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Measuring Thermal Degradation of a Polyol Ester Lubricant in Liquid Phase

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Thermal degradation of two polyol ester lubricants with the same base chemical structures from two different manufacturers at high temperature (i.e., 220 °C) has been studied. Gel permeation chromatography was used to identify the high molecular weight products formed during thermal stressing of these lubricants. The amount of high molecular weight products generated at different stages of the degradation (e.g., dimers, oligomers) was quantified. Several other techniques were utilized as a combined analytical approach to provide comprehensive measurement of lubricant degradation in the liquid phase. The mechanism of degradation and the formation of oxidation products have been presented. A significant difference in the extent of degradation of the two lubricants was observed using different analytical techniques.

1. Introduction

Lubricant degradation and oxidation have been a subject of study for different industries in the past several decades.[1−3] Several researchers have observed that, when lubricants are used at elevated temperatures (e.g., above 200 °C) in the presence of oxygen, they undergo a series of free radical chain reactions that generate unwanted gas phase and solid phase byproducts.[1,2] The gas phase products and vapors, usually in the form of smoke, not only are hazardous to the environment, but also can condense on the equipment where they are being used and undergo further degradation. At the same time, solid phase deposits interfere with heat transfer and lubrication, resulting in significant reductions in lubricant performance. Depending on the industrial application of the lubricant, this can lead to ongoing equipment shutdown for cleaning.

Palekar et al.[1] have proposed a mechanistic model for lubricant degradation. They suggested that at elevated temperatures a lubricant can be depleted in three ways: evaporation, oxidation to primary oxidation products, and thermal decomposition. According to this model, the majority of the primary oxidation products go through condensation and polymerization and are responsible for the increased viscosity of the degraded lubricant. This often results in the formation of high molecular weight products. Further heating leads to generation of gel and solid degradation products in the form of deposits due to continued polymerization.[2]

Several analytical techniques have been used in these studies to compare the extent of degradation between different thermally stressed lubricants. The Penn State microoxidation test (PSMO)[1,4] and pressurized differential scanning calorimetry (PDSC)[5,6] have been used to evaluate both physical and chemical degradation of lubricants. Although these tests provide valuable information to compare lubricant stability, they do not provide details about the quantity and chemical nature of degradation products, especially in the liquid phase.

It has been shown that gel permeation chromatography (GPC) can be a valuable technique to analyze the oxidation and degradation products of different types of esters.[7−9] Ali et al.[7] used GPC to study the liquid phase−high temperature oxidation products of three esters, namely, tridecyl pelargonate (TDP), di-2-ethylhexyl sebacate (DEHS), and trimethylol propane triheptanoate (TMPTH). In their analysis of GPC chromatograms, four molecular weight fractions were found in a typical refractive index detector chromatogram of the degraded lubricant. The four molecular weight fractions include (1) products with lower molecular weight than the original lubricant, (2) the remaining unreacted lubricant and any oxidation products with the same molecular weight as the unreacted lubricant, (3) products of intermediate molecular weight, and (4) higher molecular weight products.

In the present research, the GPC technique has been used to identify the high molecular weight products formed during thermal stressing of two polyol ester lubricants. In addition, a detailed evaluation of the chromatograms was used as a tool to quantify the amount of high molecular weight products generated at different stages of the degradation. Evaluating GPC chromatograms using the method explained in this study not only is fast and repeatable, but also gives critical information about the quantity and molecular weights of high molecular weight (HMW) products in one easy step, without a need for preparative GPC. Several other independent techniques were also utilized to quantify lubricant degradation including (1) acid value test, (2) thermogravimetric analysis (TGA), (3) Fourier transform infrared (FTIR) spectroscopy, and (4) UV−visible spectroscopy. This combined analytical ap-

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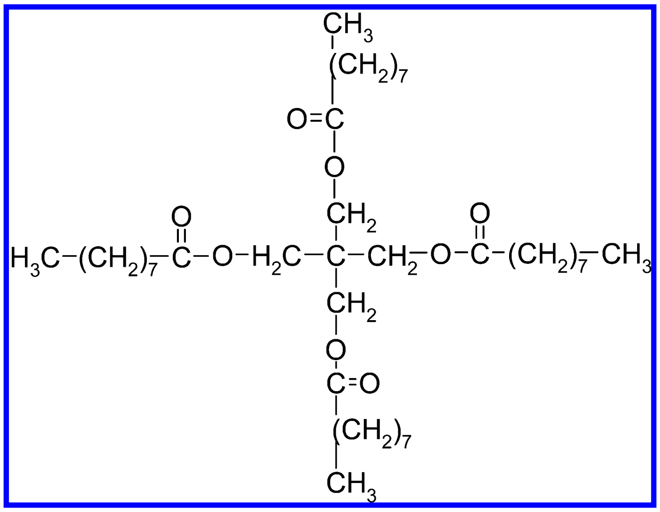


Figure 1. Chemical structure of pentaerythritol tetrapelargonate.

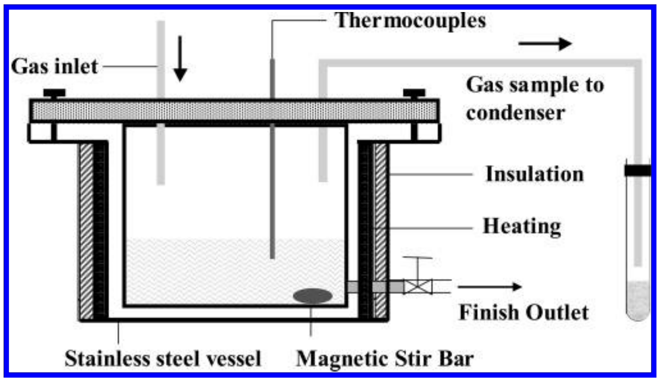


Figure 2. Heating chamber for generating thermally degraded lubricants.

proach will provide a comprehensive measurement of lubricant degradation in the liquid phase.

2. Experimental Section

2.1. 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 (Figure 1) 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. Stabilized HPLC grade tetrahydrofuran (THF) with 99.5% purity (containing 100−400 ppm butylated hydrooxytoluene 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.

2.2. Thermal Stress Experiments. A custom-built thermal experimental system was developed for the thermal stressing of the lubricant (Figure 2). The system included a 210 mL stainless steel heating chamber containing almost 140 mL of lubricant with a liquid phase outlet port, gas phase inlet and outlet ports, and thermocouple probes. The detailed description of the heating chamber and temperature controller can be found elsewhere.[10−14] A magnetic stirrer was used to maintain a uniform temperature in the heating chamber. A thermocouple was immersed in the lubricant to provide feedback to the temperature controller. A continuous flow of dry air (i.e., rate of 21.0 mL/min) entered the chamber through the gas inlet port during the thermal stressing to simulate real-world degradation in the presence of air. The air and the volatile components that exited the chamber through the outlet port were sent to a test tube and condensed at room temperature. The temperature used for thermal stressing of lubricant degradation was 220 °C. This temperature was selected since the polyol ester selected demonstrates rather good thermal stability up to 220 °C, where the C−C bonds start to break and lubricants show lower thermal stability and more degradation products. A few milliliters of liquid samples was taken from the liquid phase outlet after specific times of thermal stressing (2−8 h for short-term runs and 12−84 h for long-term experiments). Chemical and physical analyses were performed on the collected heated samples after reaching room temperature. The liquid condensates collected from the gas phase after cooling were analyzed by gas chromatography/mass spectrometry.

2.3. Analytical Measurements. Gel permeation chromatography (GPC) was performed using Waters Breeze HPLC and 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 solvent for the mobile phase and the columns and the detector temperature were maintained at 35 ± 0.8 °C. The molecular weights were obtained by a calibration curve using seven poly(ethylene glycol) standards. The concentration of the sample injected was 1 mg/mL, and the pump flow rate was set to 1 mL/min.

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 mg of lubricant was heated in a stainless steel pan to 260 ± 1 °C with a gradient of 20 °C/min. The samples were then maintained at 260 °C isothermally for 3 h. The remaining mass of the sample during the heating time was continuously obtained. TGA was performed at 260 °C; this higher temperature would allow for the lubricant to degrade in an accelerated condition, so that all the samples would volatilize in a reasonable time period.

Fourier transform infrared spectroscopy measurements were performed on a Nexus 470 FTIR spectrometer. Liquid samples were prepared by applying a thin uniform film of lubricants on a polished NaCl salt plate. The spectra were recorded over the wavelength range of 4000−750 cm^{-1} with a resolution of 4 cm^{-1} using 32 scans. Acid value tests were performed on the samples by an alcoholic titration using ASTM test method D-4662-98.[13]

The viscosities of original and thermally stressed samples were evaluated with a cone and plate type viscometer (Dynamic Stress Rheometer) at room temperature. The viscosity experiments were not performed on heated samples taken from the heating chamber due to the large amount of sample (about 18 mL) needed for each run. Instead, 50 g samples of lubricants were heated uncovered in separate glass beakers in a conventional oven at 200 ± 2 °C. After specified time periods, one sample beaker was removed from the oven and viscosity measurements were performed on the cooled samples. These sets of experiments have been performed in conditions different from those of the

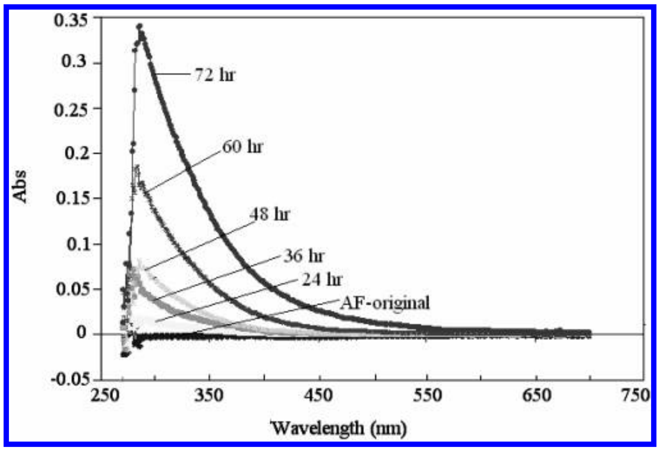


Figure 3. UV−vis spectrum obtained from samples of AF heated at 220 °C in the heating chamber.

others due to the amount of sample needed for this purpose. The reason for these sets of experiments was to observe the changes in viscosity and to compare the behavior of the different lubricants. The progress of degradation in these samples is different from that of the samples obtained from the heating chamber due to the experimental conditions, and the data obtained will solely be used for comparison between the two lubricants.

UV−vis spectroscopy was performed on AF samples using a Cary 3E spectrophotometer. Lubricant samples were diluted to 0.5 mg/mL in hexane (UV cutoff 190 nm). Hexane was used as the solvent since it had a lower UV cutoff in comparison with other solvents.

Gas chromatography/mass spectrometry (GC/MS) was done on the liquid condensed samples collected after specific periods of time at room temperature during thermal stressing of AF lubricant at 220 °C. Samples were dissolved in THF before injection into the gas chromatograph. For GC/MS experiments a capillary 30-m HP DB-XLB 0.25-m-inside-diameter equipment with 0.25-μm film thickness column was used.

3. Results and Discussion

3.1. Color. Color is the most obvious physical change observed in the heated samples of AF and ST over the duration of the thermal experiments. As these lubricants degrade in the presence of oxygen, double bonds, which are mostly related to carbonyl groups, start to form in their structures. This structural change explains the color change since the newly formed double bonds absorb visible light energy and produce color. As the degradation proceeds and more degradation products form in the liquid phase, the color of the lubricants becomes more pronounced. Eventually, the original colorless, clear pourable lubricant will change to a very dark viscous paste. To study this response, UV−vis spectroscopy was used to measure the change in color as an indicator for the amount of degradation. The spectra obtained from samples of AF heated at 220 °C in the heating chamber indicate an increase in peak area as the lubricant degrades (Figure 3). The increase in the peak height and areas of the spectrum in the visible area indicates the change in color. The peak maximum was difficult to identify due to its appearance very early in the UV zone.

3.2. Viscosity. Viscosity as a function of heating time was measured at room temperature for AF and ST lubricant samples heated in a conventional oven at 200 °C. The results are shown in Figure 4; the increase in viscosity as the sample is heated indicates a change in the composition of the heated lubricant. According to the literature,[14,15] formation of oxidation products is the major reason for increases in viscosity and the generation of sludge or varnish. The increase in viscosity is due to formation of higher molecular weight oxidation products in the liquid phase during thermal stressing. The rate of increase in viscosity of AF and ST indicates a difference between the thermal degradation behaviors of these two lubricants.

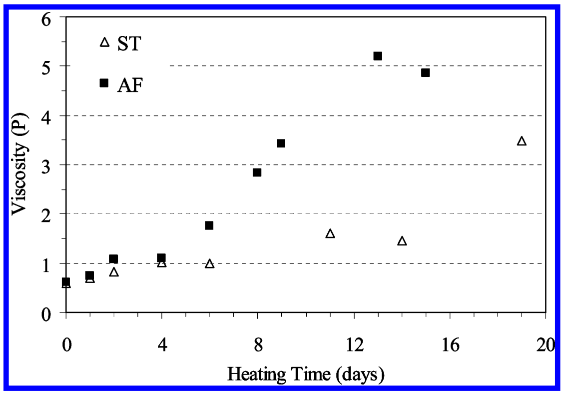


Figure 4. Viscosity change versus heating time measured at room temperature for samples heated in a conventional oven at 200 °C.

3.3. Molecular Weight Distribution. According to several authors,[14,15] lubricants in the presence of air at high temperatures undergo a series of chain reactions and produce hydroperoxides. Further reactions result in the formation of low molecular weight materials such as aldehydes, ketones, acids, and alcohols. Polymerization of these primary oxidation products results in higher molecular weight (HMW) materials during the later stages of the reactions, resulting in sludge, varnish (solid deposit), and an increase in viscosity.[14] The fact that the increase in viscosity has been observed for both lubricants suggests that high molecular weight products have been formed in the system and that they should be present in the form of liquid or solid. 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 paper, molecular weight will be used to describe molecular size in GPC for comparison, even though separation is affected by size and molecular weight.

A comparison of the chromatograms of original AF and short-term thermally stressed AF indicates that the original lubricant sample has a distinct peak at a retention time of 14.5 min (Figure 5). This peak is considered the main peak for the lubricant and it has a molecular weight of about 632; that is very close to the molecular weight of pentaerythritol tetrapelargonate (696). It is critical to notice that in gel permeation chromatography the separation is based on molecular size and not molecular weight. This results in a deviation of obtained molecular weight from the real molecular weight values. However, the molecular size distribution obtained from GPC provides enough molecular level information needed for studying the changes in the liquid phase. Also, it should be taken into consideration that the calibration is based on poly(ethylene glycol) standards, which have a different molecular structure than the HMW products that have been produced here. This also explains the difference in molecular weight.

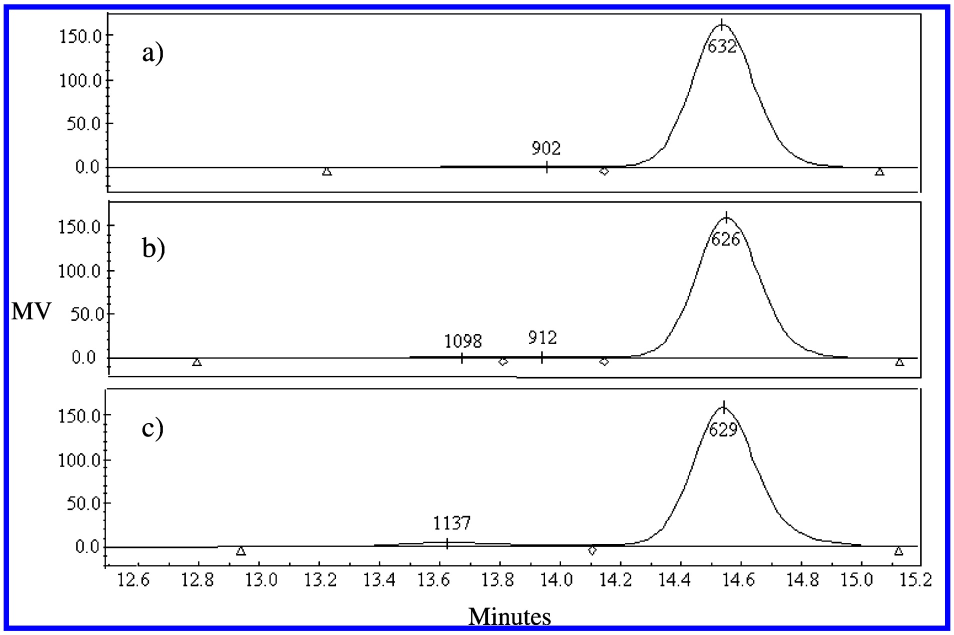


Figure 5. Stack of GPC chromatograms (RI detector) for (a) AF original lubricant and AF heated for (b) 2 and (c) 8 h at 220 °C in the heating chamber.

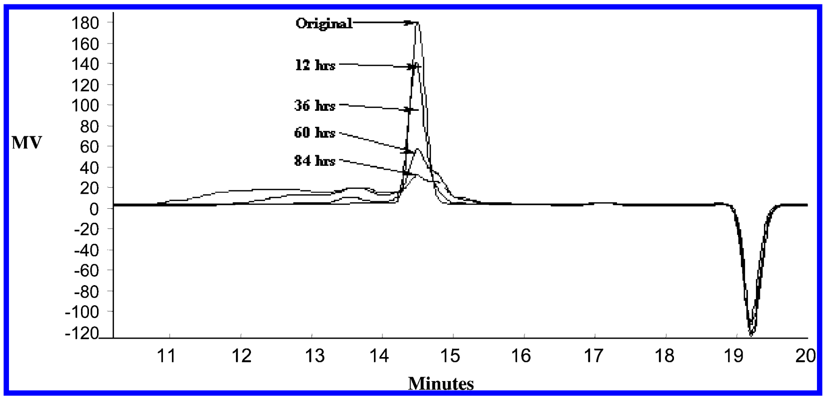


Figure 6. Overlay of GPC chromatograms (RI detector) of AF original lubricant and AF heated for 12, 36, 60, and 84 h at 220 °C in the heating chamber.

Even though the molecular weights obtained by GPC might not be the exact values, these values can be helpful for the comparison. The chromatogram of AF heated for 2 h at 220 °C (Figure 5) indicates the formation of a small peak with a maximum at a retention time of 13.9 min; that represents the existence of a small amount of high molecular weight (HMW) products (MW ~ 912) even at early stages of oxidation. Further heating of the same lubricant up to 8 h results in the growth of the first HMW peak and the appearance of the second HMW peak at retention time of 13.6 min with a molecular weight higher than the first ones (MW ~ 1282). This phenomenon suggests that the early HMW products condense and form even higher molecular weight products as the oxidation reactions proceed. This phenomenon was confirmed to occur in later stages of oxidation.[16]

A composite of the chromatograms for AF samples collected after 12, 36, 60, and 84 h of heating at 220 °C indicates a growth in both 13.9 and 13.6 min HMW peaks as well as a decrease in the main lubricant peak at 14.5 min (Figure 6). This suggests that, by increasing the heating time, the reactions proceed and more HMW products with the same molecular weight are formed. Also, the second HMW peak broadens and increases in area toward even higher molecular weights; this indicates a wide range of HMW products in the liquid phase. Chromatograms in Figure 6 also show the formation of a shoulder in the right side of the main lubricant peak during heating and increases in size up to 60 h of heating followed by a reduction in size. This shoulder relates to the formation of lower molecular weight products as oxidation proceeds. The further reduction in size of this shoulder suggests that these products either decompose and volatilize, appearing in the gas oxidation products, or condense and polymerize, forming the additional HMW products observed on the chromatograms. The same explanation can be used for the reduction of the peak area of the main lubricant peak. Similar chromatograms with the same main lubricant peak, HMW peaks, and the same retention times were obtained for the ST sample.

The percentages of area of each HMW peak and main lubricant peak were computed; in addition, the percentage of each component in the liquid samples was quantified. Figure 7a shows a decrease in area of the main lubricant peak in both AF and ST samples; this approximates the amount of original lubricant remaining in the system during heating. According to the GPC peak areas (Figure 7a) measured for the AF liquid remainder after 84 h of thermal stressing, 20% of the heated sample has a molecular size similar to that of

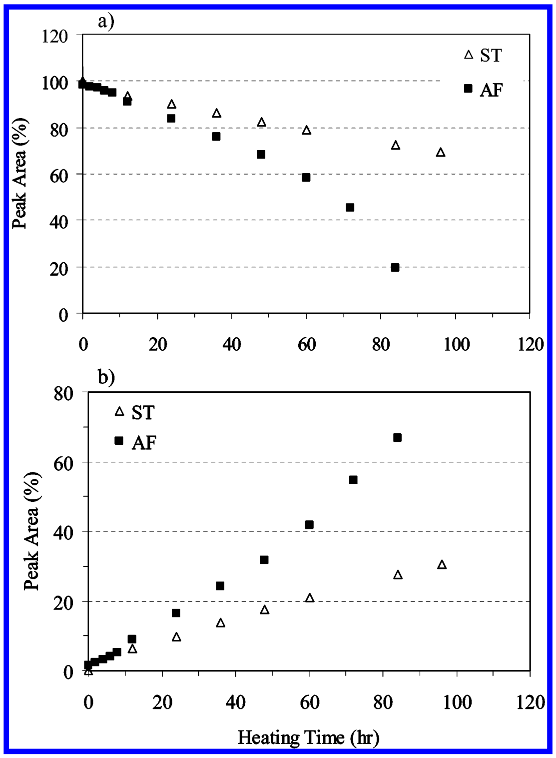


Figure 7. (a) Peak area of main lubricant peak vs heating time. (b) Combined peak area of all HMW lubricant peaks vs heating time. Obtained from GPC chromatograms with RI detector. Heating temperature 220 °C.

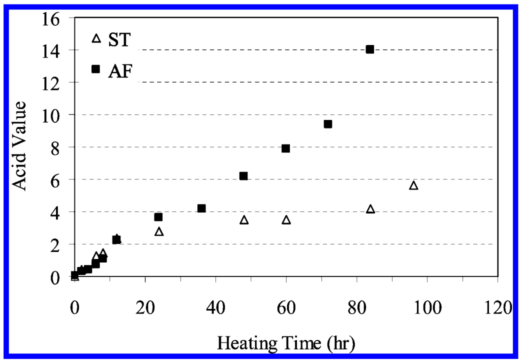


Figure 8. Total acid value versus heating time obtained from samples heated isothermally at 220 °C in the heating chamber.

the original unheated AF sample. Instead, other broader peaks with higher and lower molecular weights have been generated. The higher molecular weight peak contains about 67% of the liquid residue (as illustrated in Figure 7b), and 13% of the liquid residue includes materials with lower molecular weights than those of the original materials. In other words, after 84 h of heating, in the liquid phase only 20% of the original AF lubricant remains; the remainder has been converted to oxidation products. Also, the higher and lower molecular weight peaks were not observed for the AF samples heated for 84 h under nitrogen environment, which confirms the fact that these products are formed as a result of oxidation.[17] Other analytical methods in the current work such as FTIR and GC/MS also confirm the oxidative nature of degradation. It should be noted that this method does not recognize the percentage of the oxidation products with the same molecular size as the original lubricant. Hence, there is a small error related to the aforementioned oxidation products: the actual percentage of lubricant remaining is slightly less than the calculated value. There is an increase in the total amount of HMW products formed in the liquid phase as the reaction proceeds (Figure 7b).

As can be observed in the graphs, there is a distinct difference between the amounts of HMW products formed by ST and AF. Since these two lubricants have the same chemical structure, this could be due to the presence of some additives in one of the samples or differences in the synthesis reactions. The data suggest that, under the same conditions (220 °C temperature and same heating time), ST has fewer degradation products than AF. In other words, ST shows more thermal stability in the liquid phase than AF. This method using GPC not only easily identifies which lubricant shows a better performance in the liquid phase, but also quantitatively shows which lubricant, to what extent, has a higher resistance to oxidation. It is interesting to note that the growth of peak areas follows a linear trend, which suggests that the rate of oxidation and formation of high molecular weight products is almost the same in the liquid phase.

3.4. Acid Content. The acid value test, a standard method for measuring oxidation of lubricants, was performed to confirm the results from GPC. As degradation reactions proceed and oxidation products are formed, the free acid content of the lubricant increases (Figure 8). This is an indication of formation of new products in the liquid phase with free acid groups as a result of thermooxidative reactions. This behavior was observed for both ST and AF samples. The acid content of AF samples is higher than that of ST in every stage of heating, which indicates that there are more degradation products (with free acid groups) in the AF degraded samples. This is in agreement with the GPC results. The linear increase in the acid contents was similar to the linear change in the peak areas observed in the GPC study.

3.5. Hydroxyl Content. The FTIR spectra of original samples of AF and ST (Figure 9) show that these lubricants have the same structural chemical bonds. Comparing the spectra of the degraded samples with the original ones shows the growth of a broad peak at 3528 cm^{-1} (Figure 9). This peak corresponds to the presence of hydroxyl groups in the compound. The oxidation peak (3528 cm^{-1}) is clearly separate from the ester group oxygen in the original lubricant. Ester groups cause the strong peak at 1200 cm^{-1} related to C−O−C stretching modes and the peak at 1750 cm^{-1} related to the C═O band. The area under the peak at 3528 cm^{-1} has been normalized via dividing by the area of the carbonyl peak (1750 cm^{-1}). The increased peak ratio with heating time (Figure 10) indicates an increase in the hydroxyl content. This increase apparently has a direct relationship to the heating time and can be used as an indicator for the degree of degradation. AF shows a greater increase in the OH content compared to ST. This result further confirms the GPC and acid value results, indicating differences in the degradation behavior of the two lubricants, which have the same chemical structure.

3.6. Weight Loss. Thermogravimetric analysis (TGA) performed in both air and nitrogen environments evaluated the effect of the presence of oxygen on the lubricant degradation behavior. The amount of weight loss during the experiments was recorded; the mass percentage remaining in the TGA pan versus heating time at 260 °C is presented in Figure 11. The weight loss in a nitrogen environment is attributed to evaporation and decomposition, whereas the mass loss in the air envi-

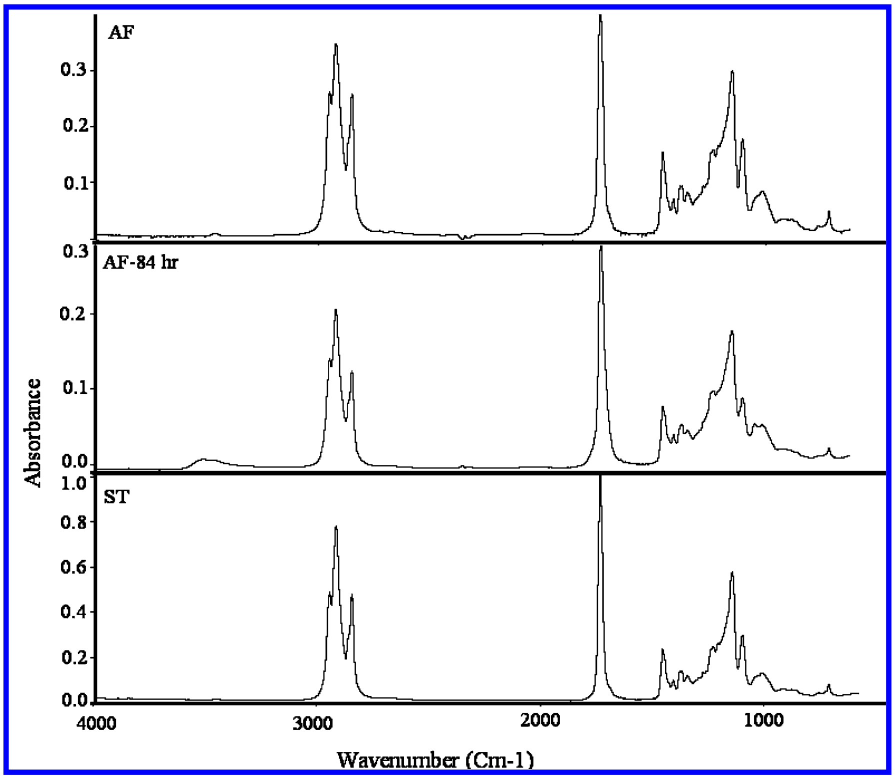


Figure 9. FTIR spectra of AF original lubricant, AF lubricant heated for 84 h at 220 °C in the heating chamber, and ST original. Spectra obtained using NaCl salt plate. The growth of the hydroxyl group peak can be observed.

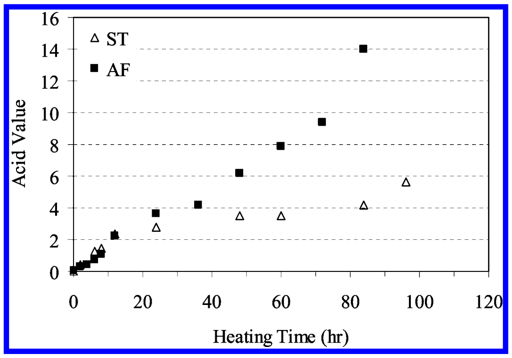


Figure 10. Area under peak at 3528 cm^{-1} (OH group) versus heating time obtained from FTIR spectra of AF and ST lubricants heated at 220 °C in the heating chamber.

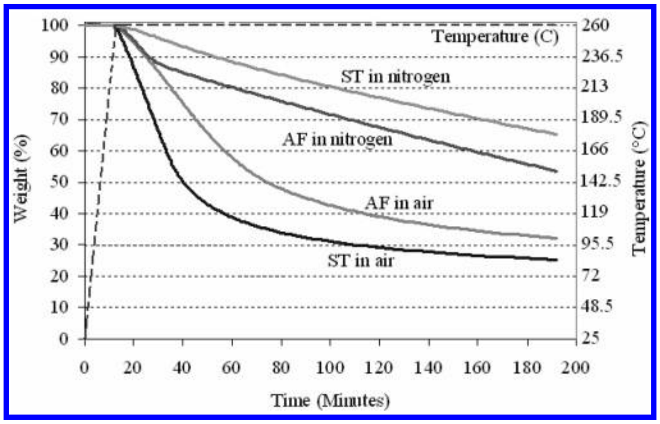


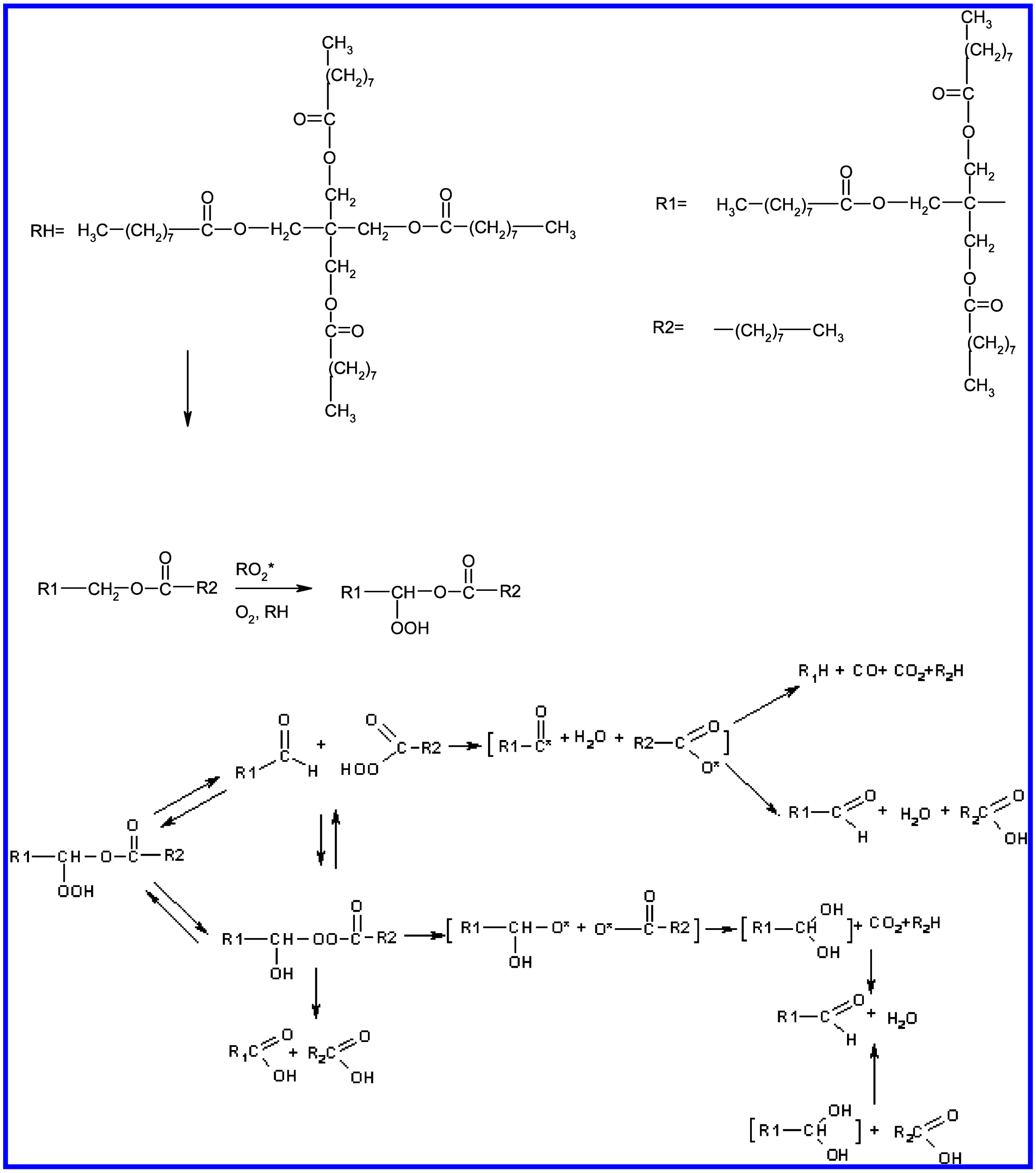
Figure 11. Weight percent of AF and ST lubricants versus heating time as they are heated at 260 °C in TGA. Environment gas: nitrogen, air (20% oxygen).

ronment is due to a combination of evaporation, decomposition, and oxidation. The difference in weight loss in air and nitrogen indicates the amount of oxidized gas phase products being produced. It is important to notice that, in the air environment, ST lubricant has a higher amount and rate of weight loss compared to AF. In contrast, in the nitrogen environment, the weight loss of AF is higher than that of ST. This means that ST generates more gas oxidation products than AF as it is heated, but AF loses its weight primarily due to evaporation or decomposition, not oxidation. At first glance, this result appears to disagree with results obtained from other experiments (i.e., GPC, acid value, FTIR, viscosity) in the current work, which suggests that ST has a higher thermal stability than AF. However, TGA only shows the amount of gas oxidation products and does not give any chemical information about the liquid or solid phases. In other words, we can conclude that ST generates more gas phase oxidation products (low molecular weight products) whereas AF generates more liquid and probably additional solid oxidation products (high molecular weight products).

It should be noted that the TGA experiment is a thin film experiment and the sample is only a few milligrams. In contrast, the degraded samples generated in the heating chamber were in a heating environment with almost 136 mL of lubricant due to the design of the chamber. Hence, a direct comparison between the percentage of weight loss in the TGA condition and the weight loss in the heating chamber will have some errors. TGA results indicate that a lubricant that demonstrates stability (in comparison to other lubricants) in the liquid phase may not be a stable lubricant in terms of weight loss (in the gas phase) and vice versa.

3.7. Mechanism of Degradation. Chemical mechanisms of the reactions occurring during thermal degradation of polyol esters have been studied by several researchers.[18-20] Oxidation reactions are the most dominating reactions of degradation. Different mechanisms have been proposed for the formation of low molecular weight products.[2,16,21] In the case of pentaerythritol

Scheme 1



tetrapelargonate, the oxidation reactions can be shown as Scheme 1, based on proposed mechanisms.[16,18,21] This scheme explains the formation of low molecular weight products, which either stay in the liquid phase or evaporate to the gas phase based on their boiling points. These low molecular weight products include acids, alcohols, aldehydes, and ketones with chain lengths from C_1 to C_9. Scheme 1 also explains that the increase in acid content and OH peak of FTIR are because of the higher formation of these products as the reaction proceeds. Earlier gas chromatography/mass spectrometry experiments[10] have proven the formation of these products in the gas phase during thermal stressing of pentaerythritol tetrapelargonate. The formation of different types of alkanes and some alkenes was reported in previous works[10−14] by online gas chromatography of the volatiles during thermal stressing of pentaerythritol tetrapelargonate (Figure 12). These volatiles form from bond scission of branches of the original molecules of lubricant or degraded products by radical dissociation. Scheme 2 depicts the formation of these products. These radicals form the volatiles by combining with hydrogen radicals. The increase in concentration of these volatiles is due to proceeding of the degradation reactions and cleavage of more bonds. The higher concentration of

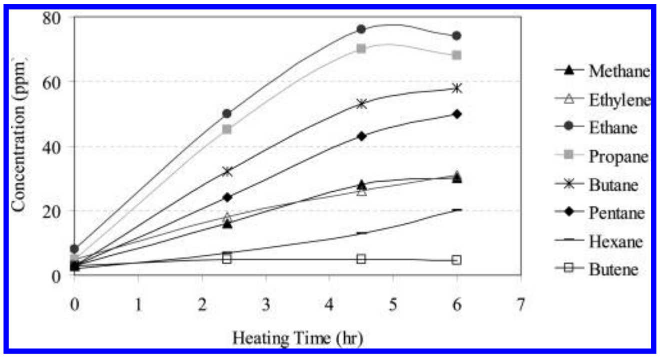
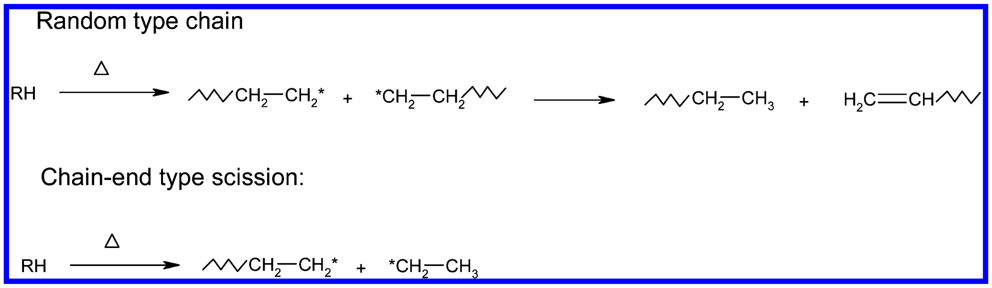


Figure 12. Concentration change of select volatilized compounds with heating time (pentaerythritol tetrapelargonate) at 200 °C.[10]

Scheme 2



smaller alkanes is due to decomposition of higher alkanes to smaller ones. The lower concentration of methane could be because of decomposition mostly by chain-end type scission, which produces fewer methyl radicals.

The approximate molecular weights obtained from GPC chromatograms indicate that the first high molecular weight peak could be due to formation of the dimer of the lubricant molecule. Based on the molecular structure of previous suggestions,[16] the formation of dimers due to condensation and polymerization can follow different schemes. Some of these schemes might be more feasible than other ones. Koch and Jantzen[2] showed the reactions that can lead to polypentaerythritol ester. Also, in other schemes, they showed different steps of a reaction that produces radicals and forms a product that can go through aldol condensation and formation of linear and branched polyesters. On the basis of the work done by Koch and Jantzen,[2] a monomer is proposed for the polymerization of pentaerythritol tetrapelargonate (Figure 13). Scheme 3 shows further reactions of oxidation by radical polymerization. The products of these reactions have susceptible sites for attack of oxygen, and they can also undergo even further reactions. Continuation of polymerization by ester interchange can lead to a variety of polyesters with different chain lengths and branches (Scheme 4).

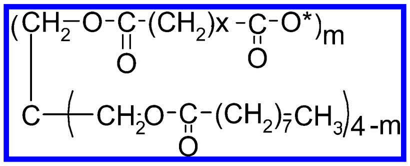
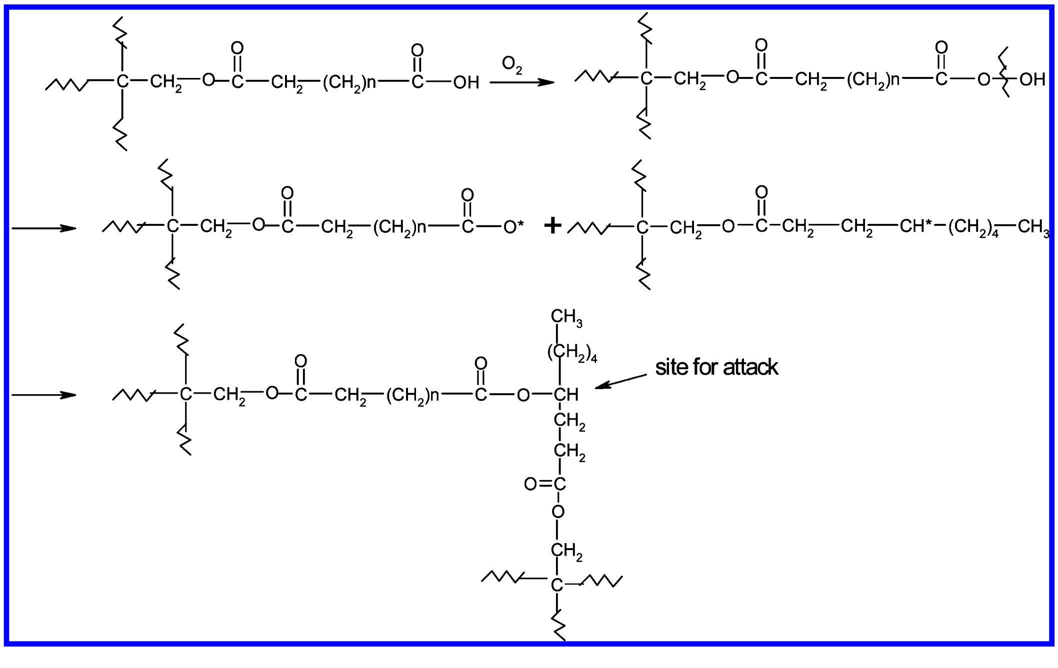


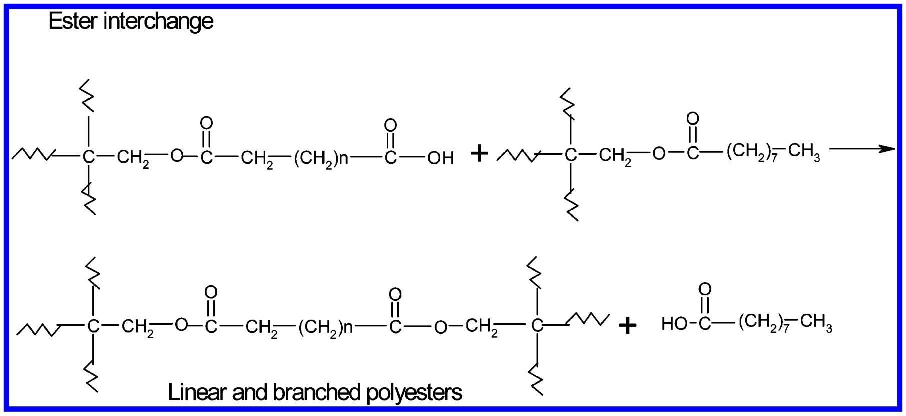
Figure 13. Proposed monomer for PETP.

GC/MS experiments on the liquid samples condensed from the gas phase showed the existence of different oxidation products in the gas phase. These liquids only include oxidation products with boiling points higher than room temperature; this was due to the collection of the volatiles at room temperature. Hence, most alkanes, some alkenes, and aldehydes were not observed in this analysis. The major peaks found in all samples were identified. These products include 2-heptanone, 2-octanone, pelargonic acid, butyl nonanoate and other esters with different lengths, 4-pentylbutane-4-olide, and 2,6-di-*tert*-butyl-4-methylphenol (BHT). The formation of ketones, acids, and esters is easily explainable by aforementioned reactions. The cyclic compound can form according to Scheme 5. The presence of BHT, which is an antioxidant, could not be related to the solvent since it was not observed in the blank solvent sample. This suggests that there was some antioxidant in the original samples. Chromatograms of condensed material collected after 72 and 84 h of heating showed a series of small peaks at very high molecular weights. These peaks exited the columns around 300 °C, which is much higher than their original boiling point (under 220 °C). These peaks could not be identified, but the molecular chains in these materials are approximately C_{20}. Since products in this molecular weight range

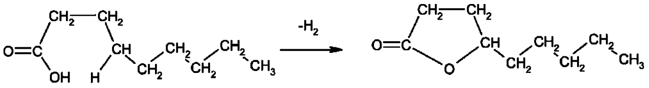
Scheme 3



Scheme 4



Scheme 5



hardly exist in the gas phase, it is suggested that these HMW products are formed in the liquid phase after condensing. This means that condensation and polymerization can continue even after evaporation in the liquid phase during the cooldown process to room temperature. Further work is being performed in our group for identification of higher molecular weight products and other low molecular weight products.

4. 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 h 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.[10] GPC results indicated a significant difference in the extent of degradation of the two lubricants under the same thermal stressing conditions.

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 showed that the results from TGA analysis and those from 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 phases. 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 and (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 the AF sample. The results obtained indicate that the combined analytical approach introduced in the present work could be utilized to further investigate and compare the extent of degradation in lubricants in both the original and stabilized forms.

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