

Improving the Thermal Stability of Textile Processing Aids

Principal Investigators: Christine S. Grant, Peter J. Hauser, William Oxenham (All NCSU)

Postdoctoral Research Associate: Paria Mousavi, Dianxia Wang

Goal

The overall objective of this project is to investigate the thermal behavior of textile finishes and their components in order to improve their thermal stability at high temperature processes.

Abstract

Producing synthetic fibers and yarns is almost impossible without applying a processing aid to the fibers during extrusion and spinning processes. The applied processing aid or 'finish' reduces static electricity, fiber-fiber and metal-fiber friction, provides integrity to the filaments, and thereby eases the manufacturing processes [1-2]. However, a finish must satisfy many requirements for high quality yarn production. During textile processes such as drawing, texturing and drying, fibers and yarns are frequently contacted with hot surfaces or pass through high-temperature ovens. The finishes applied to the fibers must have enough thermal stability to withstand this extreme condition. Since modern manufacturing equipment runs at higher speeds and subsequently at higher temperatures, the applied finish thermally degrades and generates unwanted decomposition products. These byproducts can be in the form of toxic and nontoxic gases; in liquid form, leaving a sticky residue on the yarn; or form a solid varnish on hot surfaces that is very difficult to remove [3-8]. The presence of the varnish interferes with continuous, efficient production leading to significant economic losses due to equipment shutdown and product failure. Environmental and safety issues related to the formation of toxic gases and lower quality fibers produced by oxidized finish are other important aspects associated with the thermal degradation of finishes [9-10].

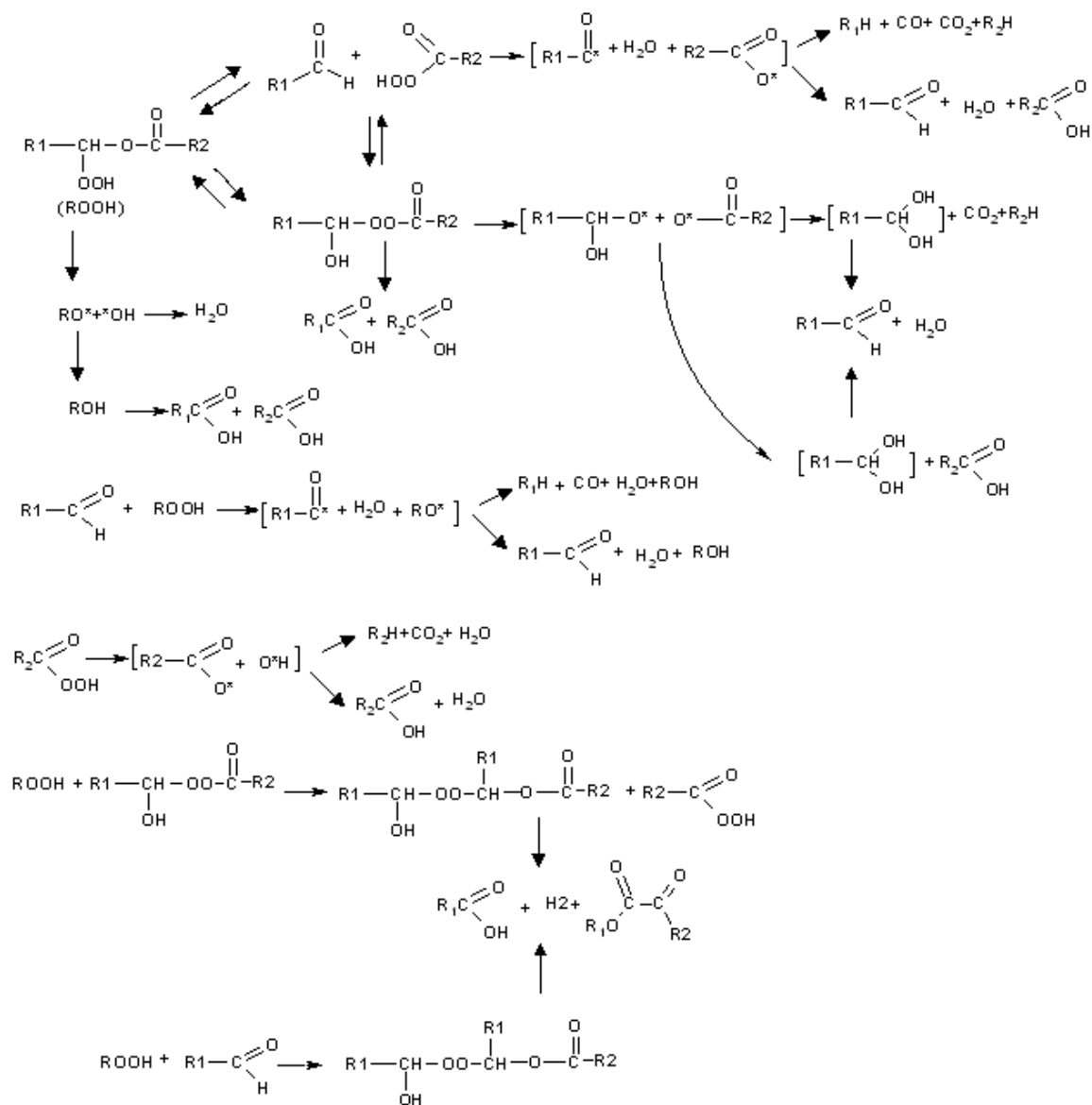
Every finish consists of different components depending on the end use of the yarn being manufactured. In general, finishes contain lubricants, emulsifiers, antistatic agents and some other components. Since lubricants are one of the main components of the finishes (about 80%), studying their behavior at elevated temperatures is an inevitable part of a research on thermal stability of the finishes.

Introduction

In the previous reports, three synthetic polyol esters based on pentaerythritol tetrapelargonate were used for the thermal degradation experiments. Different analyses showed that although the esters had the same base component, their behaviors at elevated temperatures differed from each other significantly. In general, heating the esters resulted in volatilization and chemical degradation. Increases in the heating time and temperature led to increases in viscosity, higher molecular weight products, and darkening of the initial ester. Further heating resulted in the formation of solid deposits [3-7, 11-12]. The results have provided us with critical information about the nature of the degradation process and useful insights into the makeup of the degradation products.

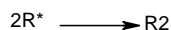
Studies on polyol ester lubricant degradation [13-21] indicate that oxidation reactions are the major reactions associated with degradation. Polyol esters typically oxidize more slowly and at higher temperatures when compared to hydrocarbons. They also produce gases like H₂, CO₂ and CO during their oxidation 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. According to several authors [15-17], 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 materials (LMW) such as aldehydes, ketones, acids and alcohols (Scheme 1). Polymerization of these primary oxidation products to form higher molecular weight materials (HMW) during the later stages of the reactions result in the formation of sludge and varnish with an associated increase in the viscosity (Scheme 2) [13-14].

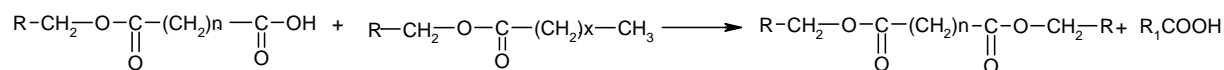


Scheme 1. Formation of low molecular weight oxidation products during oxidation of lubricants

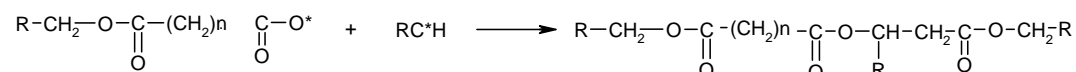
(a) Radical recombination



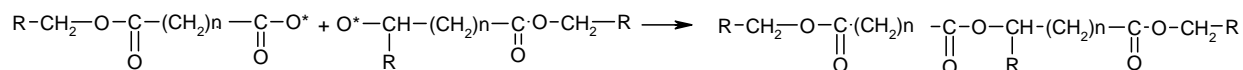
(b) Ester interchange



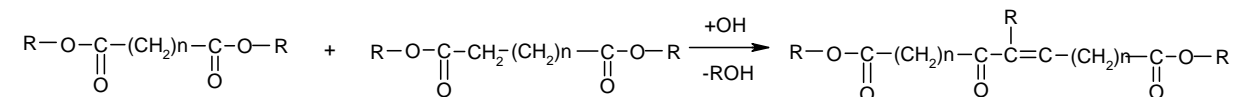
(c) Radical esterification



(d) Radical esterification



(e) Aldol Condensation



Scheme 2. Formation of high molecular weight products

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]. Antioxidants inhibit specific steps in the free radical oxidation process; hence, inhibition can occur either during the initiation or propagation steps of oxidation. The most important classes of antioxidants that inhibit the propagation step are hindered phenols, secondary alkyl aryl amines and diarylamines (radical scavengers). The mechanism of inhibition involves competing with the substrate (RH) for peroxy radicals, thus shortening the kinetic chain length of propagation reaction due to the hydrogen atom transfer to the peroxy radical in a rate-controlling step (Scheme 2). Hindered phenols can be mononuclear in nature; examples of this include: 2, 6-di-tert-butyl-4-methyl-phenol (BHT) or polynuclear such as bisphenols, 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). Introduction of long aliphatic chains to stabilizer molecules improves their performance by decreasing volatility and increases their 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. Thermally stable secondary aromatic amines such as dioctyldiphenylamine (DODPA) and phenyl α naphthylamine (PAN) have shown good oxidation protection for synthetic esters [22]. A review of both current fiber finish literature and patents has not showed evidence of using this class of antioxidants for fiber lubrication purposes.

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

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 a hindered phenolic based 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% and phenothiazine (PTZ) 99%, purchased from Acros Organics.

Lubricant AF, supplied by Dupont, with a pentaerythritol tetrapelargonate structure, 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% by weight for hindered phenolic-based (referred to as Hind) and 5% for bisphenol A-based (Bis). In case of PAN and PTZ, 1% antioxidant is added based on literature [22]. Hind, PAN and PTZ were in powder form and heating up 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 as the solvent and carrier for GPC. Zero grade compressed air and pre-purified nitrogen gas supplied by National Welders were used for experimental work.

Experimental System

A schematic diagram of the total experimental system is indicated in Figure 1. It includes a stainless steel heating chamber, a high temperature quartz crystal microbalance (QCM) system, an on-line gas chromatography (GC) system and an off-line gel permeation chromatography (GPC) system. The QCM was used to measure in situ, real-time varnish buildup on metal surfaces. The GC on-line analytical system, equipped with both thermal conductivity (TCD) and flame ionization (FID) detectors, was designed to monitor the gas phase components produced by thermally stressing finishing aids. The molecular weights and molecular weight distributions of the liquid and solid phase products were determined using GPC. Their composition was determined by gas chromatography-mass spectrometry (GC/MS). Fourier transform infrared spectroscopy (FTIR) was used to identify the new chemical bonds formed in the degraded finishing aids. In addition, thermo-gravimetric analysis (TGA) was employed to determine the amount and the rate of weight-loss during the heating of the finishing aids. Three synthetic

polyol esters based on pentaerythritol tetrapelargonate were used for the thermal degradation experiments.

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 due to its 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 ageing times (2- 8 hours for short term runs and 12- 96 hours 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 collected samples after reaching room temperature. The details of the heating chamber and the procedures are explained elsewhere [11].

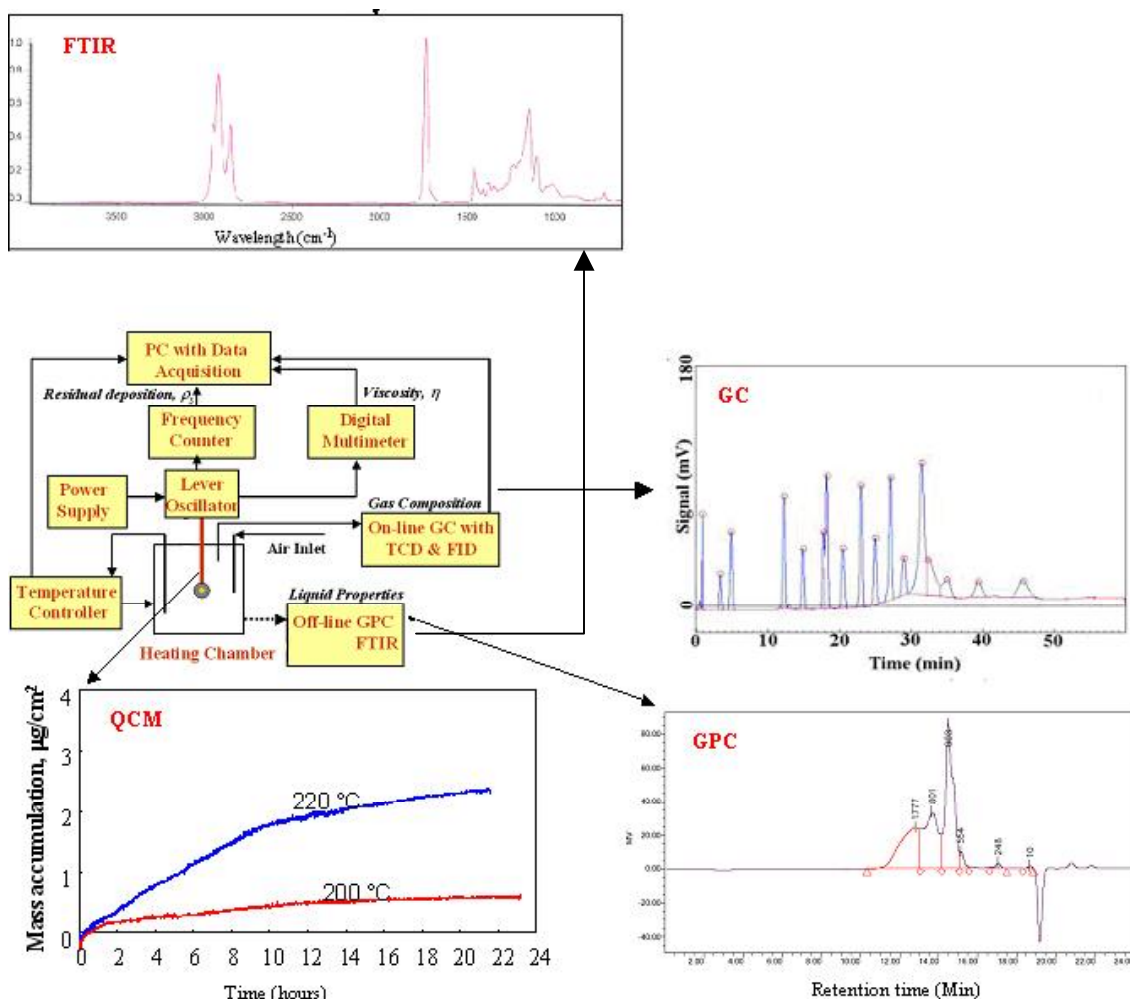


Figure 1: Schematic diagram of the experimental system and typical data output.

Analytical Measurements

It has been shown in the literature that gel permeation chromatography (GPC) can be a valuable technique to analyze the oxidation and degradation products of different types of esters [18]. In the present paper, GPC has been used to quantify and compare the high molecular weight products formed in the liquid phase during lubricant degradation [18]. GPC has also been used as a method to measure the progress of degradation of lubricants with different additives. Fourier transform infrared (FTIR) spectroscopy, acid value 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. Amount of solid deposits formed during degradation of different samples have also been measured and compared using quartz crystal microbalance (QCM). Details about evaluating mass deposition of lubricants during heating by QCM have been explained elsewhere [2-6].

GPC results show that the peak area of the high molecular weight materials formed during heating of the lubricants increased for all lubricant samples (Figure 2). 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 formation of HMW products, antioxidants PAN and PTZ have reduced the amount and also molecular weights of these products more significantly. These results suggest that antioxidants with secondary aryl amine structures improve the thermal stability of lubricants much more significantly than phenolic antioxidants commonly used for this purpose.

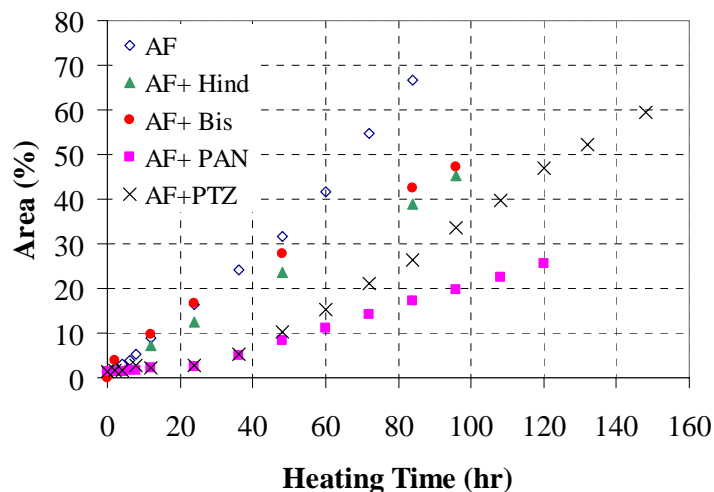


Figure 2. Peak area of all HMW peaks versus heating time for AF original sample and AF inhibited samples heated at 220°C.

The acid value test, a standard method for measuring oxidation of lubricants, was performed to confirm the results from the GPC. As oxidation proceeds and oxidation products are formed, the free acid content of the lubricants increases. This is an indication of 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 liquid phase due to the formation of less oxidized products. This decrease has been observed for all inhibited samples (Figure 3). Samples of lubricants inhibited with Hind and Bis each showed lower acid values than AF original, which indicates that the amount of oxidation products containing acid group ends are almost equal in these two inhibited samples. PAN has shown a distinctive decrease in acid values (approximately up to 70%), due to formation of less oxidation products in presence of this antioxidants and 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.

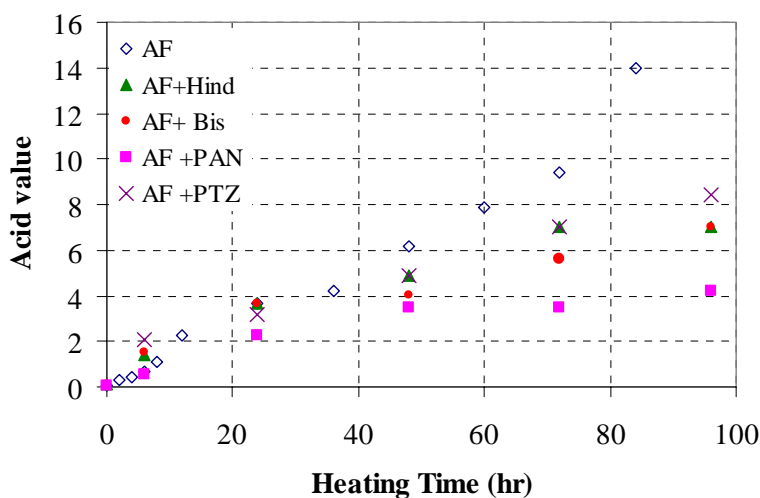


Figure 3. Acid value of original AF lubricant and inhibited AF samples versus heating time for samples heated at 220°C.

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 4). After reaching 220°C, AF lubricant does not show a significant change in the frequency for approximately 2 hours. After 2 hours at this temperature, mass loading starts and continues at an increasing rate until about 10 hours; after that deposition reaches a steady state. The three stages of lubricant mass loading observed in earlier studies are present in all lubricants. Most mass loading on the surface of crystal happens in the intermediate stages of degradation, when high molecular weight products have already started forming. Long-term experiments of mass deposition with QCM are not technically possible due to the increased viscosity of lubricant.

Conclusions

The thermal degradation of two pentaerythritol tetrapelargonate lubricants (AF and ST) was evaluated. An experimental system was developed to thermally stress the lubricants at different temperatures; degraded liquid samples were collected during heating for both chemical and physical analysis. Gel permeation chromatography was used to quantify the amounts of high molecular weight products formed in the liquid phase. It has been demonstrated that this is a fast and accurate method to identify the presence, amount and molecular weight distribution of the

HMW products. It was also observed that initial generation of HMW products occurs in as little as 2 hours of heating. This method can be used to compare and predict the amount of deposition in the later stages of the oxidation since the higher the amount of HMW products, the higher the magnitudes of the deposits. GPC results indicated a significant difference in the extent of degradation of the two lubricants under the same thermal stressing conditions.

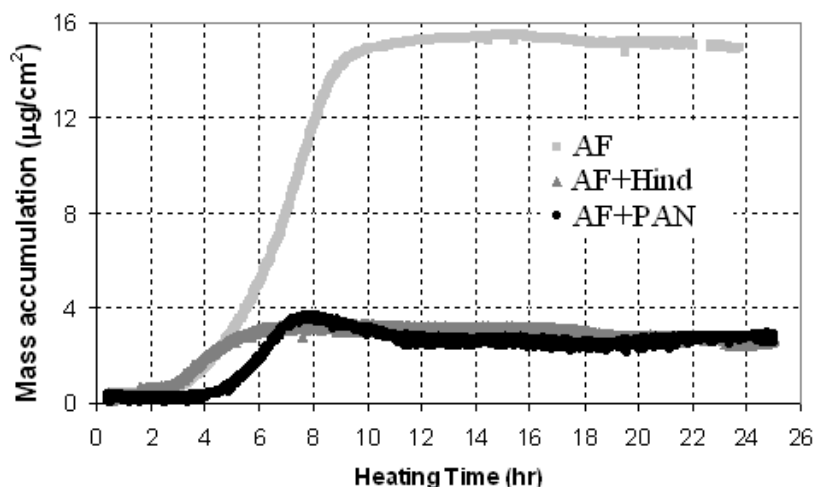


Figure 4. Mass accumulation of original AF and inhibited AF lubricant samples during heating time as they are heated at 220° C in heating chamber. Obtained using QCM in liquid phase.

Different pathways for the formation of oligomers and polymers have been suggested. FTIR, acid values, UV/Vis spectroscopy and viscosity measurements confirmed the results from GPC regarding the difference in extent of degradation of the two lubricants; ST showed a higher thermal stability in the liquid phase than AF. The oxidation products in the gas phase were identified from GC/MS measurements. A comparison of the results from TGA analysis and the liquid phase analyses were not in agreement; AF exhibited a lower weight loss due to oxidation rather than ST. This is because TGA just determines oxidative weight loss in the gas phase whereas other analytical methods utilized determine oxidation solely in the liquid phase. A series of analytical tools is required to accurately evaluate the stability of different lubricants; in the case reported in this work, two lubricants with the same base stock chemical structure exhibit different levels of stability in the gas and liquid phase. As a result, depending on the industry and application of these lubricants, one may perform better than the other. In the current study, possible reasons for the differences for the behavior of the two pentaerythritol tetrapelargonate lubricants are the differences in (i) the starting materials, or (ii) the synthesis reactions and the catalysts that may have been used in their production. TGA studies (heating up to 600°C) demonstrate that it is not likely that lubricant compounds utilized in this study are 100% pure. After heating, there was a residue related to salts and metal catalysts used for synthesis of these lubricants in the pan. In addition, the GC/MS analysis showed traces of an antioxidant in AF sample. The results obtained indicate that the combined analytical approach introduced in the present work could be utilized to further investigate and compare extent of degradation in lubricants both in original and stabilized forms.

High temperature degradation of a synthetic polyol ester textile lubricant at 220°C in the presence of different antioxidants is reported. Gel permeation chromatography on the degradation products of thermal stressing of the lubricant can be used to study the degradation and high molecular weight formation. GPC, acid value test, FTIR, TGA and QCM results indicate that antioxidants have a beneficial effect in delaying the thermal degradation of pentaerythritol tetrapelargonate. Specifically, PAN has shown a very distinctive effect in improving the thermal stability of AF lubricant. PAN has also demonstrated a larger improvement in the stability when compared with 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 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.

Thermal stressing experiments were performed on two emulsifiers, one antistatic agent, several formulated finishes prepared using different additives and two ready-to-use formulated finishes supplied by Goulston Technologies. Gel permeation chromatography has been used as a qualitative tool to study the changes in the molecular weight distributions of the degraded samples. Thermogravimetric analysis was used as a tool to study the high temperature stability of all samples in the gas phase. The antistatic agent used was found to be one of major reasons for deposit generation. Also, it was found that although antioxidants have an important role in delaying the degradation of lubricants, they do not exert a large effect on the degradation of mixed formulated finishes. Different emulsifiers presented noticeable changes in the behavior of the formulated finish at high temperature. Although GPC could give good insight about the formation of HMW and LMW products in the liquid phase, it can not separate and quantify each component after degradation. This is due to the existence of numerous different products with the same molecular sizes in the system. Further studies are needed in order to measure and quantify the extent of degradation in formulated finishes.

The web site URL address:

http://www.che.ncsu.edu/interfacial/Rsrch_Actvty/Textile_intro.htm

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