is more exposed to light, which can affect the oxidative stability of oil (3). Because the oxygen concentration in the package affects the speed of the oxidation reaction, industries use nitrogen to fill the internal space of the tanks during storage and the plastic bottles during filling to reduce the amount of oxygen in contact with the oil, delaying oxidation reactions and increasing the shelf life of the oil.

The importance of investigating the oxidative stability of oil lies in the complexity of the oxidation reactions; besides, many oxidation products (particularly of low M.W.) can have odors that consumers can perceive even at low levels. A small fraction of oil oxidation can result in development of undesirable odors, leading to rejection of the product, considering that odor and flavor are the most important characteristics of quality in edible oils (4). Therefore, in this industrial trial research work, the effect of different levels of oxygen in the headspace of PET bottles and their relation to soybean oil quality and shelf life were evaluated for a period of 6 mon.

MATERIALS AND METHODS

Soybean oil. Four lots of 45 tons each of refined, bleached, and deodorized (RBD) soybean oil, with 30 ppm of TBHQ and 45 ppm of citric acid, were produced and packaged in PET bottles at ADM (Archer Daniels Midland) in Campo Grande, MS, Brazil. Lot numbers 1, 2, 3, and 4 were produced according to the conditions described in Table 1, with headspace oxygen concentrations of <3, 5–6.5, 7–9, and >15%, respectively.

Packaging material. The RBD soybean oil was packaged in PET bottles with plastic caps made of HDPE (high-density polyethylene), but without internal seals, and packaged in cardboard boxes with 20 units in each, as done for the Brazilian market. The boxes were stacked seven high and kept at room temperature. The temperature and relative humidity of the air were measured daily during the entire period of the experiment (mean ± SD: T = 30.7 ± 2.3°C; RH = 71.2 ± 3.0%).

Experimental procedures. (i) Oil characterization and quality evaluation. Procedures for RBD soybean oil characterization...
were performed according to the American Oil Chemists’ Society official methodology (5) by the following analyses: FFA (Ca 5a-40), moisture and volatile matter (Ca 2c-25), peroxide value (PV) (Cd 8-53), saponification value (Cd 3-25), iodine value (Cd 1-25), color (Cc 13b-45), specific extinction at 232 nm (Ch 5-91), smoke point (Cc 9a-48), anisidine value (AV) (Cd 18-90), unsaponifiable matter (Ca 6a-40), chlorophyll (13d–55), refractive index (Cc 7–25), oxidative stability index (Cd 12b-92), FA composition (Ce 1-91), and metals determination (Ca 20-99). RBD soybean oil quality was evaluated for a period of 6 mon, on days 0, 30, 60, 90, 120, and 180 after packaging by the determination of FFA, moisture, smoke point, color, PV, AV, specific extinction at 232 nm, and sensorial analysis (Cg 2-83).

(ii) Oxygen concentration in the headspace and dissolved oxygen in the oil. The amount of oxygen in the headspace of the packages was determined according to Alves et al. (6) as the percentage of the gas volume, using a Pac Check 450; (MOCON© Minneapolis, MN) oxygen analyzer. An aliquot of 5 mL of the free headspace gas was collected from each bottle with a gas-tight syringe, through a septum pasted in the package, and immediately injected into the analyzer. The content of oxygen dissolved in the oil was determined using an Orbi-sphere (Geneva, Switzerland) analyzer, model 3600, with a device for penetrating the package, model 29971,29972 and 2952A membrane.

(iii) Sensorial analysis. The sensory analysis was carried out according to recommended AOCS practice Cg 2–83 (5). The Descriptive Quantitative Analysis method was used, in which samples were presented to the 10 members of the trained panel, sitting in individual booths. The trained analysts identified the attribute and the respective intensity.

(iv) Statistical analysis: The statistical analyses were done according to the Statistica program (Statistica, 1995; Statsoft, Tulsa, OK). For each experimental condition, a linear regression analysis was performed. To compare the behavior of the parameters during the storage period, the following analyses were used: ANOVA, Tukey test of multiple comparisons, linear correlation analyses, and Pearson’s. These statistical tools were used to verify the significance among all the variables and the time period studied.

**RESULTS AND DISCUSSION**

**Characteristics of RBD soybean oil.** The results related to the identity, quality characteristics, and composition of the RBD soybean oil used in this study are presented in the Table 2. The results obtained indicate an adequate refining process, according to Brazilian legislation (7,8). Soybean oil FA composition was 83.7% unsaturated and 15.6% saturated FA, indicating a high susceptibility to oxidation.

**Oxygen concentration in headspace and dissolved in oil during storage.** Oxygen concentrations in the headspace and dissolved in the oil during the storage period of 180 d are presented in Table 3.

Decreasing the quantities of nitrogen (0.5, 0.4, 0.3, and 0.0 m³/h; experimental tests 1, 2, 3, and 4, respectively) used in the stripping process resulted in significantly higher oxygen removal from the headspace, achieving increasing contents of residual oxygen (2.7, 5.7, 7.9, and 16.7%).

The use of 0.5 m³/h of nitrogen in the stripping process plus 10 m³/h of nitrogen in the blowing process, just before filling (Experimental test 1 with <3% of oxygen in the headspace) reduced the oxygen concentration 87.2% compared with the atmospheric oxygen concentration (21%) and reduced the residual oxygen concentration in the headspace 65.7% compared with the packaging condition, which used 0.3 m³/h of nitrogen in the stripping process and 7 m³/h of nitrogen in the blowing process, just before filling (Experimental test 3 with 7–9% of oxygen in the headspace).

After 30 d, a decrease in oxygen concentration in the headspace was observed in all experiments. This reduction corresponds to 70, 60, 60, and 66% of the initial oxygen content in the headspace for treatments 1, 2, 3, and 4, respectively. There was no significant difference after 30 d of storage when comparing Experimental tests 1 and 2 (0–3 and 5–6.5% oxygen content, respectively).

After 60 d of storage, there was an increase in oxygen concentration in the headspace that may have been a consequence of the entrance of oxygen through the package walls and the capping system. The content of oxygen in the headspace for the first three packaging conditions (0–3, 5–6.5, and 7–9%) presented no significant difference.

In the final storage period, the oxygen content in the headspace under all packaging conditions was less than 3.1%. Thus, oxygen disappearance/reduction was greater when the initial concentration of oxygen in the headspace was higher. The packaged samples with oxygen contents above 15% in the headspace collapsed after 180 d of storage, probably because of very low oxygen concentrations in the headspace at the end of the shelf life period, indicating that, during the storage period, a great amount of oxygen had been consumed in the oxidation reaction.