

Effect of Additive Components on Thermal Stability of Fiber Finishes

Abstract In an effort to investigate the thermal degradation of fiber finishes on fiber manufacturing equipment, different additive components (i.e., lubricants, emulsifiers, antistatic agents and anti-oxidants) of textile fiber finishes were thermally stressed at high temperature (i.e., 220 °C). Oxidative-degradation behavior of common components of formulated finishes has been evaluated independently and in mixtures with other components (formulated finish). Using chemical and physical analyses, the changes in the molecular weights and products of degradation were investigated. Thermal degradation of formulated finishes prepared in this research was compared with two ready-to-use formulated finishes from industry. Results of this work provide valuable insights that improve the thermal stability of textile fiber finishes.

Key words fiber finish, fiber lubricant, spin finish, thermal Stability, thermal degradation, polyol ester

Paria Mousavi and Peter J. Hauser¹

Department of Textile Engineering, Chemistry & Science, North Carolina State University, Raleigh, USA

Dianxia Wang and Christine S. Grant

Department of Chemical Engineering, North Carolina State University, Raleigh, USA

William Oxenham

Department of Textile & Apparel Technology & Management, North Carolina State University, Raleigh, USA

Introduction

During the production and processing of man-made fibers, an external coating is applied to the fibers to provide them with a smooth and lubricated surface and enable the process of manufacturing to be performed faster and more efficiently. Without this lubricating, coating, spinning, drawing, texturing and additional processing of synthetic fibers would have been almost impossible [1]. The applied coating or fiber finish not only provides synthetic fibers and yarns with lubrication, but also reduces the static electricity and friction as well as providing physical integrity to the filaments. During different textile processes, fibers and yarns are frequently subjected to high temperatures of ovens or contact surfaces. The finishes applied to the fibers must have enough thermal stability to withstand the severe thermal stressing. In high temperature conditions, the finish often undergoes evaporation, oxidation and chemical decomposi-

tion generating undesirable degradation products. The presence of these undesirable byproducts in gas, liquid or solid form interferes with continuous and efficient fiber processing and could lead to frequent equipment shutdown.

Depending on the end use of the fibers, fiber finishes consist of different components. Lubricants, antioxidants, antistatic agents and emulsifiers are major components of fiber finishes [1–5]. Although lubricants are the major components of finishes, a systematic study of the thermal stability of fiber finishes requires studying the thermal stability of each component separately and in the presence of other components. In our previous work [6–9], an experimental system was developed to thermally stress finishes at different temperatures and degraded liquid samples were collected during heating for chemical and physical analysis.

¹ Corresponding author: email: peter_hauser@ncsu.edu

The thermal degradation of two lubricants based on pentaerythritol tetrapelargonate was evaluated. Gel permeation chromatography was used to measure degradation by quantifying the amount of high molecular weight (HMW) products formed in the liquid phase. It has been shown that this method is fast and accurate to identify the presence, amount and the molecular weight distribution of the HMW products. In addition, high temperature degradation of the aforementioned synthetic polyol ester lubricant in the presence of different antioxidants has been reported. Results have shown that antioxidants have a positive effect in delaying the thermal degradation of pentaerythritol tetrapelargonate. Antioxidant phenyl- α -naphthylamine (PAN) has shown a significant improvement in thermal stability of the lubricants in comparison with the conventional antioxidants used in fiber finish industry.

A scientific approach to evaluate the thermal degradation of fiber finish components could not be found in the literature; the present work is an effort to investigate the thermal stability of different components of fiber finishes with a polyol ester as the base lubricant. In this paper, the thermal stability of two emulsifiers and an antistatic agent has been investigated. Mixtures of these base components have been prepared to formulate different fiber finishes according to the procedure used in industry. Thermal stabilities of the prepared fiber finishes have been investigated and compared with the thermal stabilities of two ready-to-use formulated finishes supplied by a finish manufacturer.

Experimental

Materials

Two commercial base stock polyol ester lubricants, identified here as AF and ST, provided by two different suppliers with the same base component were utilized in this research. Pentaerythritol tetrapelargonate was reported to be the base component of both lubricants with a purity of more than 98.5 and 95% for ST and AF, respectively. They were used as received from Dupont, a major consumer of these products.

Two different antioxidants were selected for experimental purposes. One of these antioxidants is a hindered phenolic-based (Hind) antioxidant, typically used for fiber finishes supplied by Goulston Technologies Inc. The other antioxidant, usually added to engine oils, is *N*-phenyl-1-naphthylamine or phenyl- α -naphthylamine (PAN) 98%, purchased from Acros Organics.

Poly(oxyethylene) (POE) (40) sorbitol hexaoleate or Sorb (Figure 1) and POE (25) hydrogenated castor oil or HCO (Figure 2) supplied by Goulston Technologies were used as high temperature emulsifiers. The exact chemical structures of these emulsifiers are trade secrets. The antistatic agent used in the current study is based on quaternary amines sup-

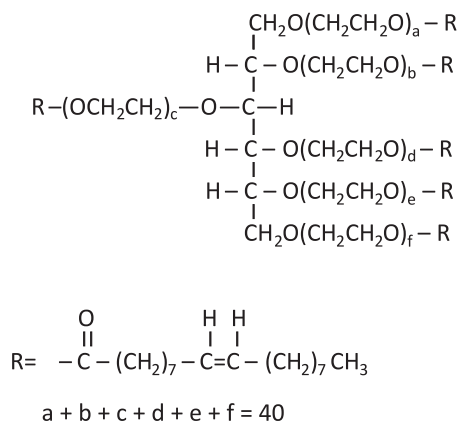


Figure 1 Chemical structure of POE (40) Poly (oxyethylene) Sorbitol Hexaoleate.

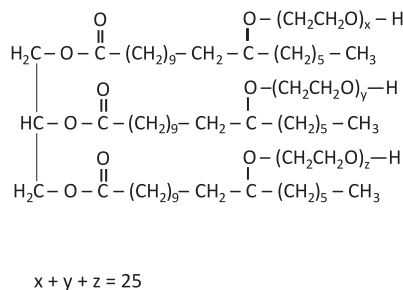


Figure 2 Chemical structure of POE (25) hydrogenated castor oil (HCO).

plied by Goulston Technologies, Inc. and is called Quat. The chemical structure of this material is also a trade secret.

Two fully formulated, ready-to-use fiber finishes, supplied by Goulston Technologies, known as TC4 and TCL, were used for the thermal stressing experiments. The exact chemical contents of these materials are trade secrets.

Fully formulated finishes were prepared using the major components mentioned above. In order to do so, the general percentage of lubricants and additive were used based on the supplier's recommendation: lubricant (original or inhibited) 60%, emulsifier 30%, and antistatic agent 10% by weight. For preparing inhibited lubricant samples, 1% antioxidant by weight was added to the original lubricant. Initial heating to 60°C was necessary to dissolve the antioxidants in the lubricants. Three different samples of finish consisting of lubricant AF, emulsifier Sorb and the antistatic agent Quat were prepared: (1) without antioxidant (AF+ Sorb+ Quat) and (2) with antioxidant Hind (AF+ Hind + Sorb+ Quat) or (3) with antioxidant PAN (AF+

PAN+ Sorb + Quat). Also, samples of finish with a different emulsifier (HCO), without antioxidant (AF+ HCO+ Quat), were made for thermal stress studies. In further studies, for evaluation of the role of lubricants, formulated samples of lubricant ST, emulsifier Sorb and antistatic agent Quat (ST+ Sorb +Quat) were prepared. Thermal stressing followed by gel permeation chromatography, acid value test and thermogravimetric analysis was performed on the original and degraded samples.

Stabilized HPLC grade tetrahydrofuran (THF) with 99.5% purity (containing 100–400 ppm butylated hydroxytoluene as a preservative) purchased from J.T. Baker, was used as the solvent and carrier for GPC. Zero-grade compressed air and prepurified nitrogen gas supplied by National Welders were used for experimental work.

Thermal Stress Experiments

Batches of emulsifiers (Sorb and HCO), antistatic agent (Quat) and the above-mentioned prepared formulated finishes were heated at 220°C in a 210 mL stainless steel heating chamber designed for the degradation studies. The heating chamber contained 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 aging times (2–8 hours for short term runs and 12–96 hours for long term experiments). 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 [6–9].

Analytical Measurements

Gel permeation chromatograms were obtained using 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 chromatography. THF was used as the sample solvent and the mobile phase. The columns and the detector temperatures were maintained at $35 \pm 0.8^\circ\text{C}$. The molecular weights were obtained by a calibration curve using seven polyethylene 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.

Acid value tests were performed on the samples by an alcoholic titration using ASTM test method D-4662-98 [10].

Thermogravimetric analysis (TGA) experiments utilized a Perkin-Elmer Pyris 1 Thermogravimetric Analyzer in two different environments: air or nitrogen with a flow of 20 mL/min. Five to 10 milligrams of sample was heated in a platinum pan to $260 \pm 1^\circ\text{C}$ with a gradient of $20^\circ\text{C}/\text{min}$. The samples were then maintained at 260°C isother-

mally for three hours. The remaining mass of the sample during the heating time was continuously obtained.

Results and discussion

Emulsifiers

Gel permeation chromatography was used to investigate the molecular weight distribution of the liquid emulsifier samples taken at different times from the heating chamber. In this paper, molecular weight will be used to describe molecular size in GPC for comparison, even though separation is affected by size and molecular weight.

The chromatogram of the original Sorb emulsifier (Figure 3) consists of three separate peaks: a rather sharp peak with a retention time of about 12.8 min (MW ~2326), a broad peak with a right shoulder showing a retention time of about 13.7 min (MW ~991), and a small peak with a retention time of about 15.7 min (MW ~343). Since in the production process of ethoxylated sorbitol esters the ethoxylation of sorbitol happens before esterification with fatty acid (in this case oleic acid), there is some unreacted fatty acid and ethoxylated sorbitol in the system. The small peak at the retention time of 15.7 min is attributed to oleic acid and according to peak area measurements; it contains 5.6% of the weight of Sorb emulsifier. The broad peak at 13.7 min is attributed to the ethoxylated but not fully esterified sorbitol molecules (with 0 to 6 esterified OH groups) containing 36.2% of the weight of Sorb emulsifier. The peak at 12.8 min is the ethoxylated hexaester sorbitol molecule, which contains 58.2% of Sorb emulsifier. Various chain lengths of ethylene oxide and the wide molecular weight of Sorb provide this emulsifier with good emulsifying properties and a hydrophilic-lipophilic balance (HLB) value of 10.4 [1]. Heating Sorb at 220°C in the heating chamber results in changes in the liquid phase that affect the peaks observed in the original sample. The fatty acid peak decreases and disappears as heating continues. This change is due to chemical degradation of oleic acid. Unsaturation of oleic acid makes its degradation progress faster due to radical generation and mostly gas phase oxidation products are formed. Peaks at retention times of 12.8 and 13.7 minutes also decrease in size as the heating continues, because of the dissociation of ester bonds in the ethoxylated hexaester, bond cleavage and thermal decomposition of the long chains. It is important to notice that the peak at a retention time of 12.8 min starts to grow a left shoulder even after 2 hours of heating of the emulsifier and this shoulder grows in peak area as heating continues. This phenomenon is due to the formation of high molecular weight products by a free radical chain mechanism, a process similar to what has been observed in the polyol ester lubricant [7, 11–14]. The high molecular weight (HMW) products form from condensation and polymerization of long chain radicals produced from thermal decomposition; the chemical reactions are indicated in earlier

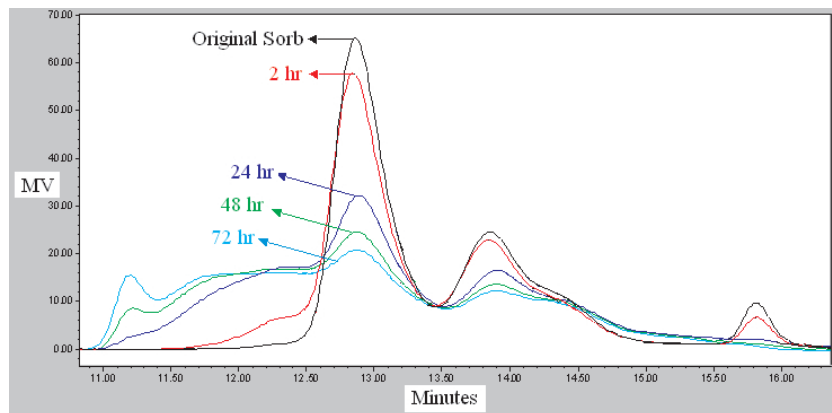


Figure 3 Stack of GPC chromatograms (RI detector) for original Sorb emulsifier and Sorb heated for 2, 24, 48 and 72 hours at 220°C in the heating chamber.

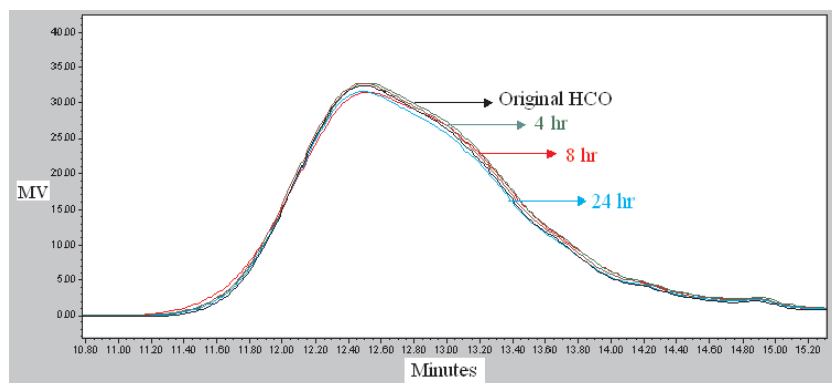


Figure 4 Stack of GPC chromatograms (RI detector) for original HCO emulsifier and HCO heated for 4, 8 and 24 hours at 220°C in the heating chamber.

papers [7, 11–15]. As degradation progresses, these HMW products increase in molecular weight and can generate solid deposits. It can be concluded that not only are lubricants responsible for solid deposition of finishes, but also emulsifiers can generate these products.

The chromatograms of hydrogenated castor oil indicate that this emulsifier has one broad peak with a maximum at a retention time of 12.6 min (Figure 4). The reason for the broadness of the peak is due to the existence of molecules of HCO with different degrees of ethoxylation on the branches and also molecules that have not been fully ethoxylated and have hydroxyl groups on the branches. Hydrogenation of castor oil saturates the double bonds on branches of castor oil and this step significantly reduces formation of varnishes [1]. Heating this emulsifier in the heating chamber at 220°C results in the reduction of the peak area of HCO. No other peaks are appearing or growing in the chromatograms of the heated sample. This is an indication of decomposition of HCO without formation of high molecular weight products. So the probability of forming high molecular weight deposits as a result of thermal degradation is almost zero. Instead, HCO molecules decompose or oxidize to products that leave the liquid phase to gas phase. These gaseous products most

probably include polyethylene oxide branch separating HCO molecules, leaving a carbonyl group on the seventh carbon of branches. These carbonyl groups can cause further degradation of the molecules by providing sites for radical formation.

Acid value tests on the original Sorb and heated Sorb samples show a distinct decrease in free acid content of this emulsifier as the heating continues (Figure 5). This shows

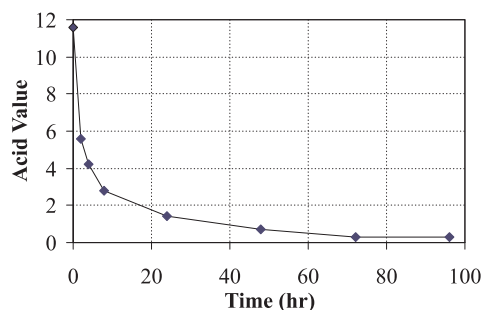


Figure 5 Acid value of Sorb emulsifier versus heating time for sample heated at 220°C in the heating chamber.

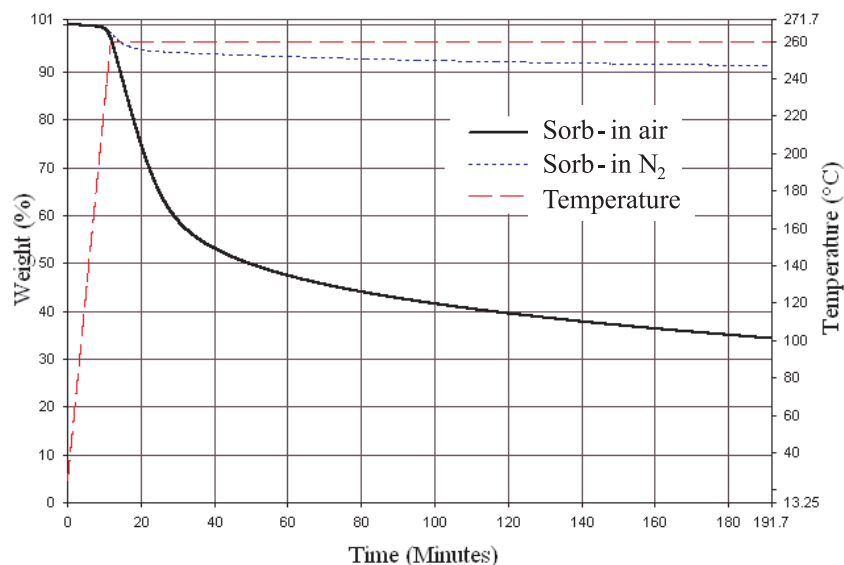


Figure 6 Weight percent mass of Sorb emulsifier samples versus heating time while they are heated at 260°C in TGA in both air and nitrogen environment.

that as Sorb undergoes degradation, chains containing acid groups in the original sample decompose and form smaller acid molecules like HCOOH and CH₃COOH that easily evaporate and exit the system. As a result, the concentration of acid groups in the liquid phase decreases significantly.

TGA was performed in air and nitrogen environments in order to evaluate the effect of the presence of oxygen in the system on the degradation behavior of the Sorb emulsifier sample. The weight loss during the experiments was recorded online and the graphs of percentage of residual mass in the TGA pan versus heating time at 260°C are presented in Figure 6. Weight loss in a nitrogen environment is attributed to evaporation and decomposition, whereas the mass loss in the air environment is due to a combination of evaporation, decomposition, and oxidation. The difference of weight loss in air and nitrogen indicates the amount of oxidized gas phase products produced. TGA in nitrogen indicates that Sorb loses 6–7% of its weight due to evaporation until it reaches 260°C and does not change in weight due to evaporation after that. However, TGA in an air environment shows a large weight loss during heating. This means that Sorb emulsifier loses most of its weight (about 57% after 3 hours of heating at 260°C) due to oxidation and production of gas phase oxidation products. This also explains that the reduction of peak areas of Sorb in GPC chromatograms is related to degradation of the original emulsifier and forming oxidation products that leave the liquid phase.

TGA results for the HCO emulsifier show that this emulsifier loses weight due to both oxidation and evaporation almost equally (Figure 7). Total weight loss in the air environment is less than the Sorb emulsifier and also oxidation in the gas phase for HCO is less than Sorb. In other words, the difference between weight loss in air and nitro-

gen for the HCO sample is less than with Sorb. The weight loss observed in TGA is responsible for the reduction of peak area of HCO in the GPC chromatograms.

Comparison of the analytical results obtained for the two emulsifiers Sorb and HCO shows that these two emulsifiers act completely differently in a high temperature environment. This makes it difficult to come to the conclusion about which emulsifier is a better choice, in terms of thermal degradation behavior, for fiber finishes. But in general, we can say that ethoxylated hydrogenated castor oil can be a good high temperature emulsifier since it does not form high molecular weight products and as a result, solid deposits. Also it forms less gas phase oxidation products in comparison with ethoxylated sorbitol hexaoleate. It is important to take into consideration that there is a high possibility that these emulsifiers act differently in the presence of lubricants and other additives due to synergistic effects.

Antistatic agent

The Quat sample was heated in the heating chamber at 220°C. Part of this antistatic agent evaporated while reaching the desired temperature and after 5 min of heating isothermally at 220°C, the liquid antistatic turned into a very viscous paste. Heating the sample could not be continued for more than 8 hours since the sample nearly turned into a solid (very viscous paste) that could not exit the tap designed for sample taking. This physical observation suggests that this antistatic agent could be one of the major contributors to the formation of solid deposits in the formulated finish.

Gel permeation chromatography was performed on the samples taken during heating of Quat for 8 hours (Figure 8).

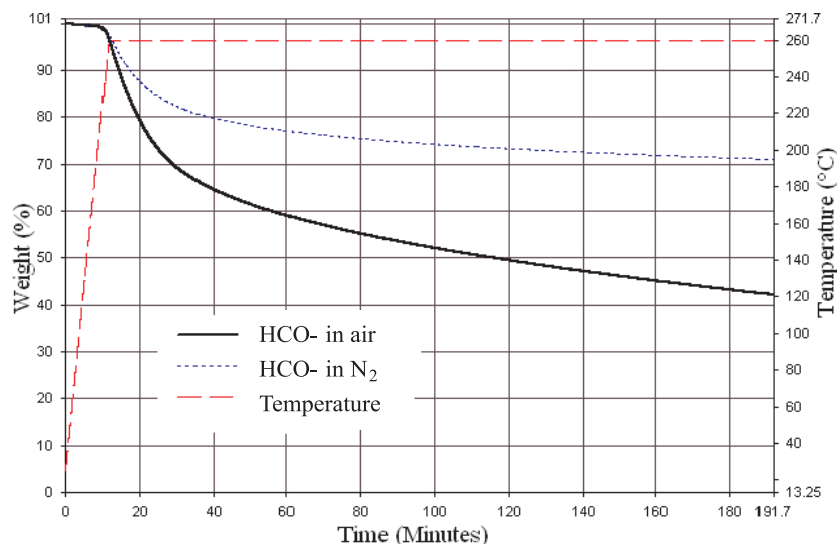


Figure 7 Weight percent mass of HCO emulsifier samples versus heating time while they are heated at 260°C in TGA in both air and nitrogen environments.

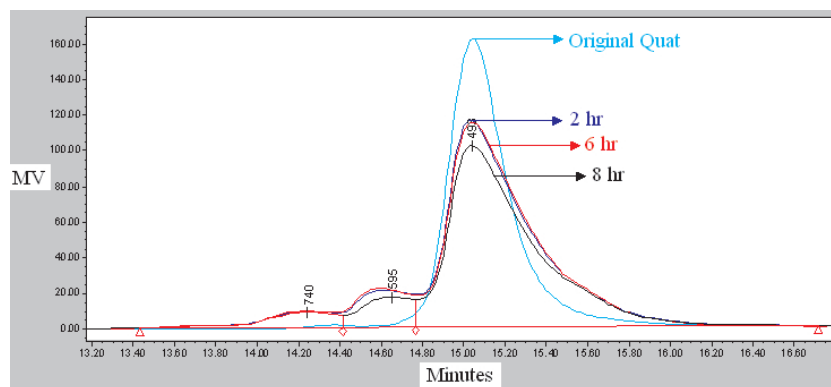


Figure 8 Stack of GPC chromatograms (RI detector) for original Quat antistatic agent and Quat heated for 2, 6 and 8 hours at 220°C in the heating chamber.

The chromatogram of the original Quat sample shows a distinct peak at a retention time of 15.1 min (MW ~469). Heating the samples for even 5 min at 220°C, results in the formation of two left shoulders (high molecular weight products). These shoulders tend to increase in area as heating continues. The change observed in the peak area of the main peak suggests that either Quat degrades quickly and produces HMW products and other products with a similar molecular weight. The growth of the HMW peaks can be related to condensation and polymerization of the alkyl chain attached to the nitrogen atom in the quaternary amine.

Thermo-gravimetric analysis of Quat shows that this antistatic agent loses weight at high temperature mostly due to evaporation and not oxidation (Figure 9). Most of the weight loss happens while heating the antistatic agent to 220°C and after that the rate of weight loss is very low since Quat becomes a solid.

Formulated finishes

Gel permeation chromatography was performed on the unheated formulated finishes and heated samples taken from the heating chamber during heating. The chromatograms of AF + Sorb + Quat (Figure 10) show four peaks as expected. Peaks at 12.8 and 13.7 minutes are related to the Sorb emulsifier, their total peak area is 30.3%, which corresponds to the concentration of Sorb in the mixture. The peak at 14.5 min is attributed to the AF lubricant, with an area of 61% for the concentration of lubricant in the formulated finish. The peak with a maximum at 15.8 min is mostly due to the Quat antistatic. However, this peak is broader than the Quat peak. This is due to overlap of Quat peak with the third Sorb peak existing at 15.7 min retention time. The peak area is 9% showing the concentration of Quat in the formulated finish.

The chromatograms of heated samples of AF + Sorb + Quat show decreases in peak area and height of the first

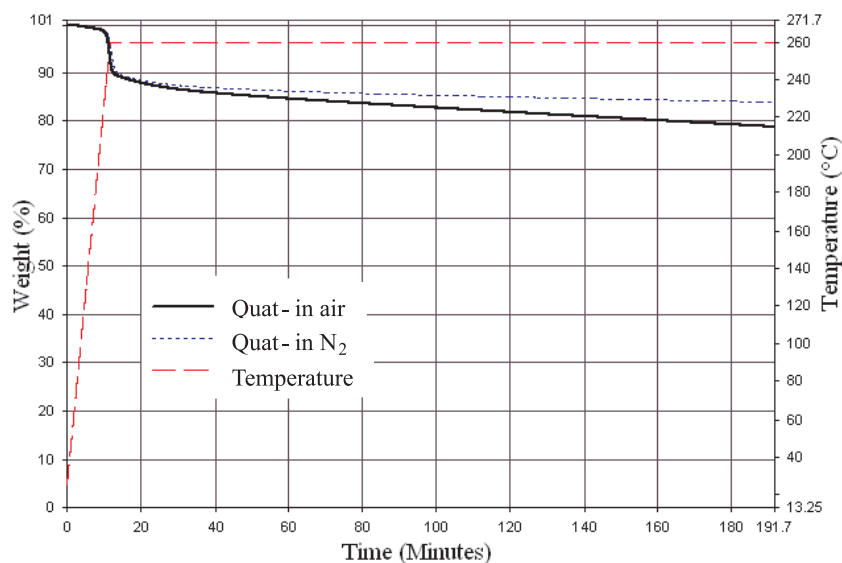


Figure 9 Weight percent mass of Quat antistatic agent samples versus heating time as they are heated at 260°C in TGA in both air and nitrogen environment.

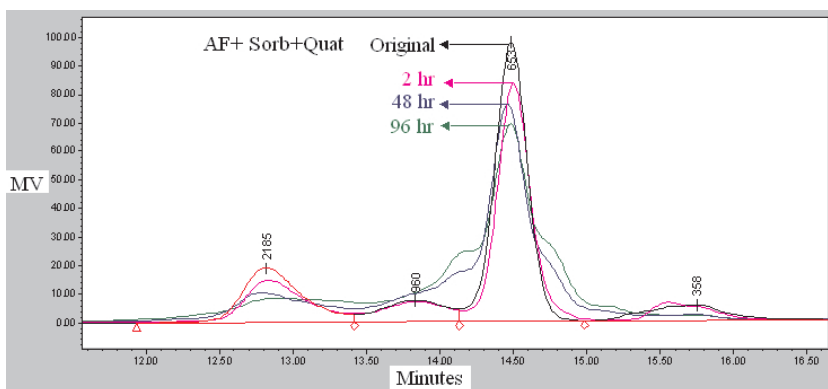


Figure 10 Stack of GPC chromatograms (RI detector) for unheated formulated finish AF + Sorb + Quat and samples heated for 2, 48 and 96 hours at 220°C in the heating chamber.

and third emulsifier (Sorb) peaks, the AF lubricant peak and the antistatic (Quat) peak. This is an indication of the original materials, undergoing degradation reactions and changes in chemical structure. It is important to note that as degradation progresses the lubricant peak grows a left shoulder that increases in area so that it totally overlaps or covers the second Sorb peak at 13.7 min retention time. This phenomenon has been observed in lubricant degradation before and is due to formation of high molecular weight products of oxidation of the lubricant. These products polymerize further so that in the samples heated for 72 and 96 hours, they cover the right side of the first Sorb peak. Comparison of these chromatograms with original AF degraded chromatograms indicates very interesting results: samples of AF that have been heated for the same time and at the same temperature as AF + Sorb + Quat show a broader and higher range of HMW products than the formulated finish samples. Not only do the HMW prod-

ucts of original AF have higher molecular weight, but also the amount of these products is greater than the HMWs in the formulated finish sample. It is hard to quantify the amount of HMW products in the heated formulated samples due to overlap with emulsifier peaks. Furthermore, the decrease in area of lubricant peak in the formulated sample is much lower than what has been observed in the original AF heated samples. Also, it has been observed that the emulsifier peak in the formulated finish sample does not show any growth of left shoulder like the ones observed in the original heated Sorb. This indicates that the degradation progress of lubricant and emulsifier in the mixed sample is slower than these components separately and this can be due to the positive synergistic effect of the mixture or the sacrificial degradation effect of antistatic in the mixture. The lubricant peak in the formulated sample also shows a growing right shoulder, which is an indication of low molecular weight (LMW) oxidation products. The

antistatic agent peak in the formulated sample also shows a reduction in size as degradation progresses, but the growth in the left shoulder that was observed in original Quat can not be distinguished from the growth of right shoulder of lubricant. From the chromatograms of degraded formulated finish, it is difficult to quantify the degradation of these materials as it has been measured for the degradation of starting materials, but useful information can be derived from them. Physical observations showed that the formulated sample has more solid deposition than the original lubricant and emulsifier alone. This, as mentioned earlier, is due to the degradation of Quat antistatic to solid products.

The chromatogram of inhibited formulated finishes before heating is similar to AF + Sorb + Quat, with additional small peaks related to the presence of antioxidant. In the case of AF + PAN + Sorb + Quat, the PAN peak appears at a retention time of 18 min (Figure not shown). This PAN peak decreases and disappears as the degradation progresses, which indicates that the antioxidant reacts with oxygen to prevent the degradation of finish. The chromatograms of degraded AF + PAN + Sorb + Quat show a similar change was observed in AF + Sorb + Quat. Chromatograms of the two above mentioned formulated samples heated for 24 hours are very similar, with AF + PAN + Sorb + Quat having an extra peak for antioxidants. However, 72- and 96-hour degraded samples show that in AF + Sorb + Quat, the emulsifier peak is still present whereas in AF + PAN + Sorb + Quat the emulsifier peak has been shifted toward a lower molecular weight. This shows that the products of emulsifier degradation are lower in molecular weight in the presence of PAN antioxidant than in its absence. The peak shape of HMW products of lubricant in both systems confirms this conclusion. The chromatogram of AF + Hind + Sorb + Quat before heating is similar to AF + Sorb + Quat. The same changes have been observed in peak areas as the formulated sample degrades. Comparison of the chromatogram of AF + Hind + Sorb + Quat that has been heated for 72 hours with those of AF + Sorb + Quat and AF + PAN + Sorb +

Quat indicates that the presence of Hind in the mixture works the same way as PAN in the reduction of molecular weight of HMW products at the left part of the chromatogram (12.8 min retention time). The peak area of degraded products at 13.5 min increases slightly, which shows formation of more degraded products of this molecular weight. Instead, the area of the left shoulder of lubricant peak shows a decrease. This indicates that in the presence of Hind, degradation products have slightly higher molecular weight than in the presence of PAN. The right shoulder of the lubricant peak also shows an increase in area, which is an indication of formation of more LMW products in the liquid phase. These comparisons suggest that, in contrast with what was observed in lubricant systems, in the mixture of formulated finish the presence of antioxidants does not have a major effect on degradation of samples in the liquid phase. The minor changes observed in the chromatograms of samples containing antioxidants suggest that PAN provides a slightly better protection against formation of oxidation products.

Gel permeation chromatography was performed on the unheated and heated samples of AF + HCO + Quat as well (Figure 11). The chromatogram of unheated sample shows three peaks: a broad area stretching from 11.5 min to 14.2 min retention time related to the emulsifier HCO; a distinct peak at 14.5 min attributed to AF and a small peak with a maximum at retention time 15.5 min due to the antistatic Quat. As it was observed with other mixtures mentioned above, the antistatic peak and lubricant peak decrease in peak area as degradation proceeds due to degradation and chemical reactions that form oxidation products with different molecular weights. Also, the lubricant peak grows shoulders at both sides, which indicates the presence of HMW and LMW products of oxidation in heated samples. The emulsifier HCO peak shows a different behavior in comparison with emulsifier Sorb in the progress of degradation. It reduces in area to some extent but there is no trace of formation of high molecular weight products at the left side of this peak. It might form some low molecular weight products. The area of the peak at 13.5 min increases

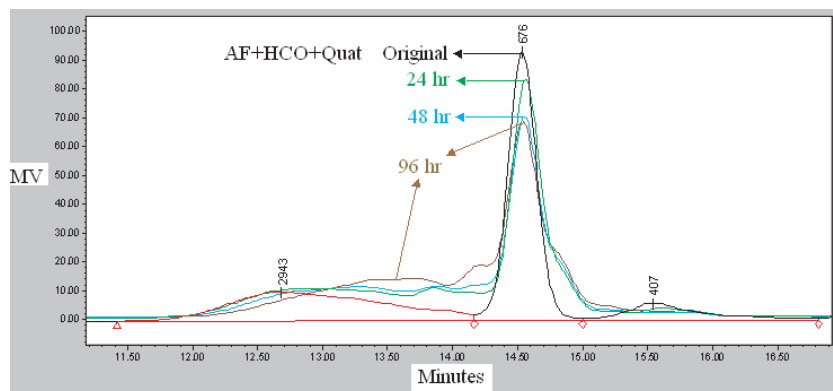
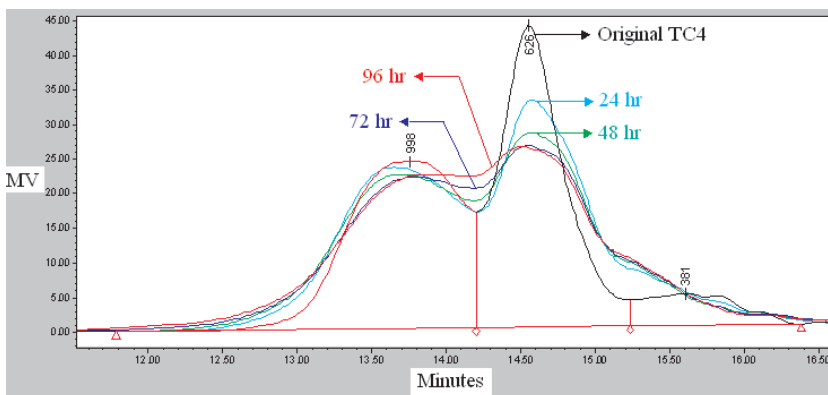


Figure 11 Stack of GPC chromatograms (RI detector) for unheated formulated finish AF + HCO + Quat and samples heated for 24, 48 and 96 hours at 220°C in the heating chamber.

Figure 12 Stack of GPC chromatograms (RI detector) for unheated formulated finish TC4 and TC4 samples heated for 24, 48, 72 and 96 hours at 220°C in the heating chamber.



because of LMW products of HCO together with HMW products of lubricant. Qualitative comparison of the chromatogram of AF + HCO + Quat with AF + Sorb + Quat does not give any suggestion about the more stable system, since the degradation of molecular weight of the emulsifiers in these two systems is different.

The GPC chromatograms of ST + Sorb + Quat before and during heating are also very similar to those of AF + Sorb + Quat since AF and ST have the same base component (figure not shown). Reduction in lubricant, emulsifier and antistatic peaks is obvious from chromatograms with an increase in the area of HMW and LMW products as degradation proceeds. In comparison with AF + Sorb + Quat, after 96 hours of heating, ST + Sorb + Quat shows fewer degradation products at 12.7 min. Also the left and right shoulders of the lubricant peak are smaller in size (14.1 min and 14.8 min respectively). This suggests that replacing AF with ST decreases the amount of oxidation products and as a result oxidation in the liquid phase. This is in agreement with previous results indicating that ST has more thermal stability in the liquid phase than AF in the presence of air [7].

GPC chromatograms of the formulated finish TC4 are shown in Figure 12. The chromatogram of unheated TC4 sample shows two partially overlapped major peaks with retention times of 13.7 and 14.5 min, respectively. Another small peak at 15.6 min with right shoulders appears in the chromatogram. After consulting with the supplier of this product, some information on the chemical contents of TC4 was provided: TC4 includes 40% high molecular weight esters mostly pentaerythritol esters, 52% non-ionic surfactant and 7% Quat. According to this information chromatogram peaks were identified. The peak at 13.7 min is related to the non-ionic surfactant, which acts both as emulsifier and lubricant. The peak at 14.5 min is attributed to HMW esters including pentaerythritol acting as a lubricant in the mixture. This peak also matches the lubricant peak corresponding to pentaerythritol tetrapelargonate in our studies. The peak with a retention time of 15.5 min is

mostly due to Quat as an antistatic in the mixture. Right shoulders of this peak could be related to other contents of the mixture or emulsifier, as it has been observed in Sorb. Chromatograms of the heated samples of TC4 show that as this sample degrades, the lubricant peak decreases in height and peak area. It forms HMW products, which fill the gap between the emulsifier peak and lubricant peak at the left side of lubricant peak. Also a right shoulder, which is attributed to LMW degradation products of lubricant, starts to appear as degradation progresses. The emulsifier peak also decreases in size to some extent. This peak broadens toward the left side, which is an indication of the formation of a small amount of HMW products. Also as degradation proceeds, these peaks move to the right side. This means that the degradation products of the emulsifier mix with HMW products of lubricant to fill the gap between the two peaks. The antistatic agent peak also decreases in size as degradation progresses. After a certain amount of heating these peaks almost disappear due to a decrease in size and the formation of other products. These newly formed products have even higher molecular weights and form part of the broad right shoulder of the lubricant peak.

A GPC chromatogram of the TCL finish was also obtained (Figure 13). According to the supplier of this formulated finish, the contents of TCL are as follows: 40% esters (20% pentaerythritol high molecular weight ester, 20% esters with lower molecular weights), 39% non-ionic surfactants, and the rest of the mixture includes two antistats: phosphate and sulfonate based and two antioxidants: Hind (0.5%) and Bis (4.5%). The chromatogram of TCL shows a distinct peak at 14.5 min related to lubricants including pentaerythritol esters. At the left side of lubricant peak, there is a broad shoulder (from 12.5 min to 14.2 min), which is related to non-ionic surfactant acting as an emulsifier and lubricant. The small peak at 15.6 min is again due to an antistatic agent. As degradation proceeds, the main lubricant peak at 14.5 min decreases significantly in size. Also its left shoulder, the emulsifiers' area, decreases in height. This emulsifier tends to broaden towards a higher molecular

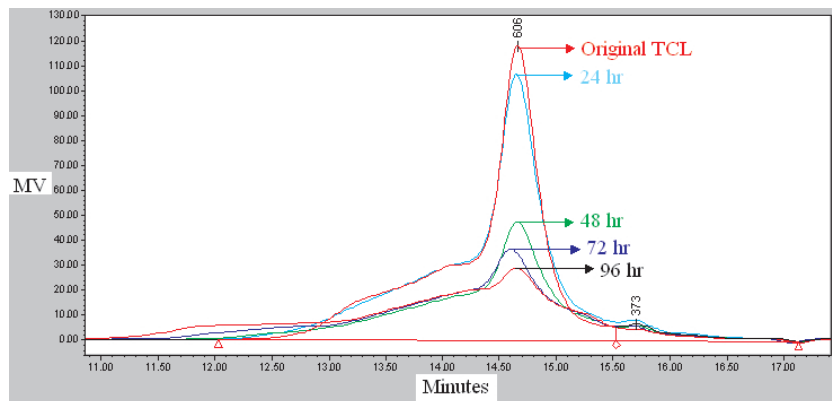


Figure 13 Stack of GPC chromatograms (RI detector) for unheated formulated finish TCL and TCL samples heated for 24, 48, 72 and 96 hours at 220°C in the heating chamber.

weight as degradation proceeds. This area of HMW grows towards 11.0 min for highly degraded samples. This is an indication of the formation of HMW products due to degradation (consumption) of both lubricants and emulsifiers. Furthermore, a small shoulder forms at the right side of the lubricant peak due to the formation of LMW products. The antistatic peak also decreases in size as heating proceeds probably due to evaporation or oxidation to gas phase products.

Acid value tests on the original formulated finishes (TCL and TC4) and their heated samples show a value of 3.51 for both. This value increases to 4.21 after 4 hours of heating at 220°C and after 24 hours, it increases to 5.61 and does not change after that. This is because the lubricant in the mixture increases in acid value as the degradation proceeds whereas other contents like emulsifier (as it was observed earlier with Sorb) decrease in acid content. These two effects neutralize each other in the mixture and

give an almost stable acid value for the mixture as it is heated. As a result, acid value can not be used as an identification of the progress of degradation in the formulated or mixed samples. This phenomenon was also observed with AF + Sorb + Quat and other mixed samples.

TGA was performed in air and nitrogen environments to evaluate the effect of oxygen on the degradation behavior of the mixed samples and formulated finishes. Weight loss during the experiments was recorded online and graphs of percentage of residual mass in the TGA pan versus heating time at 260°C were obtained. The difference in weight loss of formulated finish AF + Sorb + Quat between air and nitrogen environments is about 20% after 3 hours of heating at 260°C. This indicates that almost 36% of the total weight loss in air is due to oxidation and the rest of it is related to evaporation and thermal decomposition (Figures 14 and 15). Total weight loss of inhibited formulated finishes is less than uninhibited finish in the air environ-

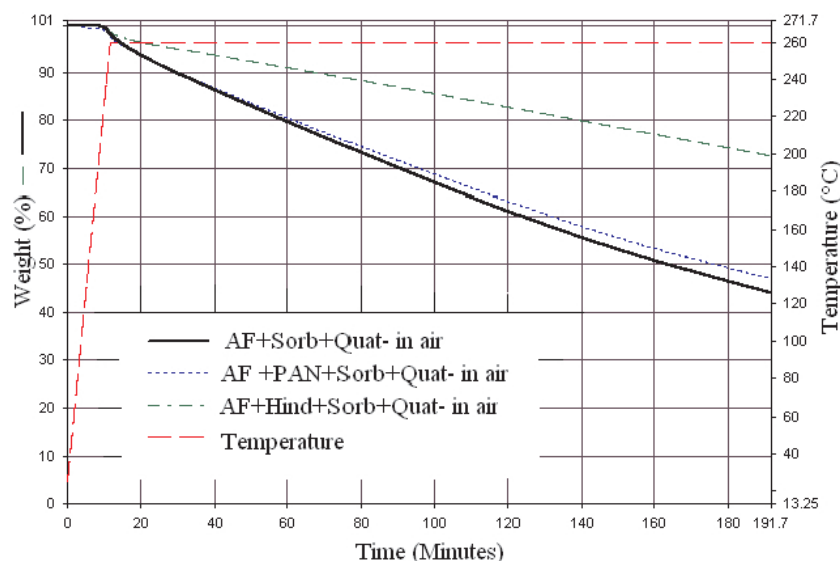


Figure 14 Weight percent mass of AF + Sorb + Quat, AF + PAN + Sorb + Quat and AF + Hind + Sorb + Quat formulated finish samples versus heating time as they are heated at 260°C in TGA in an air environment.

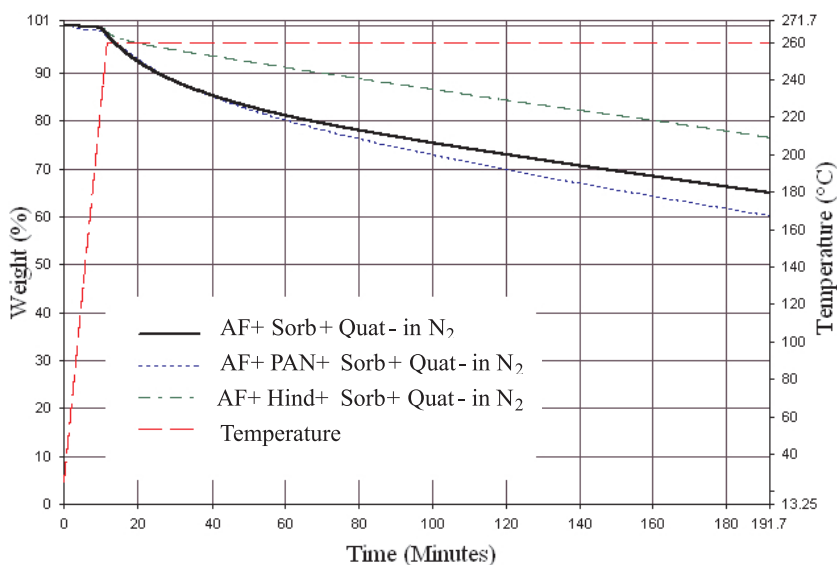


Figure 15 Weight percent mass of AF + Sorb + Quat, AF + PAN + Sorb + Quat and AF + Hind + Sorb + Quat formulated finish samples versus heating time as they are heated at 260°C in TGA in a nitrogen environment.

ment. This has also been observed in the systems without the presence of emulsifiers and antistatics [7–8]. The formulated finish AF + Hind + Sorb + Quat shows lower weight loss in both environments compared to its uninhibited form, AF + Sorb + Quat. This indicates that the presence of Hind in the mixture reduces the amount of oxidation, evaporation and thermal decomposition of the mixture. The difference of weight loss of this finish (AF + Hind + Sorb + Quat) between air and nitrogen environments is very small (about 5% after 3 hours of heating at 260°C), which indicates that Hind reduces the amount of oxidation as well as evaporation in the gas phase. So in this sample, almost 84% of total weight loss in air after 3 hours is due to evaporation rather than oxidation. The formulated finish AF + PAN + Sorb + Quat shows more evaporation than the uninhibited form (AF + Sorb + Quat) due to greater weight loss in nitrogen environment. However, the difference between its weight loss in air and in nitrogen shows that the presence of PAN in the system reduces oxidative weight loss (from 20% of weight to 12% after 3 hours of heating at 260°C). So, in this sample 24% of total weight loss in air is due to oxidation (in comparison with 36% in AF + Sorb + Quat). This result shows that Hind reduces degradation in the gas phase more than PAN. This is in agreement with the results obtained on the effect of different antioxidants on thermal degradation of lubricant systems [8].

TGA experiments were performed on AF + HCO + Quat in both air and nitrogen environments as well (figure not shown). Comparison of the TGA plot of this formulated finish with that of AF + Sorb + Quat indicates that the change of emulsifier from Sorb to HCO reduces the weight loss of the mixed sample in both air and nitrogen

environments (about 11% of weight after 3 hours of heating at 260°C in both environments). The difference between the weight losses of mixed samples in the two environments, which indicates weight loss due to oxidation, does not change by changing the emulsifier (about 21% of total weight). As a result, TGA studies indicate that using HCO in a mixture of formulated finish reduces the evaporation and thermal decomposition of the finish, but the amount of gas oxidation products will not change. This result was expected due to lower evaporation of HCO compared to Sorb in the individual studies mentioned earlier.

The effect of change in lubricant from AF to ST in the formulated finish was also studied by TGA. A previous study [7] has shown that the lubricant ST demonstrates more weight loss in the air environment compared to AF and more of its weight loss was due to oxidation rather than evaporation. The formulated finish ST + Sorb + Quat shows almost the same weight loss in air as AF + Sorb + Quat. However, in a nitrogen environment, ST + Sorb + Quat shows greater weight loss (about 8% of weight after 3 hours of heating at 260°C). The difference between weight loss in air and in nitrogen is greater with ST + Sorb + Quat (almost 27% of weight after 3 hours of heating at 260°C). This means that this finish goes through oxidation in the gas phase more than AF + Sorb + Quat. This result is in agreement with weight loss in lubricant systems without additives.

Weight losses of TC4 and TCL samples in TGA air environment are greater than observed with the above mentioned formulated samples (Figures 16 and 17). TC4 shows a lower weight loss in both environments than TCL. However, in TC4, 38% of the total weight of sample was lost, after 3 hours of heating at 260°C, due to oxidation.

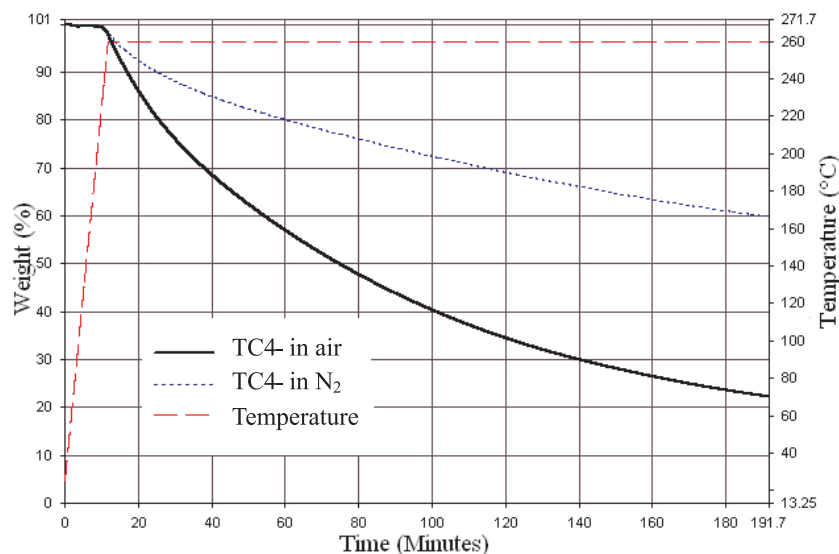


Figure 16 Weight percent mass of TC4 formulated finish samples versus heating time as they are heated at 260°C in TGA in both air and nitrogen environments.

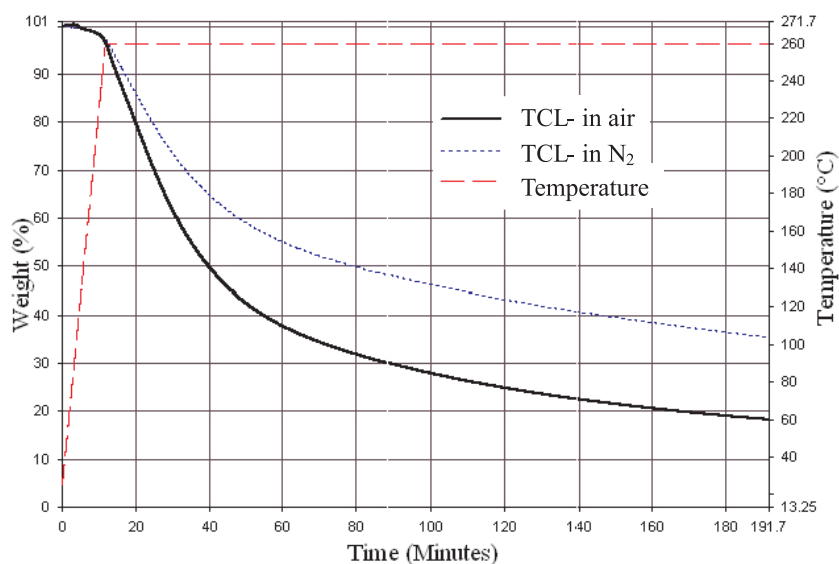


Figure 17 Weight percent mass of TCL formulated finish samples versus heating time while they are heated at 260°C in TGA in both air and nitrogen environments.

This is almost 48% of the weight loss of TC4. With TCL, 17% of the total weight was lost after 3 hours due to oxidation to the gas phase, which is only 22% of the total weight loss. In other words, although TC4 shows lower weight loss in the gas phase, most of it is due to oxidation to gas phase oxidation products. It is important to notice that according to the supplier of these products, TC4 produces more deposits in the solid phase than TCL. Therefore, it can be concluded that the lower weight loss of TC4 is due to oxidation to solid phase oxidized products and it is not an indication of greater stability.

Conclusions

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 industry. GPC has been used as a qualitative tool to study the changes in the molecular weight distributions of the degraded samples. TGA 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 the 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 a good insight into the formation of HMW and LMW products in the liquid phase, it was difficult to 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. This work is an initial effort to evaluate the oxidative degradation of formulated finishes. Further studies are needed in order to measure and quantify the extent of degradation in formulated finishes.

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