Effects of Antioxidants on the Thermal Degradation of a Polyol Ester Lubricant Using GPC

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The thermal degradation of a polyol ester lubricant used as the main component of textile fiber finishes at high temperature (i.e., 220 °C) has been studied to model the real-world degradation of finishes on fiber manufacturing equipment. Chemical and physical analyses were performed on the thermally stressed lubricants using a combined analytical technique to measure the progress of degradation in the lubricant. The effects of two commonly used antioxidants in the fiber industry and two secondary arylamine antioxidants used in turbine engine oil on the thermal behavior of the lubricants were investigated. Phenyl-α-naphthylamine (PAN) shows a significant improvement in the thermal stability of the lubricant used in this study and could be considered as a potential fiber finish antioxidant for the textile industry.

1. Introduction

Fiber finishes are introduced to synthetic fibers and yarns during extrusion and spinning processes. Finishes make the manufacturing process easier by reducing static electricity and friction as well as providing physical integrity to the filaments.[1−5] During textile processes such as drawing, texturing and drying, finished fibers and yarns frequently contact hot surfaces or pass through high-temperature ovens. The finishes applied to the fibers must have enough thermal stability to withstand these severe conditions. Because modern manufacturing equipment runs at both higher speeds and temperatures, the applied finish can lose its stability under these severe conditions. The finish often undergoes evaporation, oxidation, and chemical decomposition, generating unwanted degradation products. The resulting presence of the thermally degraded material interferes with continuous and efficient fiber production and can lead to equipment shutdown.

Because lubricants are the major component of fiber finishes used in the textile industry (about 60−80% by weight),[1] a study on the thermal stability of finishes would be incomplete without degradation studies on lubricants. Polyol ester lubricants, often utilized as high-temperature lubricants, are used extensively in the fiber lubricant industry. High thermal stability, good lubrication properties, and appropriate viscosity at low temperatures are the main features of this group of lubricants. Some of the polyol ester lubricants can retain their properties in the temperature range of −50 to 200 °C.[6]

Studies on polyol ester lubricant degradation[6−11] indicate that oxidation reactions are the major reactions associated with degradation. Polyol esters typically oxidize more slowly and at higher temperatures than hydrocarbons. They also produce gases such as H_2, CO_2, and CO during their oxidation, similar to the behavior of other lubricants. The oxidation process is accompanied with a significant viscosity increase due to the formation of high-molecular-weight materials.[12,13] According to several authors,[7−9] synthetic oil in the presence of air at high temperatures undergoes a series of free-radical chain reactions that produce hydroperoxides. Further reactions often result in the formation of low-molecular-weight (LMW) materials such as aldehydes, ketones, acids, and alcohols. Polymerization of these primary oxidation products to form higher-molecular-weight (HMW) materials during the later stages of the reactions results in the formation of sludge and varnish with an associated increase in the viscosity.[6]

To overcome the problems caused by the degradation of finishes, several additives are introduced to prevent or delay the reactions of oxidation and degradation. Several classes of antioxidants are typically used in industry for the above-mentioned purpose.[1,14−16] Antioxidants inhibit specific steps in the free-radical oxidation process; hence, inhibition can occur during either the initiation or propagation steps of oxidation.[14−15] Scheme 1 shows the steps in the oxidation of organic materials by a free-radical chain mechanism.

Two main classes of antioxidants inhibit the initiation of thermal oxidation: (1) "peroxide decomposers" and (2) "metal deactivators". Peroxide decomposers inhibit the initiation step by decomposing the hydroperoxide intermediates as they are formed during oxidation. Examples of these types of antioxidants are sulfides such as dialkylthiodipropionates, alkyl and aryl phosphites, and xanthates.[15] In contrast, metal deactivators are strong metal ion complexing agents that inhibit catalyzed reactions by chelation.[15]

The most important classes of antioxidants that inhibit the propagation step are hindered phenols, secondary alkyl arylamines, and diarylamines (radical scavengers). The mechanism of inhibition involves competing with the substrate (RH) for peroxy radicals, thus shortening the kinetic chain length of the propagation reaction through hydrogen-atom transfer to the peroxy radical in a rate-controlling step (Scheme 2). Hindered phenols can be mononuclear in nature, such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) (Figure 1), or polynuclear such as bisphenols (Figure 2), diphenols, and polyphenols. Hindering the phenolic hydroxyl group with at least one bulky alkyl group provides steric hindrance. Steric hindrance decreases the ability of a phenoxyl radical to abstract a hydrogen atom from the substrate and produce an alkyl radical capable of initiating oxidation (Scheme 3). The introduction of long aliphatic chains
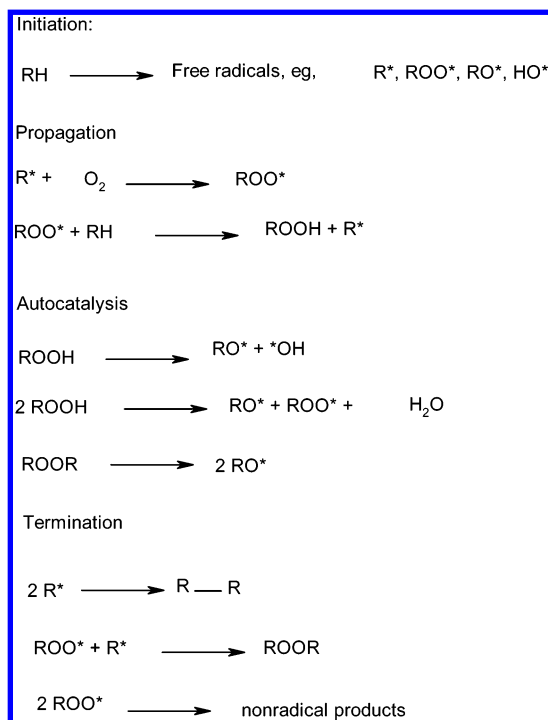
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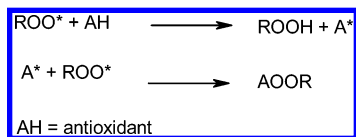† Department of Textile Engineering, Chemistry & Science.
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Scheme 1. Oxidation of Organic Materials by Free-Radical Chain Reactions

Scheme 2. Antioxidant Mechanism for Radical Scavengers

Scheme 3

into stabilizer molecules improves their performance by decreasing volatility and increasing stability.

Antioxidants derived from *p*-phenylenediamine and diphenylamine are highly effective scavengers for peroxy radicals and are more effective than phenolic antioxidants. The potential problem associated with these types of antioxidants is their staining and discoloring effect.[14] Scheme 4 shows oxidation of
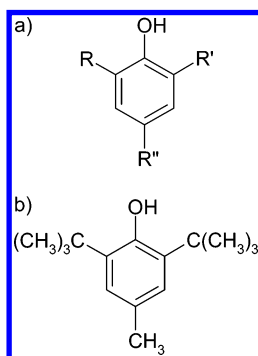

Figure 1. Chemical structures of (a) hindered phenol and (b) 2,6-di-*tert*-butyl-4-methylphenol (BHT).
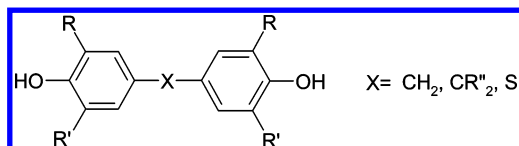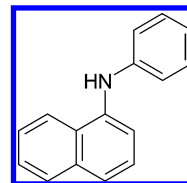

Figure 2. Chemical structure of bisphenol.

Figure 3. Chemical structure of phenyl-α-naphthylamine (PAN).

these antioxidants and production of highly conjugated products. However, alkylated diphenylamines show less color change than *p*-phenylendiamines upon heating.[14]

Thermally stable secondary aromatic amines such as dioctyldiphenylamine (DODPA) and phenyl-α-naphthylamine (PAN) (Figure 3) have exhibited good oxidation protection for synthetic esters.[17] A review of both current fiber finish literature and patents has not shown evidence of using this class of antioxidants for fiber lubrication purposes.

In the present research, the effects of different antioxidants on the chemical and physical thermal stability of a polyol ester lubricant are investigated. Antioxidants used in this study include common antioxidants used in fiber lubricants in addition to antioxidants used in turbine engine oils.

It has been shown in the literature that gel permeation chromatography (GPC) can be a valuable technique for analyzing the oxidation and degradation products of different types of esters.[10] In the present work, GPC has been used to quantify and compare the high-molecular-weight products formed in the liquid phase during lubricant degradation.[10] GPC has also been used as a method for measuring the progress of degradation of lubricants with different additives. Fourier transform infrared (FTIR) spectroscopy, acid value tests, and thermogravimetric analysis (TGA) have also been used to confirm and support the results obtained by GPC. This facilitates other methods that can be used for degradation measurements.[13] The amounts of solid deposits formed during degradation of different samples have also been measured and compared to results obtained using a quartz crystal microbalance (QCM). Details about evaluating the mass deposition of lubricants during heating by QCM have been explained elsewhere.[2,18]

2. Experimental Section

2.1. Materials. Four different antioxidants were selected for experimental purposes. Two of these antioxidants are typical antioxidants used for fiber finishes supplied by Goulston Technologies, Inc.; one is based on a hindered phenol, and the other antioxidant is based on bisphenol A. Their exact chemical structures are not known. The two other antioxidants, usually added to engine oils, are *N*-phenyl-1-naphthylamine or phenyl-α-naphthylamine (PAN, 98%; Figure 3) and phenothiazine (PTZ, 99%; Figure 4), purchased from Acros Organics.

Lubricant AF, supplied by Dupont, with a pentaerythritol tetrapelargonate structure (Figure 5), was used as the base lubricant for thermal degradation tests. Four mixtures of lubricant and antioxidants were prepared; in each mixture, one antioxidant was added to the AF lubricant. The percentage of antioxidant added was based on the supplier's recommendation: 1 wt % for hindered-phenolic-based (referred to as Hind) and 5% for bisphenol A-based (Bis). In the cases of PAN and PTZ, 1% antioxidant is added based on the literature.[17] Hind, PAN, and PTZ were in powder form, and preheating to 60 °C was necessary to dissolve the additives in the lubricant.

Stabilized HPLC-grade tetrahydrofuran (THF) with 99.5% purity [containing 100−400 ppm butylated hydroxytoluene (BHT) as a preservative], purchased from J.T. Baker, was used

Scheme 4. Oxidation of Aromatic Amine Antioxidants
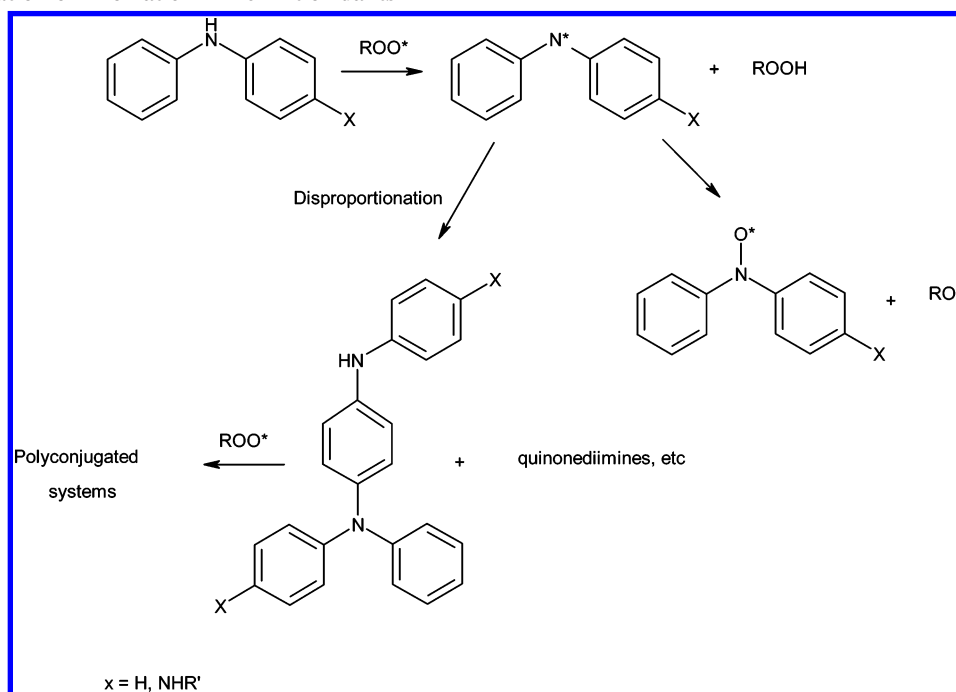
as the solvent and carrier for GPC. Zero-grade compressed air and prepurified nitrogen gas supplied by National Welders were used for experimental work.

2.2. Thermal Stress Experiments. Four different samples of inhibited lubricants and the original uninhibited AF lubricant were heated at 220 °C in a 210-mL stainless steel heating chamber designed for the degradation studies.

The heating chamber contains almost 136 mL of lubricant (which accounts for about 65% of the chamber volume) by design. A continuous dry airflow with a rate of 21.0 mL/min was passed through the chamber during heating. Liquid samples were periodically removed from the heating chamber after specific aging times (2−8 h for short-term runs and 12−96 h for long-term experiments). The same thermal stressing experiments were performed on the original uninhibited ST and two batches of inhibited ST. Chemical and physical analyses were performed on the samples collected after reaching room temperature. The details of the heating chamber and the procedures are explained elsewhere.[18]
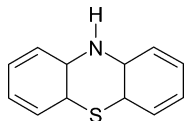

Figure 4. Chemical structure of phenothiazine (PTZ).
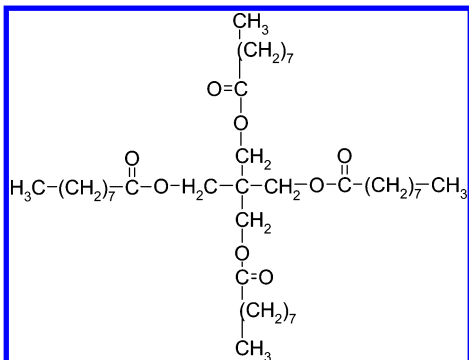

Figure 5. Chemical structure of pentaerythritol tetrapelargonate.

2.3. Analytical Measurements. Gel permeation chromatograms were obtained on a Waters Breeze HPLC pump model 1525 in GPC mode with a refractive index (RI) detector. Two Waters Styragel HR columns, HR1 and HR4E, filled with tetrahydrofuran (THF) were used for chromatographic separation. THF was used as the sample solvent and the mobile phase. The column and detector temperatures were maintained at 35 °C. The molecular weights were obtained by a calibration curve using seven poly(ethylene glycol) standards. The concentration of all standards and samples injected was 1 mg/mL, and the pump flow rate was maintained at 1 mL/min. All lubricant samples were filtered after dilution with THF to remove any insoluble solid deposits before injection into the chromatograph.

Acid value tests were performed on the samples by an alcoholic titration using ASTM test method D-4662-98.[19] This method was used to measure the acid content of the lubricant samples during degradation.

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Pyris 1 TGA instrument in two different environments: air or nitrogen with a flow of 20 mL/min. TGA was performed in order to evaluate the effect of the presence of oxygen in the system on the degradation behavior of the uninhibited and inhibited lubricant samples. In TGA experiments, 5−10 mg of sample was heated to 260 °C with a gradient of 20 °C/min and kept at 260 °C isothermally for 3 h. The remaining weight of the sample during the heating time was determined.

Fourier transform infrared spectroscopy measurements were performed on a Nexus 470 FTIR spectrophotometer. Liquid samples were prepared by applying a thin uniform film of samples on a polished NaCl salt plate.

A dual (double-sided) quartz crystal microbalance (QCM) sensor was introduced into the heating chamber and placed in the liquid phase for solid deposition studies. The quartz crystals used were 5-MHz AT-cut wafers with polished gold electrodes (purchased from International Crystal Manufacturing Co. Inc.) and driven by Lever oscillators.[2,18] The resonant frequency and dc voltage from the QCM crystal were recorded every 5 s during heating of lubricant at 220 °C. Mass accumulation on the crystal
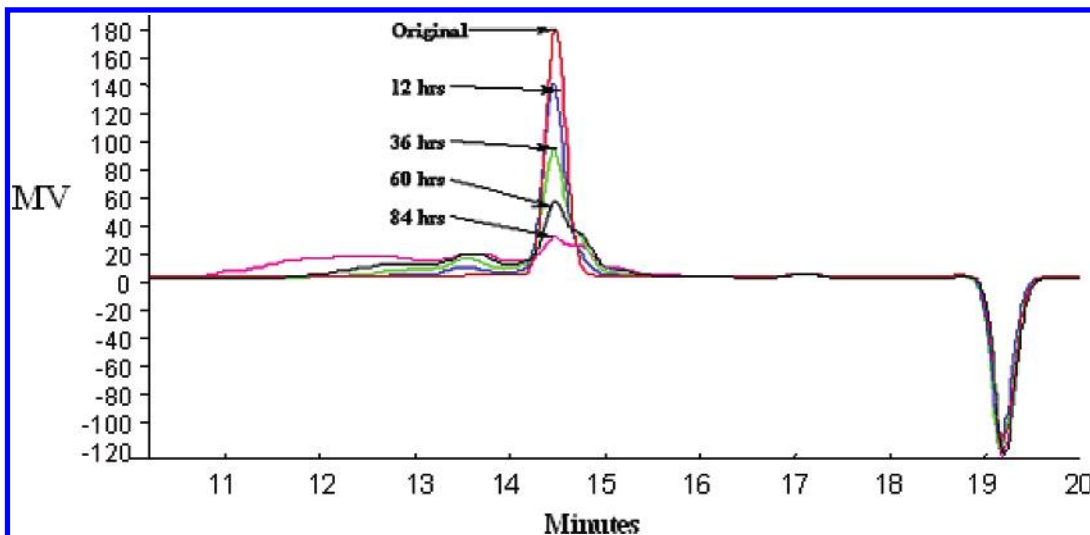
Figure 6. GPC chromatograms of original AF sample and AF samples heated for 12, 36, 60, and 84 h at 220 °C, obtained with a refractive index detector.

surface was calculated using eq 1 with the assumption that liquid properties (the product of density and viscosity) are constant[13,18]

$$\rho_s = -2.2097 \times 10^5 \, \Delta f/f_0^2 \, (\text{g/cm}^2) \qquad (1)$$

where ρ_s is the surface mass density, Δf is the change in the resonant frequency, and f_0 is the unperturbed series resonant frequency for a double-sided crystal.[18]

3. Results and Discussion

3.1. Molecular Weight Distribution. Gel permeation chromatography was used to investigate the molecular weight distribution of the liquid samples taken at different times from the heating chamber. In this article, molecular weight is used to describe the molecular size in GPC for comparison, even though separation in GPC is based on molecular size rather than molecular weight. Figure 6 is an overlay of the chromatograms obtained from original AF lubricant and heated AF samples. As the chromatogram shows, the original lubricant sample has a distinct peak at a retention time of 14.4 min. This peak is considered as the main peak for the lubricant and is present in all chromatograms regardless of the presence of antioxidants. The same figure shows the formation of a peak at an earlier retention time relative to the main lubricant peak (13.3−13.8 min). This peak, which grows as the lubricant is heated, represents the formation of materials with higher molecular weights when compared to the original lubricant. Formation of these products has also been observed in inhibited AF lubricants; as the heating continues, these peaks become broader (an indication of a molecular weight increase) and taller (an indication of an increase in concentration). The retention time (molecular weight range) of HMW products increases from 13.3−13.8 min to 11−14 min as heating continues.

The area of the main lubricant peak was measured for each sample, and the percentage area of the original lubricant remaining in the system during heating was determined. The percentage area of a peak indicates the area percentage of that peak relative to the total areas of the peaks in the chromatogram. Figure 7a shows the percentage area of the main lubricant peak as a function of heating time. The graph shows that, as the heating time increases, the lubricant is reacting and the percentage of the original material is decreasing in the system. The AF sample shows a half-life (heating time needed for the area of lubricant peak to reach one -half of its original value)
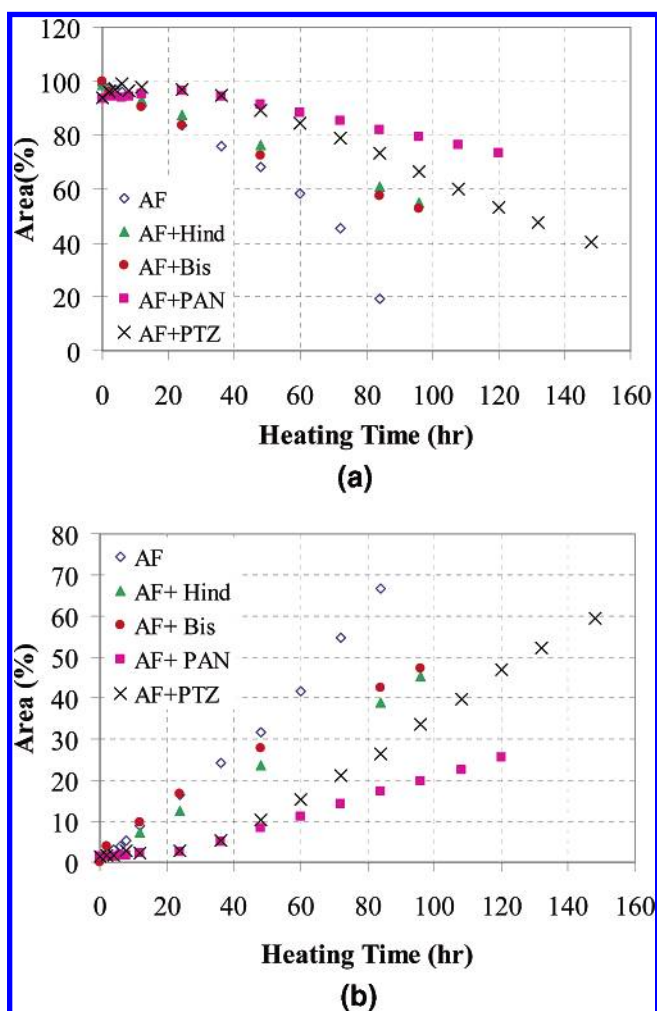

Figure 7. (a) Peak area of main lubricant peak versus heating time for AF original sample and AF inhibited samples heated at 220 °C obtained from GPC chromatograms of the liquid phase. (b) Peak area of all HMW peaks versus heating time for AF original sample and AF inhibited samples heated at 220 °C obtained from GPC chromatograms of the liquid phase.

of less than 70 h. Samples of AF with Hind and Bis additives show a much better thermal stability; the original lubricant seems to remain in the system for a longer period of time. After approximately 100 h of heating at 220 °C, these samples reach their half concentrations, with Hind showing a slightly better stability than Bis. Also, Figure 7a shows that the addition of

PAN to AF had a distinct effect on improving the thermal stability of this lubricant. Even after 120 h of heating at 220 °C, 73% of the original AF is present in the system; this point is reached after 48 h of heating AF + Hind or AF + Bis and 36 h of heating the original AF at 220 °C. The antioxidant PTZ also showed a good improvement in thermal stability almost equivalent to that of PAN.

The peak area of the high-molecular-weight materials formed in the liquid phase during heating of the lubricants increased for all lubricant samples (Figure 7b). This indicates that lubricants undergo oxidation reactions, with larger molecules formed by condensation and polymerization. Addition of antioxidants delays the formation of these high-molecular-weight (HMW) products, which later in the process of heating can continue polymerization and form solid deposits. Although the antioxidants Hind and Bis show a decrease in the formation of HMW products, antioxidants PAN and PTZ reduce the amount and also the molecular weights of these products more significantly. These results suggest that antioxidants with secondary arylamine structures improve the thermal stability of lubricants much more significantly than the phenolic antioxidants commonly used for this purpose.

3.2. Color. Because amine antioxidants are known for staining and discoloring effects,[14,15] the color change is an important parameter to determine their suitability for the textile and fiber industry. Several researchers[6] have demonstrated that, when lubricants thermally degrade, they produce color. Observations show that colorless lubricant, e.g., pentaerythritol esters, can change to dark brown to black as degradation progresses. The color change is due to the formation of carbonyl groups and other types of double bonds in the liquid-phase oxidation products. These products with unsaturated groups absorb light and produce color. The progress of degradation results in an increase in the amount of these products and leads to deeper shades. In earlier work, this effect was studied on AF degraded samples using UV/vis spectroscopy.[13] Physical observations indicate that the presence of antioxidants in the lubricant system, regardless of the type, has a color-change effect on the lubricant as it is heated. The color change was distinctly noticed in all inhibited AF samples after only 2 h of heating at 220 °C. Based on the color change they cause in the AF lubricant during heating, the antioxidants can be arranged in decreasing order as PTZ > Hind > PAN > Bis. Because PAN shows less of a color change than Hind, which is used in the textile industry, it can be concluded that there should be no problem related to the color change of PAN for fibers. However, staining experiment tests on different fibers are necessary to confirm this conclusion.

3.3. Acid Content. The acid value test, a standard method for measuring the oxidation of lubricants, was performed to confirm the results from GPC. As oxidation proceeds and oxidation products are formed, the free acid content of the lubricants increases. This is an indication of the formation of oxidation products in the liquid phase with free acid groups from thermo-oxidative reactions. Antioxidants, as inhibitors of oxidation reactions, should be able to indicate a decrease in the free acid content of the liquid phase resulting from the formation of less-oxidized products. This decrease was observed for all inhibited samples (Figure 8). Samples of lubricants inhibited with Hind and Bis each showed lower acid values than the AF original, which indicates that the amounts of oxidation products containing acid group ends are almost equal in these two inhibited samples. PAN exhibited a distinctive decrease in acid values (approximately up to 70%), as a result of the formation
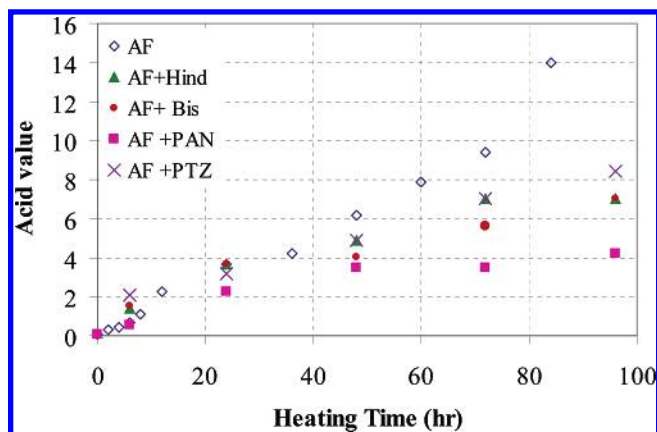

Figure 8. Acid values of original AF lubricant and inhibited AF samples versus heating time for samples heated at 220 °C.
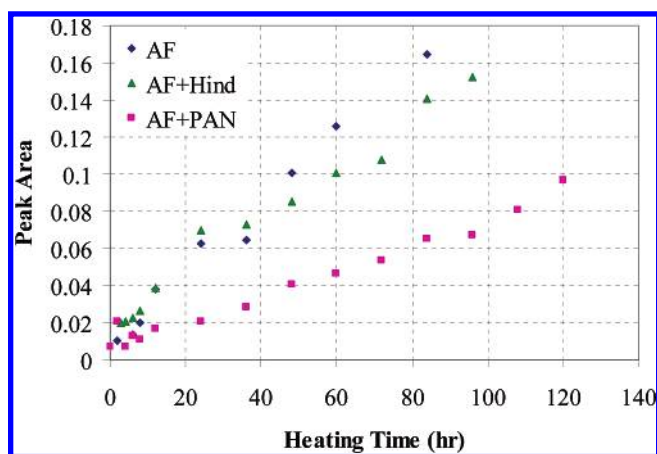

Figure 9. Area under the peak at 3528 cm^{-1} (OH group) versus heating time obtained from FTIR spectra of original AF lubricant and inhibited AF lubricants heated at 220 °C in the heating chamber.

of less-oxidized products in the presence of this antioxidant and the neutralization of acid by the amine group in PAN. These results are in good agreement with GPC results indicating that PAN is a better antioxidant for AF.

3.4. Hydroxyl Content. A comparison of the FTIR spectra of the original AF lubricant and heated AF lubricant samples indicates the growth of a broad peak at 3528 cm^{-1} that reflects an increase in the concentration of OH groups in the liquid phase[13] (spectra not shown). The area under the peak at 3528 cm^{-1} was normalized by dividing by the area of the carbonyl peak (1750 cm^{-1}). This peak ratio was measured for the original AF and inhibited AF samples. Measuring the same peak area for degraded samples indicates the amount of growth of this peak during the thermal stressing of AF and inhibited samples (Figure 9). The uninhibited AF sample exhibits a larger increase in OH concentration than AF+ Hind and AF+ PAN as they are thermally stressed. This means that the antioxidants have partially eliminated the presence of oxidation products with hydroxyl groups during thermal stressing; this includes carboxylic groups as well. AF+ PAN shows much smaller growth of this peak than AF+ Hind, which indicates that PAN is a better antioxidant than Hind. Because oxidation products with OH groups are some of the major degradation products of polyol ester lubricants, these results are valuable in determining the effects of antioxidants. The FTIR results are also in good agreement with the GPC and acid value data.

3.5. Weight Loss. In thermogravimetric analysis (TGA) experiments, the weight loss during heating was recorded online, and graphs of the percentage of residual mass in the TGA pan
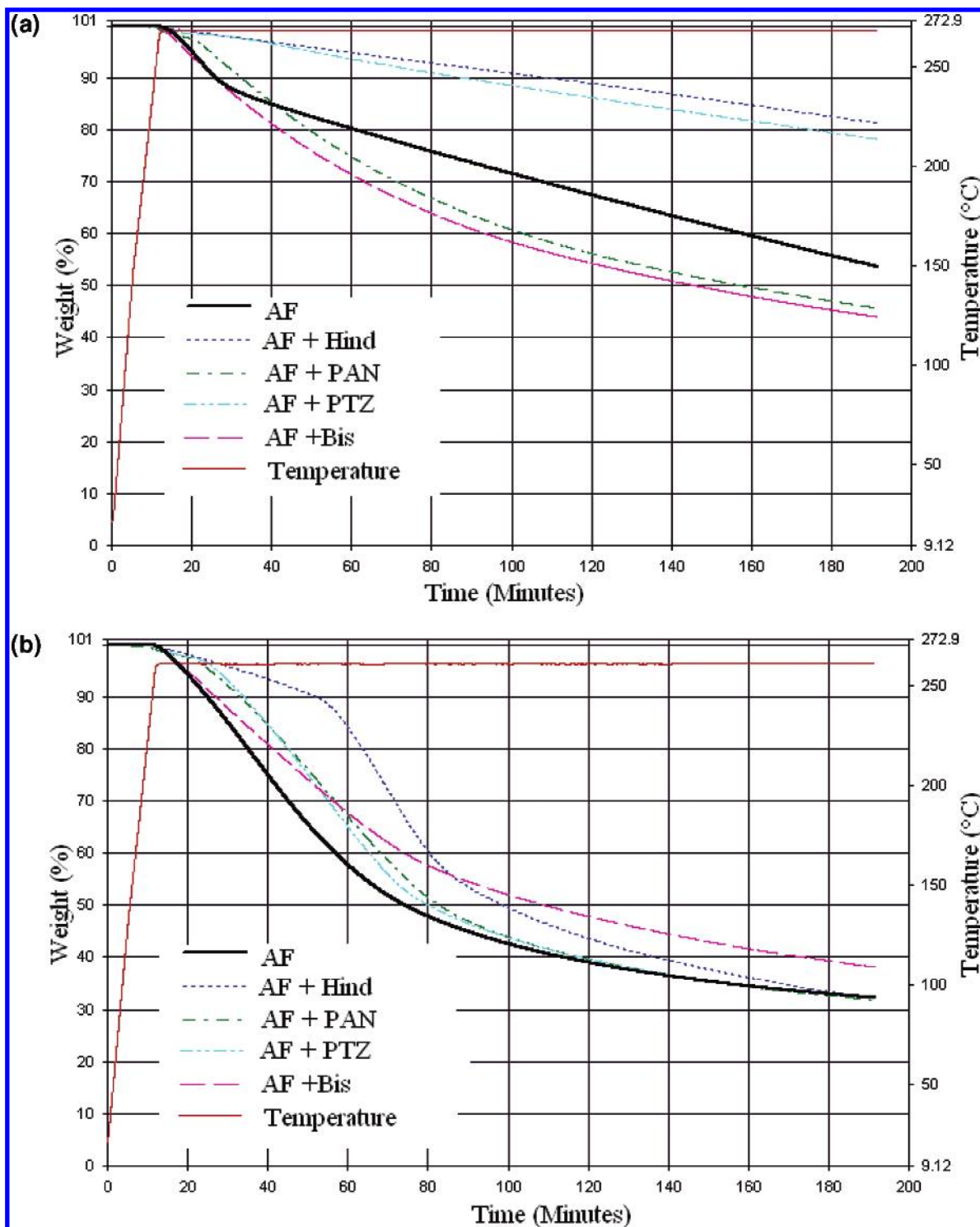
Figure 10. Weight percent mass of original AF lubricant and inhibited AF lubricant samples versus heating time as they are heated at 260 °C in TGA. Environment gas: (a) nitrogen, (b) air.

versus heating time at 260 °C are presented in Figure 10. The weight loss in the nitrogen environment is attributed to evaporation and decomposition, whereas the weight loss in the air environment is due to a combination of evaporation, decomposition, and oxidation. The difference between weight loss in air and nitrogen is an indication of the amount of oxidized gas-phase products produced. All antioxidants used in this study improved the amount and rate of weight loss of AF in the presence of air. In other words, addition of antioxidants helped to reduce the amount and rate of generation of gaseous oxidation products. However, it is important to note that not all above-mentioned antioxidants reduce the amount of evaporation/

decomposition. TGA results indicate that the antioxidants Bis and PAN show an increase in the amount of evaporation/ decomposition (in the presence of nitrogen), whereas they decrease the amount and rate of lubricant oxidation (in the presence of air). The difference in the amount of weight loss obtained for AF+ Bis between air and nitrogen is very small (i.e., almost 8% of the original weight after 3 h of heating at 260 °C in TGA), which shows that there are small amounts of oxidized products in the gas phase. This behavior was also observed for AF+ PAN (about 14% of original weight after 3 h of heating at 260 °C), whereas AF+ Hind and AF+ PTZ show up to 50% difference in weight loss between the two
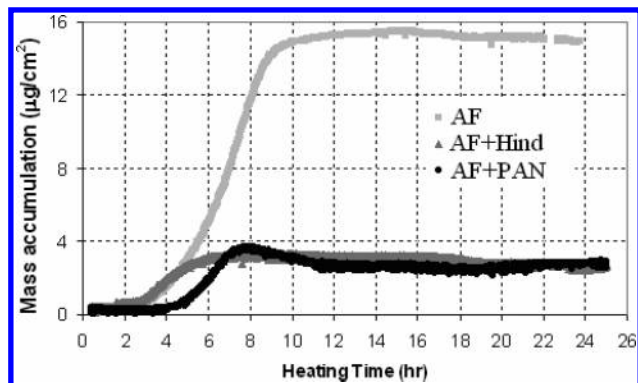
Figure 11. Mass accumulation of original AF lubricant and inhibited AF lubricant samples during heating time as they are heated at 220 °C in heating chamber. Obtained using QCM in liquid phase.

Figure 12. Oxidation products of phenyl naphthylamines.

Scheme 5

environments (50% and 46% of the original weight, respectively). This value for the original AF lubricant is approximately 22% of the original weight after 3 h of heating at 260 °C. This means that, although the TGA results at first glance suggest that Hind is a better antioxidant than others because of the generation of fewer gaseous products, a detailed analysis of these results indicates that this is not a correct conclusion. Most of the weight loss for AF+ Hind (about 75% of the total weight loss) is due to oxidation, whereas for PAN, for instance, most of the weight loss is related to evaporation/decomposition of the lubricant without chemical oxidation and a small amount of weight loss (about 25% of the total weight loss) is due to oxidation.

3.6. Mass Accumulation. Mass accumulation results using QCM quantify the amount of solid deposition during isothermal heating of original AF and inhibited AF lubricant at 220 °C (Figure 11). After reaching 220 °C, AF lubricant does not show a significant change in frequency for approximately 2 h. After 2 h at this temperature, mass loading starts and continues at an increasing rate until about 10 h, after which deposition reaches a steady state. The three stages of lubricant mass loading observed in earlier studies are present for all lubricants.[18] Most mass loading on the surface of the crystal occurs in the intermediate stages of degradation, when high-molecular-weight products have already started forming. Long-term experiments of mass deposition with a QCM are not technically possible because of the increased viscosity of lubricant.

The effect of antioxidants on the amount of mass loading is apparent. The inhibited AF samples show a distinct decrease in the amount of mass deposition relative to the original AF. AF+ Hind shows the same onset time for deposition as AF, whereas PAN delays the onset of deposition from 2 h for AF to 4 h. The amounts of mass loading during the second stage for the two inhibited samples are similar, with PAN showing a maximum at about 8 h and decreasing slightly in the later stage of deposition. After 24 h of heating of the hindered lubricants at 220 °C, PAN-inhibited AF shows a similar mass accumulation as AF+ Hind, which indicates that PAN decreases the amount and rate of deposition of AF as much as Hind does.

In summary, the results indicate that PAN, as an antioxidant for polyol esters, can increase the thermal stability of AF significantly, even more than common antioxidants used for fiber finishes. This effect is due to the mechanism of antioxidation of PAN, which is different from that of other antioxidants. The inhibitors usually reduce the oxidation of lubricants by termination of the free-radical chain processes of oxidation.[14,15] However, as reported by Hunter et al.,[17] in the case of PAN, the inhibitor molecules eliminate the first step of the oxidation
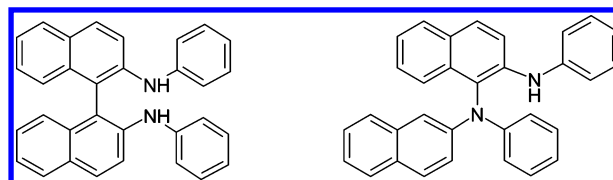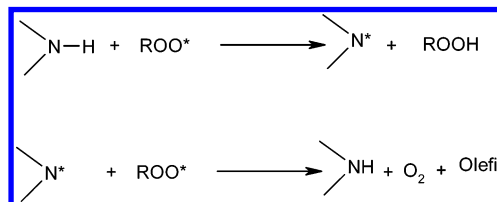
process. In other words, the inhibitor and its oxidation products prevent the formation of lubricant radicals and hydroperoxides. Hunter et al.[17] related this effect to the ability of PAN to exist in several resonating states and to absorb energy by moving between these resonating states. Because PAN can absorb energy from molecular collisions with oxygen without reaction, it can survive many collisions before oxidizing and forming oxidation products. This effect makes PAN a good inhibitor. A similar mechanism is shown with the oxidation products of PAN,[17] so even oxidized PAN inhibits the oxidation of lubricant.

Formation of the aminyl radical (N^*) according to Scheme 5 is the first step of sacrificial transformation of secondary amines in the antioxidant mechanism.[20] Some of these aminyls participate in amine regeneration via reaction with ROO*. $N-N$, $C-C$, or $C-N$ coupling products and more complicated trimer and tetramers are formed from PAN (Figure 12). However, it has been shown that the principal attack of ROO* on PAN is on the naphthyl ring, forming quinone imines and naphthoquinones.[20] These products also exhibit free-radical oxidation activity. This explains the better performance of PAN as an antioxidant and makes PAN a good potential inhibitor for the fiber finish industry.

4. Conclusions

High-temperature degradation of a synthetic polyol ester textile lubricant at 220 °C in the presence of different antioxidants is reported. Gel permeation chromatography of the degradation products of thermal stressing of the lubricant can be used to study the degradation and the formation of high-molecular-weight products. GPC, acid value tests, FTIR spectroscopy, TGA, and QCM results indicate that antioxidants have a beneficial effect in delaying the thermal degradation of pentaerythritol tetrapelargonate. Specifically, PAN exhibits a very distinctive effect in improving the thermal stability of AF lubricant. PAN also demonstrates a larger improvement in the stability than conventional antioxidants (e.g., hindered-phenolic-based) used in fiber finishes. Although the addition of PAN makes a significant improvement in thermal stability, further studies on other requirements of a good finish (e.g., performance, lubrication, chemical interaction, and viscosity) in a pilot plant are needed to introduce PAN as an antioxidant for fiber finishes. Further studies on the compatibility of the PAN-inhibited lubricant with other components of fiber finishes (e.g., emulsifiers and antistatic agents) are required to develop a more thermally stable finish.

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