Toluenesulfonate-Acyl Esters of Ethylene Glycol and Other 1,2-Diols as Industrial Antioxidants with Cupric Ion

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ABSTRACT: Ethylene glycol esters of soybean oil FA increased in viscosity much more slowly than methyl or glycerol esters when oxidized at 105°C in the presence of flowing air and colloidal copper. This increased stability was caused by a minor constituent of the ethylene glycol esters, which was shown by MS to be a mixed ethanediol fatty acylate *p*-toluenesulfonate (EFAT). The *p*-toluenesulfonate group came from the catalyst used in the formation of the ethylene glycol esters. EFAT was quantified by UV spectrometry, HPLC, or GC of the acyl group that it contains. EFAT could be synthesized in good yield by reacting ethylene glycol, a FA, and *p*-toluenesulfonic acid (TSA) in a 1:1:1 molar ratio using a benzene azeotrope to remove water of esterification. EFAT increased the time required for the polymerization of soybean oil by about 27 times but required concentrations of 2–5% by weight. EFAT made with a variety of FA were active in delaying viscosity increase. Ethyl and decyl *p*-toluenesulfonate were inactive. Replacing ethylene glycol by glycerol and 1,2-propylene glycol but not by 1,3-propylene glycol resulted in active EFAT. TSA itself delayed the polymerization of soybean oil, especially in the presence of free ethylene glycol and FA, but this probably was caused by formation of EFAT during the oxidation test. Colloidal copper could be replaced by cupric ion. EFAT–copper appeared to act as an antioxidant by destroying hydroperoxides without initiation of free radical chains.

Paper no. J10091 in *JAOCS 79,* 791–796 (August 2002).

KEY WORDS: Antioxidant, copper, cupric ion, EFAT, ethylene glycol toluenesulfonate fatty acylate.

Because of the poor biodegradability of petroleum-based fluids there is growing interest in using vegetable oils for industrial applications, such as lubricants and hydraulic fluids, especially in ecologically sensitive settings. In addition, vegetable oil-based lubricants are said to have an enhanced lubricity that can result in significantly decreased gasoline consumption (1,2). The use of many vegetable oils in these applications is limited because of their rapid oxidation and polymerization. Ruger *et al.* (3) advocated testing the effectiveness of antioxidants for such applications by their ability to prevent viscosity increase in soybean oil at 105°C with bubbling air in the presence of colloidal iron and copper. He concluded that TBHQ was particularly effective in this application, and its effectiveness was slightly enhanced by the addition of citric acid.

We theorized that the polymerization and viscosity increase of soybean oil resulting from oxidation should be a function of the number of oxidizable fatty acyl groups per molecule. It follows that esters of a particular FA composition should increase in viscosity in the following order when oxidized under similar conditions: methyl esters < ethylene glycol esters < glycerol esters. To test this hypothesis we compared the rates of viscosity increase of these three types of esters of soybean oil FA when they were oxidized under the conditions of Ruger *et al.* (3). We found that the glycerol esters increased in viscosity faster than the methyl esters, but the ethylene glycol esters were unusually stable in the presence of colloidal copper and had hardly increased in viscosity long after the methyl and glycerol esters had increased to about five times their original viscosity. This paper tells of our identification of a minor constituent in the ethylene glycol esters that was responsible for this antioxidant effect, our attempts to determine the structural elements necessary for antioxidant action, the role of copper ions, and information about a possible mechanism of action.

MATERIALS AND METHODS

Materials. Refined commercial soybean oil (Crisco; Procter & Gamble, Cincinnati, OH) was purchased locally. Unless otherwise specified, the solvents and reagents were purchased from Fisher Scientific (Fair Lawn, NJ) and were certified grade. Colloidal copper and iron and ethyl *p*-toluenesulfonate were purchased from Aldrich (Milwaukee, WI).

Synthesis of esters. Soybean oil was converted to methyl esters by mixing 500 mL of oil with 55 g of methanol and 15 g of 30% sodium methoxide in methanol (Fluka, Milwaukee, WI) at room temperature for 15 h. The product was washed with water and dried with sodium sulfate.

To make ethylene glycol esters, 500 mL of oil was saponified with 130 g potassium hydroxide, 750 mL water, and 25 mL ethanol and stored at 70°C under nitrogen for 16 h. FFA, recovered from the soaps with acid, were dried with sodium sulfate. The FFA and ethylene glycol were reacted in a 2.04:1 molar ratio in refluxing benzene for 18 h with 3 g *p*-toluenesulfonic acid (TSA) catalyst. A Dean–Stark trap was used to remove the water of esterification. The milliliters of benzene were set at 2.5 times the weight of the FA plus 30 mL to fill the leg of the Dean–Stark trap. The reaction mixture was neutralized with 5% aqueous sodium carbonate solution and washed

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*To whom correspondence should be addressed at Dept. of Food Science and Human Nutrition, Food Sciences Bldg., Iowa State University, Ames, IA 50011. E-mail: hammond@iastate.edu gently with water five times; the benzene was removed with a rotary evaporator (Buchi, Flawil, Switzerland). Ethylene glycol monoacyl esters of soybean oil FFA was produced similarly using a 3:1 molar ratio of ethylene glycol to FFA.

Ethylene glycol fatty acylate *p*-toluenesulfonate (EFAT) was synthesized with various FA (lauric, palmitic, stearic, linoleic, and linolenic) using a molar ratio of ethylene glycol/TSA/FFA of 1:1:1 and using benzene and a Dean–Stark trap as before. Excess TSA was removed by washing with sodium carbonate solution. The same method was used to make esters using 1,2- and 1,3-propylene glycol in place of ethylene glycol. To make the decyl ester of TSA, the molar ratio of decanol to TSA 1:1 was used. To substitute glycerol for ethylene glycol, the molar ratio of glycerol/TSA/FFA was 1:2:1 to maximize the yield of glycerol esterified with two TSA and one FFA.

Stability measurement. Oxidative stability was measured in duplicate using the apparatus described for the Active Oxygen Method (AOM) in the American Oil Chemists' Society Method Cd-12-57 (4). Air, supplied by an aquarium pump, was regulated at 2.33 mL/s by controlling the pressure with a water column. The heating block was maintained at 105ºC with a Barnant controller model 689 (Barrington, IL). Samples consisted of 20 mL of oil to which approximately 10 mg each of colloidal iron and copper were added. In some experiments only colloidal copper was added, or the colloidal copper was replaced with various amounts of an ethanolic solution of cupric acetate. Samples (1 mL) of the soybean oil were withdrawn periodically, and their viscosities were measured using a Brookfield LV-DV-II+ cone and plate viscometer (Stoughton, MA) operated at 40ºC. After measuring the viscosity, the oil samples were returned to their respective AOM tubes. A value of 150 cP was chosen as an arbitrary end point.

Initial isolation of EFAT. A column, 2 × 54 cm, was filled with 120 mL hexane, and 150 g of 80–200 mesh alumina, activated at 260°C for 15 h (5), was added and allowed to settle under gravity. Ethylene glycol esters of soybean oil FA (50 g) dissolved in 30 mL hexane were added, and the column was eluted with hexane, hexane/ethyl acetate (7:5, vol/vol), and methanol. The eluates were collected in 20-mL portions, each of which was checked for its composition by TLC.

TLC. Mixtures produced by ester syntheses (50 mg) were applied to Adsorbisil-Plus 1 silica thin-layer TLC plates, 20 × 20 cm, 0.5 mm thickness (Alltech Assoc., Deerfield, IL) with a streaker (Applied Science Laboratories, Inc., State College, PA). The plate was developed with hexane/ethyl ether/acetic acid (70:30:1, by vol), and the components were visualized by spraying lightly with 0.1% (wt/vol) 2′,7′-dichlorofluoresein (Sigma Chemical Co., St. Louis, MO) in methanol. Silica containing visible bands was collected, and each band was extracted with freshly distilled ethyl ether. The ether was evaporated, and the residues were weighed and used for further analysis.

GC. The GC was a Hewlett-Packard (Avondale, PA) (HP) 5890 Series II instrument with an HP3396 Series II integrator and FID detector. A Supelco (Bellefonte, PA) 2330 column, 15 m × 0.25 mm i.d., 0.20 µm film, was operated with injector and detector temperatures at 250°C; initial column temperature was 170°C for 3 min, programmed at 20°C/min to 225°C, and held 6 min. Carrier flow was 1.5 mL/min, and other gases were at the setting recommended by the manufacturer.

GC/MS. For EI-MS an HP 5890 Series II instrument with an HP5790 mass detector was used. The column was a Supelco SPB-1 30 m × 0.25 mm i.d., 0.25 µm film. Injector and detector temperatures were 320°C; initial oven temperature was 170°C for 3 min, programmed at 10°C/min to 320°C, and held 6 min. For atmospheric pressure chemical ionization (APCI) a Finnigan JSQ 700 (Finnigan Instruments Corp., San Jose, CA) mass spectrometer fitted with a Finnigan APCI ion source was used. Samples were injected in the loop injection mode. The vaporizer temperature was maintained at 400°C. For exact mass MS a Kratos MS-50 double-focusing magnetic sector mass spectrometer (Kratos Instruments, Manchester, United Kingdom) was used, with a solid probe introduction, electron ionization mode, and manual peak matching at 10,000 resolution (10% valley definition) with perfluorokerosene as the reference compound.

Quantification of EFAT. The amount of EFAT was determined by dissolving the sample in acetonitrile (HPLC grade) and measuring the absorbance of the TSA moiety at 273 nm with a Hitachi TU-2000 Spectrophotometer (Hitachi Instruments, Inc., Conroe, TX). EFAT also was quantified by using GC to determine the amount of acyl group it contained. EFAT preparations were fractionated by TLC, the EFAT band was recovered, converted to methyl esters with methanolic sodium methoxide (6), and extracted with hexane. Methyl heptadecanoate was added as an internal standard, and the sample was analyzed by GC.

To follow the synthesis of EFAT, 0.05 moles each of ethylene glycol, lauric acid, and TSA were esterified as before. Samples of ~0.3 g were taken periodically and washed with water to remove unreacted TSA and ethylene glycol. The solvent was evaporated, and the residue was weighed and dissolved in acetonitrile. Dibenzyl (1 mg/mL) was added as an internal standard. Analysis was accomplished with a Shimadzu LC-600 instrument with an SPD-6 AV UV detector (Kyoto, Japan), Zorbax SB-C18 4.6 × 25 mm column (Agilent Technologies, Palo Alto, CA), and a mobile phase of acetonitrile at 1 mL/min. The eluate was monitored at 273 nm, and the data were corrected for the relative absorbance ratio of lauric EFAT and dibenzyl. The amount of ethylene glycol dilaurate was determined by GC, using methyl heptadecanoate as an internal standard and an SP-2330 column. The data were corrected for the relative GC response.

Proton NMR. Measurements were carried out at room temperature using a Varian VXR-300 instrument. $CDCl_3$ (δ = 7.26 ppm) was used as solvent and reference standard.

Peroxide decomposition. To test EFAT's effect on hydroperoxides, four 20-mL soybean oil samples that were approximately one millimolar in cupric acetate were oxidized in the AOM apparatus at 40°C for 26 h. Lauric EFAT was added at 5% by weight to two of the samples, and the other samples served as controls. The sample and control oils were gassed with nitrogen for the remainder of the experiment. Samples were taken periodically, and their PV were determined by the Stamm method (7).

RESULTS AND DISCUSSION

We tested the relative rates of oxidation of methyl, ethylene glycol, and glycerol esters of soybean oil FA to test the hypothesis that more FA per molecule would increase the rate of polymerization. Table 1, lines 1–3, shows the AOM times to 150 cP for glycerol and methyl esters of soybean oil FA. Ethylene glycol esters oxidized unexpectedly slowly, and the sample was exhausted before 150 cP was reached. The addition of iron to these esters did not change their oxidation rate appreciably (data not shown), but in the presence of added colloidal copper the rate of oxidation of the methyl and ethylene glycol esters decreased while that of the glycerol esters remained about the same (Table 1, lines 4–6). The effect of copper on the rate of oxidation of the ethylene glycol esters was particularly striking. The slower oxidation of ethylene glycol esters, especially in the presence of copper, was contrary to our hypothesis. The addition of copper to lubricants has been advocated to slow oxidation (8).

To understand the unexpected stability of the ethylene glycol ester, we subjected it to TLC and discovered three components of R_f 0.7, 0.3, and 0.2. The main component was diacyl ester of R_f 0.7. The ethylene glycol ester mixture was fractionated on an alumina column to obtain enough material for our oxidation tests. Table 1, lines 7–9, shows the relative stability in the AOM test of glycerol, methyl, and ethylene glycol esters of soybean oil that had been purified by chromatography on alumina, which was expected to remove tocopherols and other polar constituents. The relative rates of oxidation of these esters were more nearly in agreement with our hypothesis. The addition of copper to the ethylene glycol esters had a much smaller effect than before (Table 1, line 10). But when the materials of R_f 0.3 and 0.2 were added back to ethylene glycol esters, they greatly enhanced the esters' stability (Table 1, line 11). Similar effects were obtained when these unknown components were added to soybean oil (data not shown).

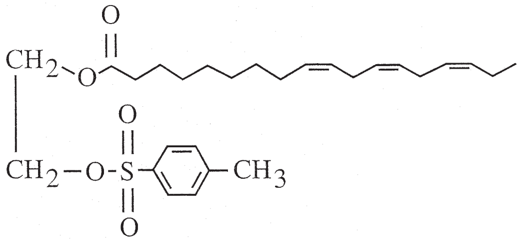
The component of R_f 0.2 was the monoacyl ester of ethylene glycol and was the primary component of syntheses that had a high ratio of ethylene glycol to FA. By itself this component had no effect on oil stability. The unknown component of R_f 0.3 was treated with methanolic sodium methoxide, and GC on an SPB 2330 column revealed the presence of methyl esters of the FA of soybean oil. By substituting palmitic, oleic, linoleic, or linolenic acids individually for soybean oil in the synthesis, materials analogous to the unknown spot were obtained but with only one kind of acyl group.

The unknown containing linolenate was chosen for further study by GC/MS. By electron impact GC/MS there was one major component with its mass fragments (*m/z*, %) at 99 (100), 55 (74), 139 (20), 79 (20), 67 (17), 91 (18), 112 (18), 153 (16), 86 (9), and 125 (9). The parent compound seemed to have an M.W. of 304, and the spectrum was consistent with a lactone formed from ethylene glycol monolinolenate by splitting out water from the free hydroxy group and a β-hydrogen from the

TABLE 1
Initial Viscosity and Hours to Reach a Viscosity of 150 cP for Soybean Oil and Its Derivatives Oxidized at 105°C with Air Bubbling Through at 2.33 mL/min

Oil	Initial viscosity (cP)	Hours to viscosity[a] 150 cP
1. Soybean oil	30.1	29.6
2. Soybean methyl esters	3.4	148
3. Soybean ethylene glycol esters	14.3	>83; 31.4 cP[b,c]
4. Soybean oil + Cu^0	30.1	25.2
5. Soybean methyl esters + Cu^0	3.4	248
6. Soybean ethylene glycol esters + Cu^0	11.6	>315; 20.8 cP[c]
7. Soybean oil, alumina-treated	26.0	20.8
8. Methyl esters, alumina-treated	3.4	144
9. Ethylene glycol esters, alumina-treated	12.7	33.3
10. Ethylene glycol esters, alumina-treated + Cu^0	12.7	42.0
11. Ethylene glycol esters, alumina-treated + Cu^0 + unknown #1	12.7	>83; 17.5 cP[c,d]
12. Soybean oil + Cu^0 + 5% EFAT	28.6	>900; 64.9 cP[c]
13. Soybean oil + Cu^0 + 5% TSA	45	164
14. Soybean oil + Cu^0 + ingredients for 2% EFAT	28.6	658
15. Soybean oil + Cu^0 + 2% EFAT	28.6	>900; 74.5 cP[c]
16. Soybean oil + 5% EFAT + no Cu	28.6	384
17. Soybean oil + 5% EFAT + 0.01 mM Cu^{2+}	28.6	588
18. Soybean oil + 5% EFAT + 0.1 mM Cu^{2+}	28.6	640
19. Soybean oil + 5% EFAT + 1.1 mM Cu^{2+}	28.6	>645; 54.4 cP[c]

[a] Average of duplicate determinations. Overall least significant difference (LSD) was 37.7 at $P < 0.05$. When divided into groups of <100 cP and >100 cP, the LSD were 8.3 and 61.3, respectively.
[b] The rate of increase for methyl esters was greater than for ethylene glycol esters.
[c] Viscosity 150 cP was not reached. The average viscosity at the final reading time is given.
[d] Single determination because of lack of material.



SCHEME 1

linolenate. But lactones were not polar enough to account for the TLC properties of the unknown.

The APCI-MS of the unknown based on linolenate revealed peaks at 477 (100), 305 (46), 261 (18), and 243 (4). This is consistent with an M.W. of 476, with a major fragment at 304. The peaks at 305 and 261 were shown to be fragments of the 477 peak. This molecular weight is consistent with ethanediol *p*-toluenesulfonate linolenate, and the 304 and 261 peaks probably represent the loss of toluenesulfonic acid and a linolenyl group, respectively. This structure was confirmed by exact mass measurement of the molecular weight as 476.26088, which was best fit by $C_{27}H_{40}O_5S$. The exact mass spectrum also contained a strong peak at mass 91, indicating a toluene ring. We suggest the trivial name EFAT for the compound for ethylene glycol, fatty acylate, and *p*-toluenesulfonate (Scheme 1).

We concluded that the concentration of EFAT in our original ethylene glycol esters was about 5%. This yield was improved considerably by increasing the molar ratio of TSA to ethylene glycol and FA to 1:1:1 during synthesis. When this ratio was used, the concentration of EFAT in the reaction product rose quickly to ~50% and then more slowly rose to ~60% as shown in Figure 1. The formation of diacyl ester was faster than that of EFAT, but it decreased with reaction time.

Table 1, line 12, shows the effect on the stability of soybean oil of copper plus 5% EFAT in which the acyl groups were soybean oil FA. The viscosity of the soybean oil with EFAT slowly rose to about 65 cP in 900 h compared with the control (line 1) that reached 150 cP in ~30 h. EFAT is much more effective in stabilizing the oil than TBHQ-citric acid, which was the best antioxidant reported by Ruger *et al.* (3). But the ability of EFAT to prevent the polymerization of soybean oil requires a fairly high concentration compared with other antioxidants. EFAT was active at 2% or more but had no antioxidant activity at 1%.

Modifications of EFAT. Various modifications in the structure of EFAT were tried to determine the structural features required for antioxidant activity. Purified FA as short as lauric acid were substituted for soybean oil FA to alter the acyl group in EFAT. All of these acyl group variations were active in stability tests. When we tried octanoic acid, most of it distilled with the benzene azeotrope and was lost, so the yield was too poor for testing.

Mono alcohol esters of TSA were tested. Neither ethyl *p*-toluenesulfonate nor decyl *p*-toluenesulfonate, made using benzene azeotrope distillation, gave antioxidant activity in the AOM test at the 5% level.

EFAT analogs were synthesized using glycerol and 1,2-

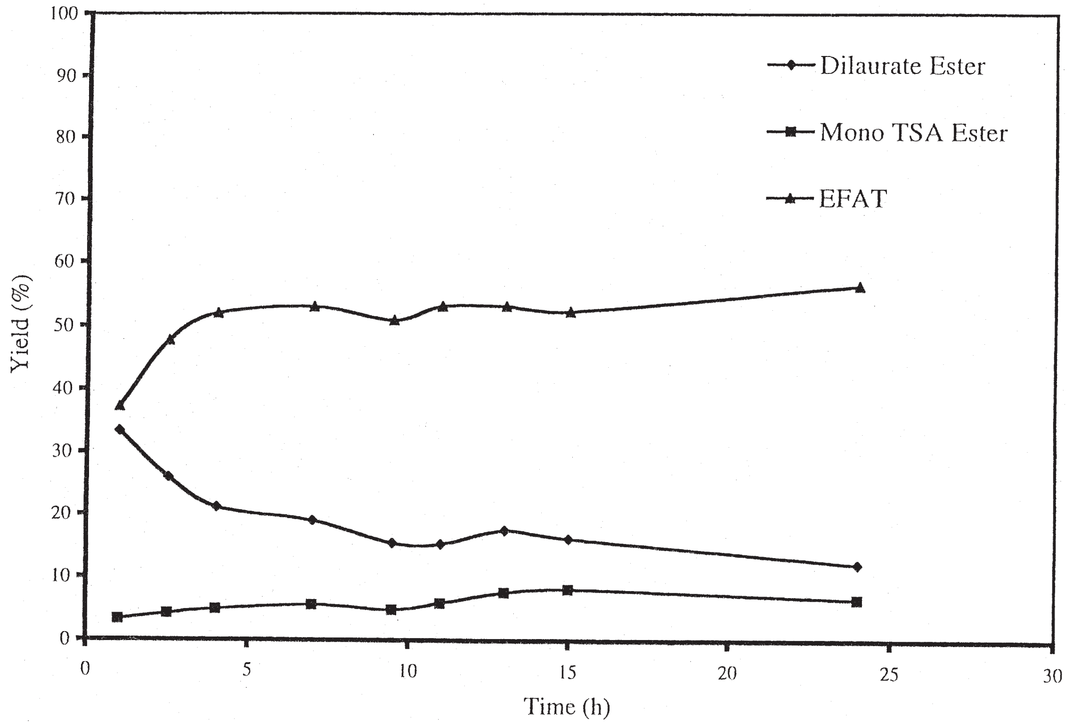


FIG. 1. Weight percent yield of ethylene glycol fatty acylate *p*-toluenesulfonate (EFAT), ethylene glycol dilaurate, and ethylene glycol mono-*p*-toluenesulfonic acid (mono TSA) vs. time. Conditions: 1:1:1 molar ratio of TSA/ethylene glycol/lauric acid in refluxing benzene with water removal by a Dean–Stark trap.

and 1,3-propylene glycol in place of ethylene glycol. The structures of the latter two products were verified by MS and NMR. Chemical shifts for the propylene glycol esters are given in ppm (δ), and multiplicities are indicated by *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *qn* (quintet), and *m* (multiplet). ^{1}H NMR (300 MHz, $CDCl_3$, 16 mg/mL) for the 1,2-propylene glycol product δ: 0.87 (3H, *t*), 1.30 (22H, *s*), 2.16 (2H, *m*), 2.45 (3H, *s*), 4.03 (2H, *m*), 4.91 (1H, *m*), 7.35 (2H, *d*), 7.79 (2H, *d*). For the 1,3-propylene glycol product δ: 0.88 (3H, *t*), 1.25 (18H, *s*), 1.98 (2H, *qn*), 2.21 (2H, *t*), 2.45 (3H, *s*), 4.09 (4H, *m*), 7.35 (2H, *d*), 7.79 (2H, *d*). The two spectra are similar. The 1,3-isomer had a methylene group in the middle of the 1,3-propylene glycol backbone that gave a quintet at 1.98 ppm, and the two methylene groups adjacent to the ester bonds gave two triplets at 4.09 ppm. For the 1,2-isomer the methyl group at the end of 1,2-propylene glycol joined with methylene groups on the FA chain at 1.25 ppm, and the –CH group in the middle of the propylene glycol gave a multiplet near 4.91 ppm. This multiplet arose because the product is a mixture of two compounds that vary in the position of tosyl and lauryl groups. The 1,3-propylene glycol product gave APCI-MS peaks at *m/z* 413, 241, 104, and 183, using hydrogen as the ionizing gas. The peak at *m/z* 413 is the expected mass + 1. The *m/z* 241 fragment is produced by the loss of the tosyl group. The *m/z* 183 fragment probably comes from the lauryl group split between its ester oxygen and carbonyl group. For the ethylene glycol product no peak representing the intact molecule was obtained; only the *m/z* 241 peak resulting from the loss of the tosyl group was observed.

The EFAT made with glycerol and 1,2-propylene glycol were active as antioxidants in the AOM test at the 5% level, but the EFAT made from 1,3-propylene glycol was not (data not shown). These results suggest that for antioxidant activity the EFAT must, for unknown reasons, have its acyl group and tosyl groups on adjacent carbons.

EFAT was made with sodium dodecylbenzenesulfonate in place of TSA. The APCI-MS of this product ionized with hydrogen gave peaks at *m/z* 401, 227, and 353. None of these represented the intact molecule, but the *m/z* 227 peak represents the loss of the dodecylbenzenesulfonyl group, and the *m/z* 353 peak represents the loss of the lauryl chain. This version of EFAT was active as an antioxidant in the AOM test at the 5% level (data not shown).

Table 1, line 13, shows that when free TSA was tested in the modified AOM test, it prolonged the time for viscosity increase to 150 cP from about 30 h to 164 h. But TSA is an interesterification catalyst and may react with soybean oil under AOM conditions to form a glycerol-based version of EFAT. Table 1, lines 14 and 15, shows that if ethylene glycol and FFA are put into the reaction mixture with TSA, an antioxidant effect is observed that is better than that of TSA alone but not as great as that of 2% preformed EFAT. These observations suggest that EFAT is formed to some extent during the AOM test. If no source of hydroxy groups is present, EFAT formation may be limited to the amount of MG and DG in the test oil.

The level of copper needed. Cupric acetate could successfully replace colloidal copper in the modified AOM stability test, so presumably the colloidal copper was furnishing cupric ions. The use of cupric acetate made it possible to measure the amount of copper ion needed. A comparison of Table 1, lines 16 and 12, shows that with no added cupric ion and 5% EFAT, the AOM time was reduced to about 384 h rather than the >900 h observed with colloidal copper. Increasing levels of copper ion from 0.01 mmol up to about 1.1 mmol or ~76

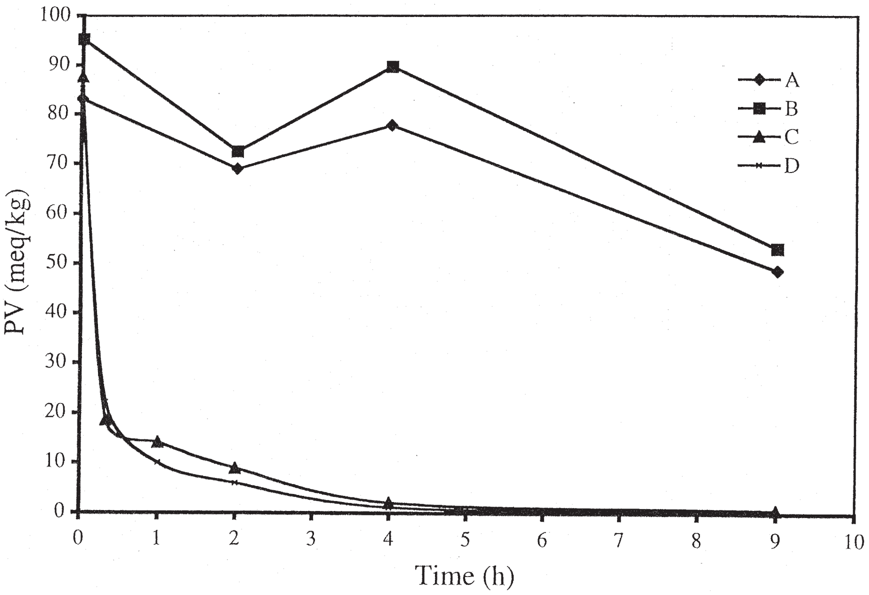


FIG. 2. Decomposition of soybean oil hydroperoxides in soybean oil that was 1 mmol in Cu^{2+} vs. time under nitrogen at 40°C. Curves A and B are controls with no EFAT; C and D contain 5% EFAT. For abbreviation see Figure 1.

ppm increased the AOM time (Table 1, lines 17–19). The copper content of refined soybean oil has been reported to be ~0.02 to 0.06 ppm (9), which would be about 0.001 mmol. It may be that if the level of copper in refined soybean oil could be reduced another order of magnitude, EFAT would have no effect by itself in stabilizing the oil. EFAT at 2% in the oil is ~41 mmol, which is ~37.5 times greater than the moles of copper necessary to give good stability.

Effect of EFAT on hydroperoxides. Figure 2 shows that the addition of EFAT to oxidized copper-containing soybean oil samples held under nitrogen at 40°C caused a much more rapid decrease of PV than controls. These results agree with our observation that samples of soybean oil containing EFAT accumulated much less peroxide during AOM testing than controls. These results suggest that EFAT exerts its antioxidant action by destroying peroxides and thus reducing the rate of free radical initiation. Normally the thermal decomposition of hydroperoxides in the presence of oxygen leads to the formation of free radicals that results in further accumulation of hydroperoxides. It is not clear how EFAT prevents this.

ACKNOWLEDGMENTS

To Eric Klinker for mass spectra of the EFAT made with propylene glycols and with dodecylbenzene sulfonic acid and the Hatch Act, State of Iowa and to the United Soybean Board for financial support. Journal Paper No. 19517 of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa, Project No. 3702.

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[Received September 17, 2001; accepted June 14, 2002]