

Abilities of Some Antioxidants to Stabilize Soybean Oil in Industrial Use Conditions

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ABSTRACT: Antioxidants, chelators, and alcohols were screened at 0.01 and 1.28% by weight for their ability to delay viscosity increase in soybean oil in the presence of metallic colloidal copper and iron at 105°C with air flowing through the sample. Most substances did not significantly enhance the effect of the natural tocopherols in the soybean oil at 0.01%. A few substances were mildly prooxidant, and a few delayed the increase in viscosity significantly. TBHQ at 0.01% was the best antioxidant of those tested. At 1.28% ascorbyl palmitate, BHT, hydroquinone, and TBHQ increased the stability significantly. Again, TBHQ was the most effective. As measured by viscosity increase to 150 CP, TBHQ increased stability about five times over that of soybean oil controls.

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The poor biodegradability of petroleum and its rising cost have caused renewed interest in the use of vegetable oils as lubricants and industrial fluids. In addition, there is evidence that vegetable oil-based lubricants have better lubricity and can improve gas mileage (1,2). But the use of vegetable oils in these applications is limited by their poor oxidative stability relative to petroleum. Oxidation leads to increased viscosity that limits the useful life of vegetable oil-based fluids. Most industrial uses entail contact of the oil with metals such as iron and copper at elevated temperatures, all of which can accelerate the oxidation reaction. These problems are particularly severe with soybean oil because of its relatively high content of PUFA.

Lubricant scientists have developed a variety of methods for assessing the oxidative stability of their fluids, mainly petroleum and synthetics. Food chemists also have developed methods for assessing the stability of fats and oils. Generally, both groups use elevated temperatures to bring the reaction rates that they are studying into a more convenient time frame, particularly when testing potential antioxidants, and they hope that the parameters that they measure will correlate well with the factors limiting the life of their products in the real world. Because petroleum is more stable than vegetable

oil, lubricant scientists have generally used harsher methods. For example, Erhan and Asadauskas (3,4) heated fluids at 150°C in a thin film to facilitate oxygen transfer and measured the loss of volatiles and formation of oxypolymers. Even higher temperatures are not uncommon (5). Adhvaryu *et al.* (5) concluded that typical soybean oil formed polymers at a rate an order of magnitude greater than mineral oil and typical lubricant bases. High-oleic sunflower oil formed polymers about threefold slower than soybean oil. Food chemists have been able to work with gentler methods, and the active oxygen method (AOM) (6) and its variants have typically been used to screen antioxidants in fats and oils at ~100°C, where oxygen transfer is not much of a problem.

Primary phenolic antioxidants usually have little effect in stabilizing soybean oil in food use (7,8), presumably because the oil's normal complement of tocopherol is adequate. Metal chelators, however, can have beneficial effects on soybean oil flavor, and citric acid is widely used for this purpose (8,9).

Our purpose was to develop methods suitable for screening antioxidants for their effectiveness in vegetable oils used in industrial applications and to see which available antioxidants and chelating agents were the most effective additives for soybean oil under these conditions. We modified the AOM method (6) by exposing the samples to copper and iron and by measuring viscosity, the parameter that limits the oil's useful life in many industrial applications. We particularly looked at antioxidants that have proven effective in applications with fats and oils but we also included some that are not permitted in food. The antioxidants recommended by lubricant specialists for use with vegetable oils are proprietary and available only in mixtures of unknown concentration in petroleum bases. To test the efficacy of the phenolic antioxidants in these mixtures, we isolated them and added them to soybean oil.

MATERIALS AND METHODS

Soybean oil was purchased from a local grocery store. Colloidal copper and iron were purchased from Aldrich (Milwaukee, WI). Antioxidants and chelating agents were obtained from Fisher (Pittsburgh, PA) or Aldrich or were isolated from an industrial lubricant additive.

To isolate antioxidants from the industrial lubricant additive, 50 μ L was streaked on an Absorbosil Plus 1 preparative thin-layer plate (Alltech, Deerfield, IL), and the plate was

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developed with hexane/methanol (85:15, vol/vol). Bands were viewed under UV light after spraying the plate with 0.1% 2',7'-dichlorofluorescein in methanol. The bands were scraped from the plate and eluted with hexane. The eluted products were examined by GC-MS using a Hewlett-Packard (Avondale, PA) 5890 Series II instrument fitted with a 5970 mass selective detector and a 30-M SPB-1 capillary column. The oven temperature was programmed from 170 to 270°C.

Antioxidants were screened in duplicate using the apparatus described for the AOM in the American Oil Chemists' Society Method Cd-12-57 (6). Air was bubbled through the oil by an aquarium pump and was regulated at 2.33 mL/s by using a water column to control the pressure. The heating block was maintained at 105°C with a Barnant controller model 689 (Barrington, IL). The antioxidants to be tested were dissolved in ~1 mL ethanol and added to 20 mL of soybean oil at a concentration of 0.01% by weight. A similar amount of ethanol was added to control samples. The ethanol was evaporated from the samples in about 30 min because of the elevated temperature and air flow through the sample. Each sample and control also contained ~10 mg each of colloidal iron and copper. Samples of 1 mL were withdrawn periodically, typically about every 10 h, and their viscosities were measured using a Brookfield LV-DV-II+ cone and plate viscometer (Stoughton, MA) operated at 40°C. A value of ~150 cP, which is an increase of about five times the viscosity of unoxidized soybean oil, was chosen as an arbitrary end point.

The mean viscosities for samples and controls were calculated over all the sampling times, and the mean viscosities of antioxidant-containing samples and controls were compared using a *t*-test at the 95% confidence interval.

RESULTS AND DISCUSSION

A test temperature of 105°C was chosen as typical of the operating temperatures of the crankcases of gasoline engines. The addition of 10 mg of the colloidal metals (typically 1- μ m spheres) to the test oil provided about 70 cm² of each of the metal surfaces. The 0.01% level is traditional for testing antioxidants because this is the level that may be added in food applications. Refined soybean oil typically contains 0.05 to 0.1% tocopherols (10), so additional phenolic antioxidants typically do not increase its stability (7) and sometimes increase its rate of oxidation.

Because TBHQ increased stability at the 0.01% level, it was tested at higher levels, and these were even more effective up to 1.28% by weight. For comparison, the other antioxidants were then tested at 1.28%, and several of them also were found to be effective at this higher concentration. Typical plots of average viscosity for the duplicates vs. time using our test are shown in Figure 1. Table 1 shows the antioxidants that were tested and the hours required to reach 150 cP at levels of 0.01 and 1.28%. Soybean oil controls and most samples reached 150 cP in ~30 h. The soybean oils used to test the two antioxidant concentrations were from different lots and varied slightly in their stability.

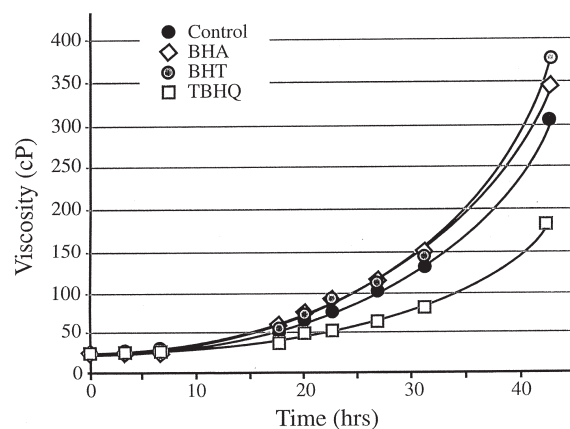


FIG. 1. Average change in viscosity vs. time for soybean oil containing selected additives at the 0.01% level. Oxidation was at 105°C with flowing air at 2.33 mL/s for a 20-mL sample.

TBHQ significantly stabilized the soybean oil at both the 0.01 and 1.28% levels. It was the most effective antioxidant and increased the AOM time of the oil about fivefold at the 1.28% level. Hydroquinone, BHT, and ascorbyl palmitate (AP) were also effective at the 1.28% level, but their effectiveness at the 0.01% level was not significant. Indeed, BHA tested significantly less stable than the control oil at 0.01%. Statistical significance, when the AOM times show small deviations from the control, must be interpreted cautiously because significance can be influenced by the agreement between duplicates in a particular experiment. Also, when using a 1 in 20 probability, one can expect some false positives

TABLE 1
Hours to Viscosity of 150 cP of Soybean Oil Containing Various Substances

Antioxidant	0.01% by weight	1.28% by weight
Control oil	31 ^a	27 ^a
Ascorbyl palmitate	33	55.5 ^b
BHA	30	30 ^b
BHT	30 ^b	69 ^b
BHA/BHT	33	—
Caffeic acid	33	27
Castor oil	31	24 ^b
Citric acid	31.5 ^b	20.5 ^b
Ethoxyquin	31	27.5
EDTA	30	26
Ferulic acid	31.5	18.5 ^b
Gossypol	29 ^b	12 ^b
Hydroquinone	33	126 ^b
Oleyl alcohol	33	27.5
Propyl gallate	33 ^b	27.5
Phenolic isolate from commercial product	33	—
Quercetin	31	29.5
Soy lecithin	33	—
TBHQ	37 ^b	188 ^b

^aThe soybean oils for the 0.01 and 1.28% tests were from different lots of slightly different stability.

^bIndicates statistical difference from controls at 0.05 by *t*-test.

when one makes a number of comparisons. Propyl gallate showed a slightly significant antioxidant effect at 0.01% but not at 1.28%. Gossypol proved to be a prooxidant at both concentrations and ferulic acid at the higher concentration. The lack of effect by most of the antioxidants at 0.01% agrees with previous investigations (7) that showed the addition 0.01% of most phenolic antioxidants does relatively little to improve the oxidative stability of soybean oil.

Polar components isolated by TLC from a commercial additive recommended for use in vegetable oil lubricants were shown by GC-MS to be a mixture of phenols. One of the chief components had a mass spectrum matching that of 2,4-bis(dimethylbenzyl)-6-*tert*-butylphenol. The other phenols had similar structures but differed in their degrees of substitution. The phenolic mixture was tested at 0.01% and, like many of the other phenols, did not have a significant antioxidant effect. This mixture was not tested at 1.28% because of the difficulty of isolating sufficient material, but its similarity in structure suggests that it would behave like BHT. The benzyl groups undoubtedly decreased the volatility of the phenols, which may be important for their effectiveness in high-temperature applications.

Of the chelators citric acid, EDTA, and lecithin, only citric acid showed a significant difference from the control in our tests and acted as a slight antioxidant at a level of 0.01% and a slight prooxidant at 1.28%. These results were surprising considering the reputation of chelators for increasing the flavor stability of soybean oil (8,9). But it was difficult to obtain solutions of citric acid and EDTA in soybean oil even with the aid of ethanol and especially at 1.28%. Lecithin foamed too much to be tested at 1.28%.

Castor oil and oleyl alcohol were tested because fatty alcohols are included in some vegetable oil lubricant formulations (2), and Kortenska and Yanishlieva (11) reported that fatty alcohols exerted a prooxidant effect. They believed that this effect resulted from the formation of hydrogen bonds between the fatty alcohols and phenolic antioxidants. In our tests, oleyl alcohol did not affect the oxidation rate significantly at either concentration, but castor oil slightly accelerated oxidation at 1.28%.

Many of the antioxidants showed signs of distilling out and accumulating on the cooler parts of the test tubes. This is a general disadvantage of testing at elevated temperatures. This crystalline accumulation may be a disadvantage in engines depending on where cool spots occur, the size of the crystals, and their adhesion to metal. Distillation of the antioxidants undoubtedly affects their effectiveness in our tests and in some uses. It is possible that some of the advantage of TBHQ over hydroquinone is attributable to TBHQ's lower volatility.

We tested TBHQ at 0.16, 0.32, 0.64, 1.28, and 2.56% by weight. The effect of TBHQ increased with concentration. A level of 1.28% was significantly better than 0.64%, but 2.56% did not give any improvement over 1.28%. At a level of 1.28%, TBHQ increased the time to 150 cP for soybean oil about fivefold. Although citrate by itself was not effective,

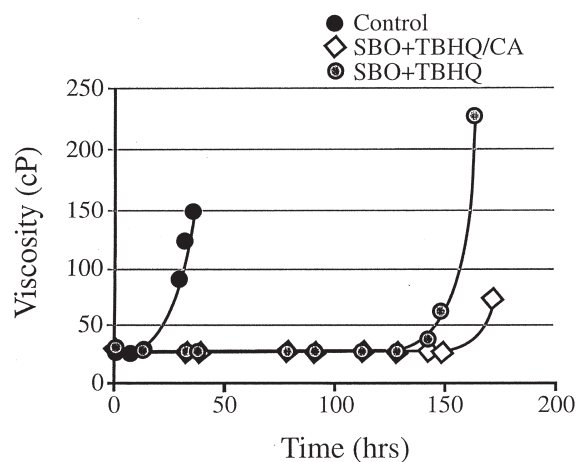


FIG. 2. Average change in viscosity vs. time for soybean oil (SBO) containing 1.28% TBHQ and 1.28% TBHQ + 0.02% citric acid (CA). Oxidation conditions were as in Figure 1.

inclusion of 0.02% citric acid with 1.28% TBHQ increased the time further to about sixfold (Fig. 2). These results agree with the findings of others that TBHQ is a superior antioxidant in soybean oil (8). It is not clear why TBHQ performs better than other phenolics in foods and in our test.

If the estimate by Erhan and Asadauskas (3), that typical soybean oil is about an order of magnitude less stable than petroleum-based fluids, can be compared with our results, one can overcome more than half of this difference by the addition of TBHQ and low levels of citrate.

Our method of testing antioxidants seems a good one for vegetable oils in industrial uses. The modifications we have made should make it a good predictor of performance. This method probably would not be good for use with petroleum-based fluids because the observation times would be inconveniently long, and if the temperature were increased substantially to reduce the time, oxygen transfer and antioxidant volatilization could affect the results.

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