FUNCTIONAL PRODUCTS INC.
Innovative Chemistry for Lubricants

Tackifiers for High Temperature Lubricants

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Overview

Tackifiers are polymeric additives that add tack, or stringiness, to oil and are typically used to provide lubricant adherence and anti-mist properties to fluids. Conventional tackifiers based on polyisobutylene (PIB) are not thermally stable. Tack and viscosity are lost as PIB begins to spontaneously degrade above 90˚C. An increasingly important performance requirement for modern lubricants, however, is better thermal stability and lubricant formulators are turning to API Group III base oils. In this study, components of less refined lubricant oils were individually added to refined Group III oil to isolate the effects of each compound on PIB stability in oil at high temperature. From these results a novel 'preservative' was identified and used to formulate a PIB-based tackified lubricant which greatly resisted loss of tack during high temperature degradation tests.

I. Introduction

Tackifiers provide a unique form of non-Newtonian behavior separate from viscosity that aids a lubricant in remaining on a surface under shear. This is seen as tackiness or stringiness in that the modified lubricant will produce fine filaments of oil due to the tackifier additive. High molecular weight polymers (M_n > 200k, M_v >1M) pre-dissolved into oil are the active ingredient in these additives. Large polymers are known for their ability to impart many new properties to their solutions in oil or solvent.[1]

Unlike simple liquids like solvent or water, polymer solutions have unique properties due to the connectivity between many repeat units. The molecules in solution are in constant movement and though they collide there is very little restriction in their motion. Their diffusivity, the ability to diffuse through the molecules of the solution, is very high. These liquids will flow spontaneously. Polymers are linear chains of many small molecules in one large molecule. This much larger particle with a larger cross-sectional area experiences more drag as it diffuses through the solution. As a consequence, its diffusivity is greatly reduced versus the sum of its parts. The diffusivity of polymer chains in an oil-based solution scales by a factor of $N^{-3/2}$, where N is the number of repeat units ($N = M_n/M_1$).[1] [2]

If many sufficiently long polymers are in the solution then the polymer chains create additional obstacles for one another. The chains will become entangled like spaghetti and at this point the polymers cannot diffuse through solution in three-dimensions. The polymers may only travel in a snake-like manner backward or forward in one-dimension through 'tube-like' openings between the many entangled chains. The prevailing theory of how polymers diffuse under these conditions was developed by de Gennes and is appropriately called the 'reptating tube model' after the reptating (the term for how a snake moves) way a chain must travel through a network of tube-like openings created by the other polymer chains in solution.[3] The longer a polymer chain is, the longer it takes for the polymer to snake through the tubes of entangled polymer chains.

This condition greatly slows down the physical response of the polymer solution, such as flow under gravity or response to shear. A given polymer solution with chains of length N and concentration φ has a characteristic timescale, τ, for responding to interactions such as shear, gravity, surface tension, or flow. For a dilute solution or non-polymers τ is negligible and action-reaction occurs ‘instantly’. On the contrary, concentrated or polymeric solutions have a noticeable τ value where mundane interactions such as pouring the solution exceed this timescale. Returning to de Gennes’s tube-like theory, polymer solutions take a long time to flow because the individual chains must work their way through the entangled network. Very long chains move slowly as it takes proportionally longer for them to travel a distance equal to their own length. The time required for a polymer to diffuse its own length is the fundamental definition of τ.[1] When physical interactions occur faster than τ the solution behaves in a non-Newtonian manner since the polymers cannot flow fast enough to respond. Tack or stringiness in oil is an example of one application of non-Newtonian behavior. Efficient tack-producing polymers achieve this effect at concentrations as low as 0.01wt% for $M_n > 100K$ ($M_v > 1M$).

A tackifier product largely consists of two components: the base oil and a dissolved polymer of high molecular weight. Olefin copolymers (OCP) or polyisobutylene (PIB) at M_n>100K (M_v>1M) are typical polymers in the current state-of-the-art. Their structures are shown below in Figure 1. The tackifier is added to lubricants at treat rates of less than 1wt% to provide adherence between the oil and surfaces. The tack of a lubricant may be characterized by methods as simple as working the oil between one’s fingers to more quantitative methods like ductless siphon.[4] However, tack tests are performed at room temperature and do not encompass the range of conditions the tackifier product will experience during its service life.

Polyisobutylene (PIB)

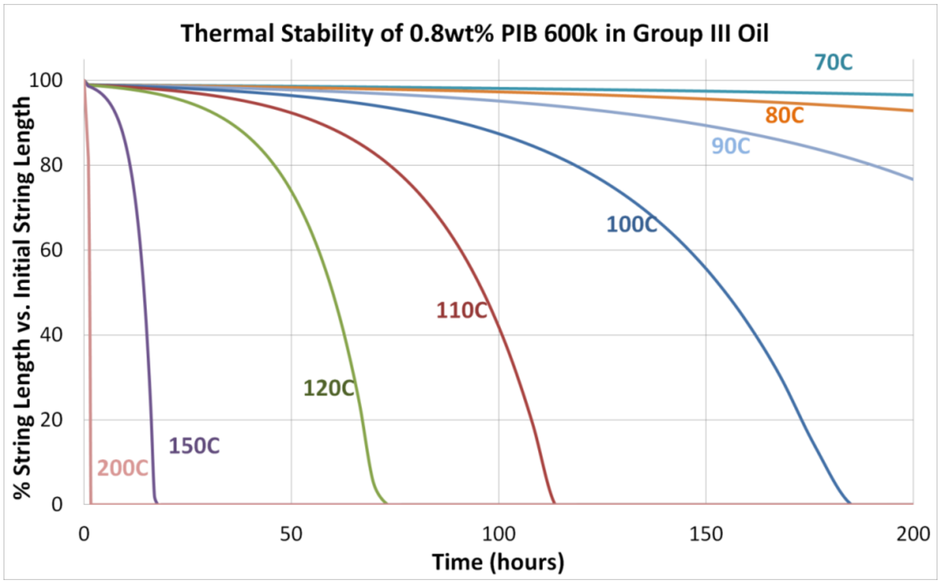
Polyolefin copolymer (OCP)
R = H, methyl, hexyl, and/or octyl

Figure 1: Chemical structure of PIB and OCP polymers

It is well-known that long polymers are sensitive to thermomechanical degradation. Continual shear acting on a polymer coil in solution will stress the chemical bonds along the backbone and cause scission of the bonds.[5] Since viscoelastic properties like viscosity index and tack are inherently tied to chain length this chain scission causes loss of performance.

The thermal contribution to thermomechanical degradation is less studied. Chain scission along the polymer backbone spontaneously occurs beyond a specific temperature for each polymer. This may occur due to reaction with oxygen or thermally generated radicals for olefin-copolymer (OCP) tackifiers. For polyisobutylene (PIB) tackifiers the chain scission occurs as an inherent property of the polymer-monomer chemistry. While PIB, given the same chain length, is more efficient at producing tack than OCP the PIB's structure introduces a critical vulnerability to temperature.

Figure 2 is a plot of % string length remaining versus the time at which a sample PIB tackifier (0.8wt% PIB 600k, 98.2% Group III oil, no antioxidant) has been held at a set temperature. These curves were extrapolated from individual data points to fit the equation %S = 100 – exp(αt), where α is a degradation coefficient that scales exponentially with temperature. String length was measured via ductless siphon.[6] From these curves, high MW PIB-oil solutions will last for months at <u><</u>80˚C, weeks from 80-100˚C, days from 100-150˚C, and hours >150˚C in Group III oil. Greater stability is reported for solid, bulk PIB.[7]



<u>Figure 2</u>: Extrapolated curves of string length versus time for a high MW PIB tackifier show that string length is very stable below 90˚C but is rapidly lost at higher temperatures.

PIB is well-known for its unique properties due to the dialkyl substitution at the 1- position of ethylene.[8] Polyethylene and polypropylene possess symmetry in their structures which limits the rotation of C-C bonds along the backbone. As a result the polymer chains do not expand or entangle as readily in oil. Entanglement is critical for viscosity and tack. PIB has two alkyl groups at the 1- position which remove the symmetry bias from the rotation of the C-C backbone and allow it to turn freely. This increases the flexibility of the PIB polymer chain and allows it to entangle more effectively. This polymer also has the benefit of producing water-white solutions in oil with high clarity even at very high molecular weights due to its very low crystallinity. However, the same structural elements in the polyisobutylene chain which allow high tackiness also enable special temperature sensitivity only observed in highly substituted polyolefins.

During polymerization, strong reactive C=C bonds are converted to weaker C-C bonds as monomers are added to the polymer chain. The excess energy is released as heat, called the ‘enthalpy’ of reaction ($-\Delta H^\circ$).[9] This confinement of once freely moving monomer units to the polymer chain also causes a loss of disorder or ‘entropy’ ($-\Delta S^\circ$). However, the second law of thermodynamics requires *all* processes to increase the total entropy of a system ($-\Delta S_{total}<0$).[10] For polymerization to occur successfully the thermal disorder from the heat released by the reaction ($-\Delta H^\circ$) must overcome the entropy lost from the monomers ($-\Delta S^\circ$).[9] This balance is expressed as the Gibbs free energy ($-\Delta G^\circ$), where T is temperature:

$$-\Delta G^\circ = -\Delta H^\circ + T(-\Delta S^\circ)$$

A process may only proceed forward and yield a stable product while $-\Delta G^\circ>0$. The process is then called ‘favorable’. Polymerization conditions are engineered to achieve $-\Delta G^\circ>>0$ and one way to do so is by varying temperature, T. If $-\Delta G^\circ<0$ during or after the polymerization then the process is ‘unfavorable’ and may spontaneously reverse itself at some rate. This rate is governed by the field of ‘kinetics’ which describes the speed at which a process moves between the initial and final states of a process that were determined by thermodynamics.[11]

Several key thermodynamic parameters of polymerizations are listed in Table 1 for different polymer families. The general trend is that $-\Delta H^\circ$, $-\Delta S^\circ$, and $-\Delta G^\circ$ of a monomer decrease with increasing ‘steric hindrance’ from additional alkyl groups on the monomer in polyolefin and polystyrene series. Steric hindrance is an effect of overcrowding in a chemical structure that prevents the structure from rotating into an efficient, energy minimized orientation. As a result, the final polymer structure is higher energy which causes a lower difference in energy between reactants and product. Therefore a lower enthalpy of polymerization is released and less capable of offsetting the loss of entropy. Unsaturated polymers like polybutadiene and polyisoprene benefit from additional alkyl groups due to stabilization of the double bonds in the polymer. As previously stated, higher $-\Delta H^\circ$ and $-\Delta S^\circ$ are more thermodynamically favorable.

Table 1: Enthalpy, entropy, and free energy of polymerization, reproduced from Wiley[12]

Monomer	**$-\Delta H^\circ$ (kJ/mol)**	**$-\Delta S^\circ$ (J/mol-K)**	**$-\Delta G^\circ$ (kJ/mol)**
Ethylene	93 – 108	142 – 177	51 – 57
Propylene	87 – 104	167 - 205	37 – 43
Isobutylene	54	120	18
Styrene	70 - 76	105 - 148	31 - 39
α-Methylstyrene	35	104	4
Butadiene	74	86	48
Isoprene	75	101	45

1,1-disubstituted olefins like isobutylene and methylstyrene exhibit low enthalpies ($-\Delta H^\circ$) of polymerization due to the steric hindrance of two functional groups on the active chain end.[9] Typical monomers have a $-\Delta H^\circ$ of 80-100 kJ/mol and $-\Delta S_p$ of 100-140 J/mol-K.[12] Isobutylene has a $-\Delta H^\circ$ of only 54 kJ/mol with a $-\Delta S^\circ$ of 120 J/mol-K. The resulting temperature-dependent $-\Delta G^\circ$ of isobutylene is much lower than usual and $-\Delta G^\circ<0$ is possible at less than 100˚C. The cross-over point when $-\Delta G^\circ=0$ is called the ceiling temperature, T_c. Below T_c, depolymerization of PIB to its monomeric units occurs. The equilibrium concentration of monomer, [M], from the depolymerization may be expressed in terms of T_c, -ΔH˚, and -ΔS˚ as:[9]

$$\ln[M] = -\frac{-\Delta H^{\circ}}{RT_c} + \frac{-\Delta S^{\circ}}{R}$$

Actual T_c may differ from estimated T_c due to additional complex interactions.[12] Depolymerization of a polyolefin backbone is understood to be a homolytic cleavage of the C-C bond into two alkyl radicals. In PIB, these two radicals can reassemble back into bond to restore the original chain. The radicals may also graft to other parts of the polymer to reconstitute the chain in a slightly different, more stable configuration. This effect delays PIB degradation in bulk.[12] However unsaturated compounds and heteroatoms in a PIB-oil solution may scavenge these radicals as chain-transfer agents and prevent reassembly.[9]

Since tackifier additives are two-component systems of oil and polymer it is worth discussing the role of the oil used to dissolve the additive and to prepare the lubricant. Previous work has shown that even low (<5wt%) concentrations of Group I/II base oils added to Group III can drastically affect PIB stability at elevated temperatures.[13] These less refined oils may contribute components which disrupt the equilibrium between polymerization and depolymerization of PIB at high temperature and accelerate decomposition.

Group I oils are produced through the cracking of crude oil into lighter products which are solvent refined. This solvent process reduces the content of ‘aromatics’ like benzene and non-carbon ‘heteroatoms’ like sulfur (S), nitrogen (N), and chlorine (Cl) but does not eliminate them. Aromatic content may be 10-20% of the oil by weight while S, N, and Cl occur at up to 300 ppm concentration. Group II oils are hydrogenated to >90% saturated hydrocarbons and minimal heteroatom content. Group III oils are hydrocracked using a more aggressive hydrogenation that breaks C-C bonds of cyclic components in the oil. Naphthenic content is greatly reduced. While Group III oils possess high viscosity indexes and purity these oils come at higher cost and often exhibit poor compatibility with additives for Group I/II oils.

As discussed, tackifiers are two-component systems of polymer and oil. This study uses multiple approaches to measure and improve the thermal stability of tack from PIB. In the first section, we focus on base oil impurities as a follow-up to prior work in Group I/III oils.[13] In the second section, we report a ‘tack preservative’ based on beneficial impurities of Group I oils. In the final section, we describe preliminary work in finding alternatives to OCP and PIB chemistries for use in tackifiers. The goal of this effort is to understand the foundations of tackifier polymer stability, improve on this established technology, and identify new polymer chemistries to advance the state-of-the-art.

II. Experimental

II.a. Base Oil Impurity Study

Polymer-oil solutions were prepared in two stages.

Stock Solutions: Commercial linear PIB and OCP polymers were chosen to examine the effects of composition on viscosity, tack, and thermal stability. A short PIB (M_n = 200k, “PIB 200k”) and long PIB (M_n=600k, “PIB 600k”) were chosen to examine dependences on molecular weight. A relatively long OCP (M_n=200k, “OCP 200k”) was included to compare performance and thermal stabilities with the short PIB of the same molecular weight.

Stock solutions of these three polymers (PIB 200k, PIB 600k, and OCP 200k) were prepared at 1wt% polymer in Group III oil. The same lot number of Group III oil was used throughout the experiments. Due to thermal instability and oxidation the polymers were dissolved into the oil via gentle mixing at 80˚C for 72 hrs. No antioxidant was included unless where noted.

Tackifiers with Impurity: Tackifier products containing 0.8 to 1.0wt% polymer and 0.1wt% of one impurity (see below) were prepared from the tackifier stock solutions. Polymer content was varied to obtain initial viscosities of 20-25 cSt at 100˚C and initial string lengths of 70 – 99 (via ductless siphon). PIB 200k and OCP 200k solutions contained 1wt% polymer while PIB 600k solutions contained 0.8wt% to account for higher tack with longer chain length. Control groups were prepared for each polymer with no added impurity.

The impurities chosen for this study are single representative species from within varying classes of ‘bad actors’ in less refined lubricant and crude oil stocks.[14] [15] A bad actor in oil is assumed to cause a qualitative loss in performance or stability in the product. Compounds containing rings, unsaturation, sulfur, nitrogen, and chlorine are known to promote the degradation of polymers and base oils through the formation of radicals or reactions with active ingredients. Four classes of impurity were tested by preparing four tackifiers with impurity, each containing one representative species:

- Monocyclic aromatics – Alkylated benzene (0.1wt% C_6H_5 in tackifier)
- Polycyclic aromatics – Naphthalene (0.1wt% naphthalene in tackifier)
- Sulfur – Thiosulfates (0.1wt% S in tackifier)
- Nitrogen – Primary alkyl amine (0.1wt% N in tackifier)

II.b. Tack Preservative Study

Tackifiers with Tack Preservative: From screening of good and bad actors in the dilute tackifiers a novel additive described as a ‘tack preservative’ was identified. Tackifiers were prepared from the PIB and OCP stock solutions previously described with varying wt% of the preservative added.

Sample High Temperature Lubricants. Lubricants were prepared to assess the performance of the novel tack preservative with both PIB tackifier and OCP-based viscosity modifier. These contain 0.01 – 0.1wt% polymer, 25wt% of a Group II-based OCP viscosity modifier with PSSI 22%, and Group III diluent oil. The dilution of tackifier polymer and tack preservative along with the inclusion of the Group II-based OCP represents a worst-case scenario. This condition aided in optimizing a robust, high-temperature product.

II.c. Thermal Degradation Testing

Two methods of high temperature degradation were performed: long-term degradation at 150˚C for 16hrs and rapid degradation at 200˚C for 2hrs. These two testing regimes were found to induce tack loss to varying degrees. Similar oven-based tests are common in evaluating antioxidants for lubricants under milder conditions (60-70˚C).[16] These conditions were sufficient to observe loss of tack across a range of different tackifier products and lubricants. The long-term test is convenient for overnight trials while the high temperature 2hr degradation allows multiple trials per day for rapid optimization of formulas.

Samples were pre-heated in 600mL beakers on a well-ventilated hotplate to the desired oven temperature. Once the temperature was reached each beaker was placed into a PID-controlled heating oven (±1˚C) for a period of up to 24hrs. Portions of each sample were taken periodically (90g per string length test; 20g per viscosity test) within minimal disturbance to the samples. It is important to pre-calculate the total sample mass required.

II.d. String Length and Viscosity Testing

Prior studies on tackifier stability at high temperature primarily focused on viscosity to characterize these materials.[13] In this study, string length chosen as the primary metric for measuring tackifier stability to expand on the available data for tack loss at high temperature.

String length was measured on 100mL samples at 25˚C via the ductless syphon method.[6] [17] This method is used by Functional Products Inc. as an arbitrary but quantitative measure of the tackiness of oil-polymer samples. The reported value is the maximum length of a single thread of tackified oil withdrawn from a standard 100mL graduated cylinder (Kimax 20025-H) by vacuum capillary tube. String lengths are only reported up to 99. Strings longer than 99 tend to be thin enough to be buoyant in air and complicate the measurement.

The lubricants were tested for viscosity at 40/100˚C using a capillary viscometer (ASTM D445) to ensure similar starting viscosities. Viscosity values are reported as needed.

III. Results and Discussion

III.a. Tackifier Stability

Tackifiers of 1wt% PIB or OCP (M_n = ~200k) in pure Group III oil were initially prepared to demonstrate the short- and long-term temperature stabilities of these major tackifier chemistries. Due to the structure of the oil and polymer, the OCP has better initial string length than the PIB at the same treat rate in oil. It is worth noting that string length and viscosity will vary by the specific compatibility between a given oil and polymer. This compatibility determines K and a in the Mark-Houwink equation, $[\eta]=KM^a$.

Two testing regimes were developed for slow and fast thermal degradation of samples based on the plots in Figure 1. Since the rate constant of reactions scale by $\exp(-\Delta H_{rxn}/T)$ increasing the temperature will cause exponentially faster degradation.[10] 16-24hrs at 150˚C and 1-2hrs at 200˚C produced adequate string length loss for samples of initial string 60-99 to provide useful information in optimizing formulations.

Figure 3 shows the remaining % string length of M_n=200k PIB and OCP tackifiers held at 150 and 200˚C over several hours. While PIB degrades significantly in both cases these two regimes show different behavior in the OCP. 1hr 200˚C degradation produces roughly the same remaining string length as 16hrs at 150˚C in PIB. This is due to the thermally induced chain scission due to unfavorable thermodynamic stability of isobutylene polymers.

In the OCP sample (Figure 3) the shorter 200˚C degradation did not produce the same level of string length loss as the longer, cooler 150˚C trials. OCP degradation occurs through slower oxidation of the polyolefin which requires diffusion of polar oxygen through a dense hydrocarbon fluid. Degraded OCP samples were yellowed or light orange while degraded PIB remaining water-white and clear. Mono-substituted polyolefins are more prone to oxidation due to the tertiary carbon, CR_3H, which generates radicals more easily due to the radical-stabilizing effect of the alkyl group along the polymer backbone. Oxidation occurs more readily on that tertiary alkyl site for the same reason. In general, the OCP string length survives thermal degradation better than in PIB of equivalent length. High temperature tackifiers have thus far relied on OCP chemistries for this reason.[18] However, they are not as efficient at producing tack as PIB in most oils at low wt% as demonstrated in Figure 4: below 0.5wt% polymer the PIB 200k polymer provides better string length than OCP 200k, given the same chain length.

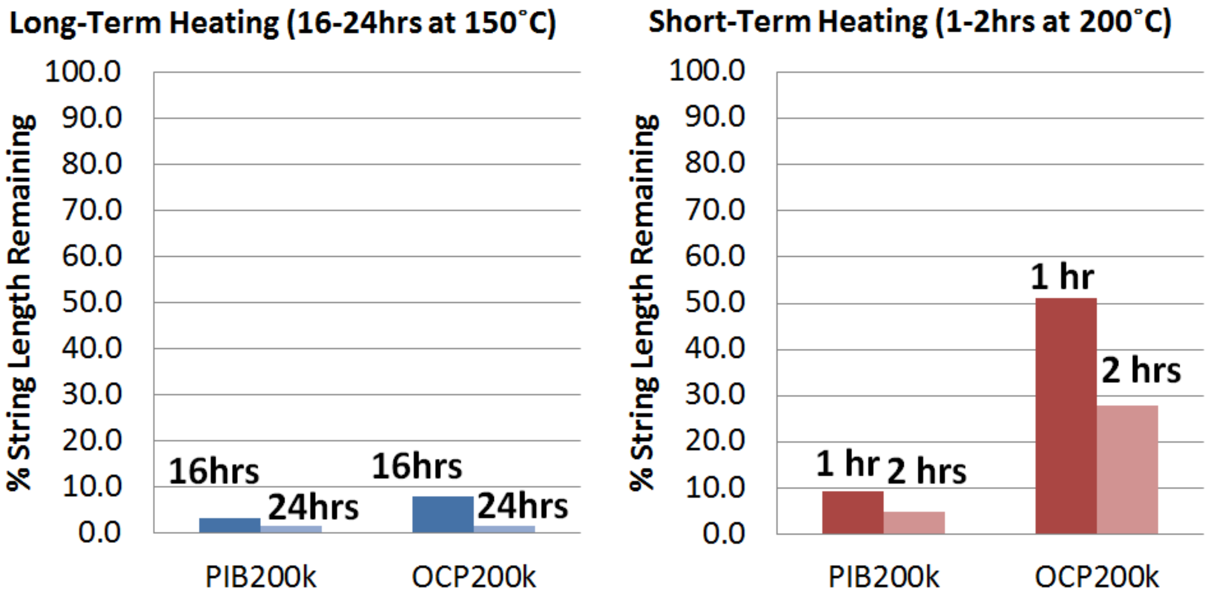


Figure 3: OCP tackifiers possess better high temperature resistance than PIB tackifiers at high, rapid heating (200˚C) but fail over long periods of lower heat due to oxidation

PIB remains desirable, despite its temperature sensitivity, due to its production through well-controlled cationic polymerizations which produce extremely high MW grades of pure PIB.[19] PIB-based tackifiers have lower initial color and better oxidative stability than OCP which allows them to remain dominant in non-high temperature applications.

This access to high MW grades of PIB is beneficial to high temperature tackifiers. If string length at high temperature is lost incrementally over time then starting with greater string length would provide a longer time before the polymer is degraded to a length too small to provide sufficient tack. This was tested with a higher grade of PIB (M_n=600k, M_v=6M).

Figure 4 shows the relationship between wt% PIB and string length for two grades of PIB (200k and 600k) in Group III oil. String length by treat rate in very high MW polymers is not a simple exponential curve like viscosity in viscosity modifiers.[20] Tripling the chain length can provide up to twice the string length and produces a viscoelastic plateau from 0.3 to 0.8 wt%. This plateau corresponds to the transition from semi-dilute to dilute concentration regions for an entangled polymer solution.[1] From this plot, the longer polymer (PIB 600k) is obviously better at providing tack however it also possesses this unique plateau where loss of polymer concentration from 0.8 to 0.3wt% does not incur a loss in string length. High temperature tackifiers should target this concentration regime. The tackifier samples produced in this study were prepared with these considerations in mind.

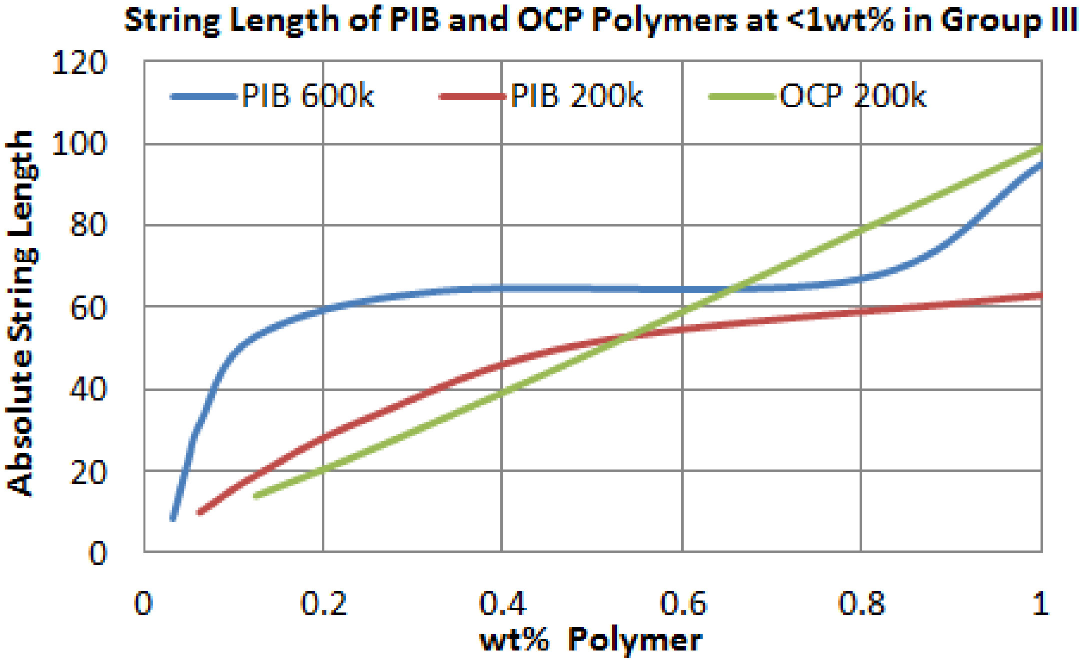


Figure 4: String length for PIB and OCP tackifiers prepared with 0-1wt% polymer. PIB 200k and 600k are better than OCP 200k at providing string length at under 0.5wt% in oil, such as after dilution of the tackifier product in the lubricant; PIB 600k is understandably better at providing tack than PIB 200k. PIB 600k experiences a ‘plateau’ from 0.3 to 0.8wt% due to its long chain length.

III.b. Base Oil Impurity Study

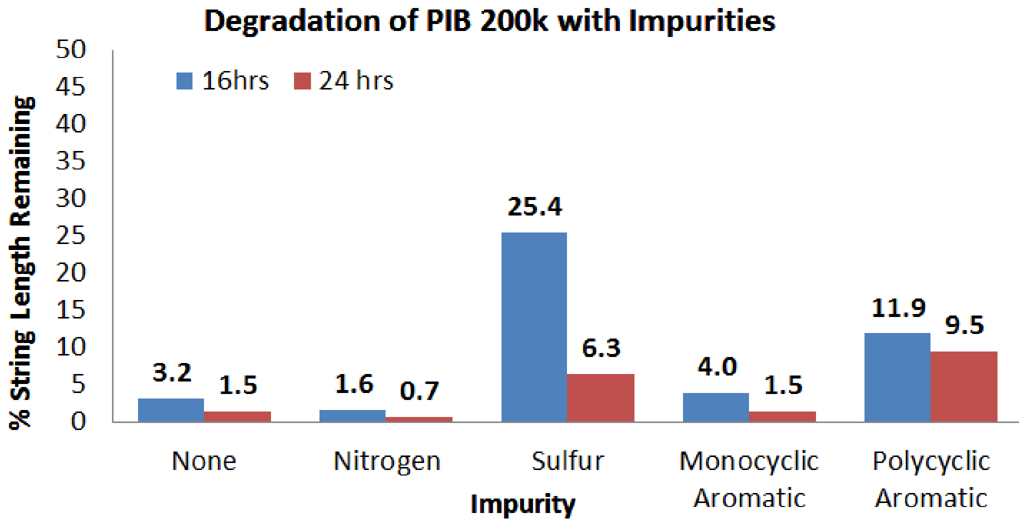
This work was initiated to complement a prior study on PIB and OCP tackifier stability in pure and impure Group III oils.[13] The results suggested that even low concentrations of impurities present in the Group III diluent oil of a lubricant additive can compromise the tack of a Group III-based lubricant at high temperature.

As discussed in the experimental section, several modified Group III oils containing a single representative species of impurity from Group I and II oils were prepared for tackifier formulation. Monocyclic aromatics (via alkyl benzene), polycyclic aromatics (via naphthalene), sulfur (via thiosulfates), and nitrogen (via alkyl amine) were solubilized in oil at 0.1wt% of the functional group or element of interest. A control with no impurity was also prepared. Samples of PIB 200k and PIB600k were solubilized at 1wt% and 0.8wt%, respectively, in the Group III oils to initial viscosities 20-25 cSt @ 100˚C and string lengths of 63-67. % string length remaining for degraded samples was calculated versus these initial string lengths.

Thermal degradation was performed under the long-term high temperature condition (150˚C for 16 and 24hrs) with string length samples pulled from the sample beakers at those prescribed times. Figure 5 shows the 16 and 24hr string lengths for PIB 200k (top) and PIB 600k (bottom) tackifiers.

Without any impurity, both PIB 200k and 600k degrade to 1-5% of their initial string lengths in 16hrs. The PIB 600k maintains better string length in 16hrs however they both reach the same negligible string length by 24hrs. These results are expectable based on the difference in initial chain size. The addition of heteroatoms (N and S) and aromatics (monocyclic and polycyclic) produced varying effects in the two PIB samples.

Heteroatoms accelerated string loss in PIB 200k but reduced string loss in PIB 600k at 16hrs. Phenolic compounds like butylated hydroxytoluene (BHT) use oxygen as a heteroatom to abstract and stabilize radicals from interacting with lubricants.[16] Nitrogen and sulfur compounds are generally reserved for anti-corrosion and extreme pressure additives but their electronegativity would grant them some affinity for the spare electron on radicals.[21] This would slow the attack of thermally generated radicals on the large PIB 600k chains. 0.1wt% nitrogen reduced both PIB string lengths below the pure Group III (none) PIB samples by 24hrs. Nitrogen compounds are oxidized to reactive nitrates species over time. Nitrogen may initially absorb radicals from the oil to initially slow degradation but will later be easily oxidized by addition of O_2 to give the reactive oxides. NO_2 will proceed to oxidize the alkyl chains and its effect will add to the thermal chain scission breakdown of PIB.



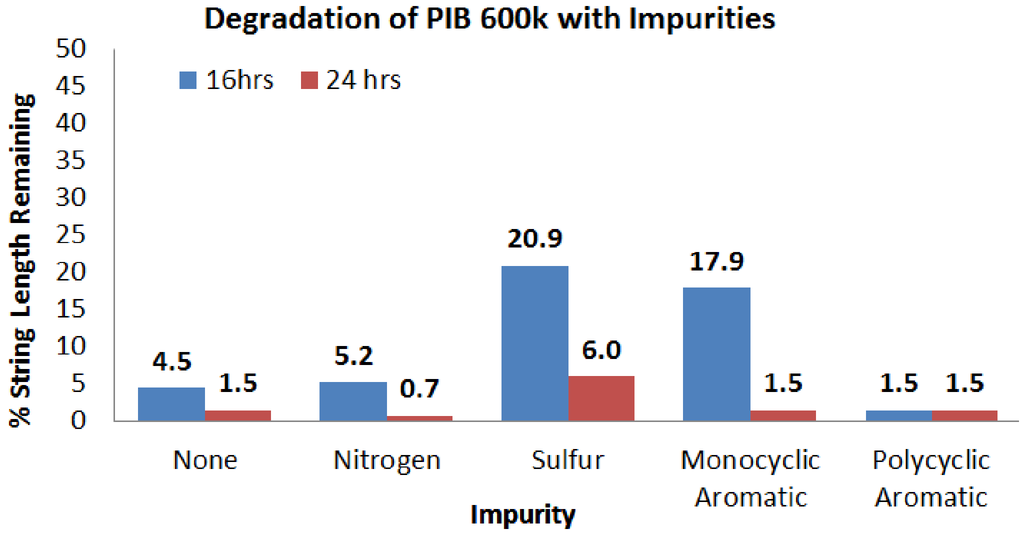


Figure 5: % string length results from PIB 200k and PIB 600k tackifiers degraded at 150˚C show a benefit from heteroatoms and aromatic compounds at 0.1wt% over 16-24hrs of thermal treatment. This is contrary to the conception of these compounds as ‘bad actors’.

Sulfur-treated PIB 600k maintained high string lengths for 16 and 24hrs. Sulfides and thiols have high affinity for radicals due to their electronegativity, multiple lone pairs, and ability to form bonds to many atoms at one time. Like nitrogen, sulfur compounds are eventually oxidized to reactive SO_2 however sulfur did not produce the same degree of string loss as nitrogen. The slower rate of string length loss may be due to nitrogen and sulfur intercepting oxygen before it react with the polymers, essentially acting as antioxidants.

Aromatics, both mono- and polycyclic, had an inverse effect with respect to MW. PIB 200k string length loss was reduced during150˚C treatment with mono- and polycyclic aromatics impurities. PIB 600k was generally unaffected after 24hrs though the benzene-doped sample gave a high % string length value at 16hrs. The results for these two categories are shown in Figure 5. Lower MW PIB produced lower string length loss after the 150˚C. This was unexpected since aromatic compounds have been identified as promoting the formation of radicals in oil.[14] The difference in outcome may be due to the fixed 0.1wt% concentration used for all the modified Group III oils prepared. Unsaturation may be as high as 10-20% in some base oils. Aromaticity of a compound stabilizes the radical, making it easier to form, through resonance which disperses the high energy radical over a large area.[9] Aromatic compounds tend toward generating radicals through breakage of the C-H bond but also tend to recombine with alkyl radicals rather than hydrogen radicals.[9] Recombination occurs when two radicals, essentially two half bonds, react to form a stable single bond. Multiple PIB radicals attacking the same aromatic compound could temporarily build chain length and prolong tack loss in principle. This would occur, for example, when the larger portions of two broken PIB chains attached to a single aromatic molecule to produce a chain of similar or larger size than the original PIB chains. If this effect occurs then it is observed more prominently in the shorter PIB chain with polycyclic aromatics where the % string length remaining after 16 and 24hrs was the highest among degraded PIB 200k samples.

Further study is needed to determine the concentration limits for the benefit effects of heteroatoms and aromatic impurities. Both types of impurities have some interaction with radicals generated from the oil or polymer at high temperature. As discussed, PIB is continually breaking bonds into radicals and recombining radicals back into chains in a temperature-dependent equilibrium. Above its ceiling temperature the breakage is favored and a net amount of radicals is generated as the chains revert to monomer. These excess radicals may proceed to accelerate degradation by attacking other sections of polymer. When impurities that interact with radicals are added this complex exchange of reactions becomes much more complicated. Impurities may help prevent further attacks on the PIB chains by PIB radicals but the additives will also prevent reassembly of broken chains when two PIB radicals recombine. There is precedent for this type of reaction in polymerization and it is the basis for the field of 'reversible addition-fragmentation (RAFT)' polymerization.22 RAFT agents work by selectively binding ("addition") and releasing ("fragmentation") alkyl radicals to sulfur groups at high temperature to control the speed of radical-initiated polymerizations and produce narrow molecular weight distributions. Many such RAFT agents are capable of adding two or more alkyl radicals. In effect, these sulfur-based compounds add two alkyl radicals together. Since PIB breaks down at high temperature into multiple radicals a compound with two or more sulfur groups could potentially reconnect the PIB chain at the site of breakage.)

This study did not include species which are a combination of the different impurity types. Crude oil feedstocks contain many species of heteroatoms and unsaturated components but also combinations of unsaturated heteroatom compounds.[15] Aromatic nitrogens like aniline will have a different interaction than alkyl amines, for example. It is difficult to establish a representative sampling of all these components for testing since there are very few published works about the composition of lubricant base oils at the molecular scale.

From these results we may draw a few conclusions. First, the representative species of impurities in less refined oils (Group I and II) are not equally or always responsible for the degradation of PIB tackifiers at high temperature. Cases were observed with neutral, positive, or negative outcomes to the addition of the impurities at 0.1wt%. These effects are summarized in Table 2. Polycyclic and sulfur compounds had beneficial effects on the string length of PIB 200k and 600k with long- and short-term thermal degradation. Second, 24hrs at 150˚C appears to be sufficient in determining the long-term stability of tackifiers with impurities at high temperature. Multiple samples gave higher % string length remaining than the pure control group but gave the same or worse results after 24hrs. A 16hr overnight trial is not sufficient for anticipating this loss. Third, this work has shown that there are alternative chemistries to butylated hydroxytoluene (BHT) in preserving the string length of tackifiers at high temperature.

Table 2: Summary of the observed effects of 0.1wt% impurity in PIB-based tackifiers

Impurity Group	Representative	Effect on PIB 200k	Effect on PIB 600k
None	None	Loss of tack	Loss of tack
Monocyclic Aromatics	Alkyl Benzene	No Change	Reduced Loss
Polycyclic Aromatics	Naphthalene	Reduced Loss	No Change
Sulfur	Thiosulfate	**Reduced Loss**	**Reduced Loss**
Nitrogen	Alkyl Amine	Increased Loss	Increased Loss

III.c. Tack Preservative

Based on the initial findings from the base oil impurity study a larger selection of ‘beneficial’ impurities was surveyed for their effectiveness in preserving tack at high temperature. Upon further review it was determined that one compound in particular showed promise as a new type of additive.

This novel ‘tack preservative’, TP, acts partially as an antioxidant however its structure also provides additional functions specific to PIB-based tackifiers at high temperature unlike butylated hydroxytoluene (BHT) tested in a prior study.[13] While BHT added to PIB tackifiers in Group III reduced string loss considerably it did not confer high temperature resistance at 0.001wt% BHT after addition of a few percent Group I oil. High treat rates of BHT may have been effective but BHT has poor compatibility

Optimization of this high temperature tack preservative was performed using results from the fast 1hr and 2hr 200˚C degradation method. This is reliable for generating substantial PIB string length loss and observing any effects of an additive. Throughout a series of different experiments we can propose how and under what conditions this tack preservative operates.

PIB 200k, PIB 600k, and OCP 200k were compared as simple two-component polymer-oil tackifiers with and without the new additive using the long- and short-term thermal treatments. The resulting string lengths after thermal degradation, shown in Figure 6, were used to assess the effectiveness of the additive for varying tackifier polymers.

Figure 6 compares the % string length remaining versus OCP and PIB tackifiers containing 0 and 0.1wt% of the tack preservative. In the 150˚C trials, top of Figure 6, the tack preservative provides long-term stability of tack for both OCP and PIB chemistries. The preservative's chemical structure allows some anti-oxidant behavior. Remarkably, in the case of the high MW PIB there is no loss of string length versus the original unheated PIB tackifier. The performance is similar between OCP 200k and PIB 200k, both having roughly the same chain length, but works best with longer chains (PIB 600k). It is also notable that the % string length value is stable between 16 and 24hrs for PIB while OCP varies over time.

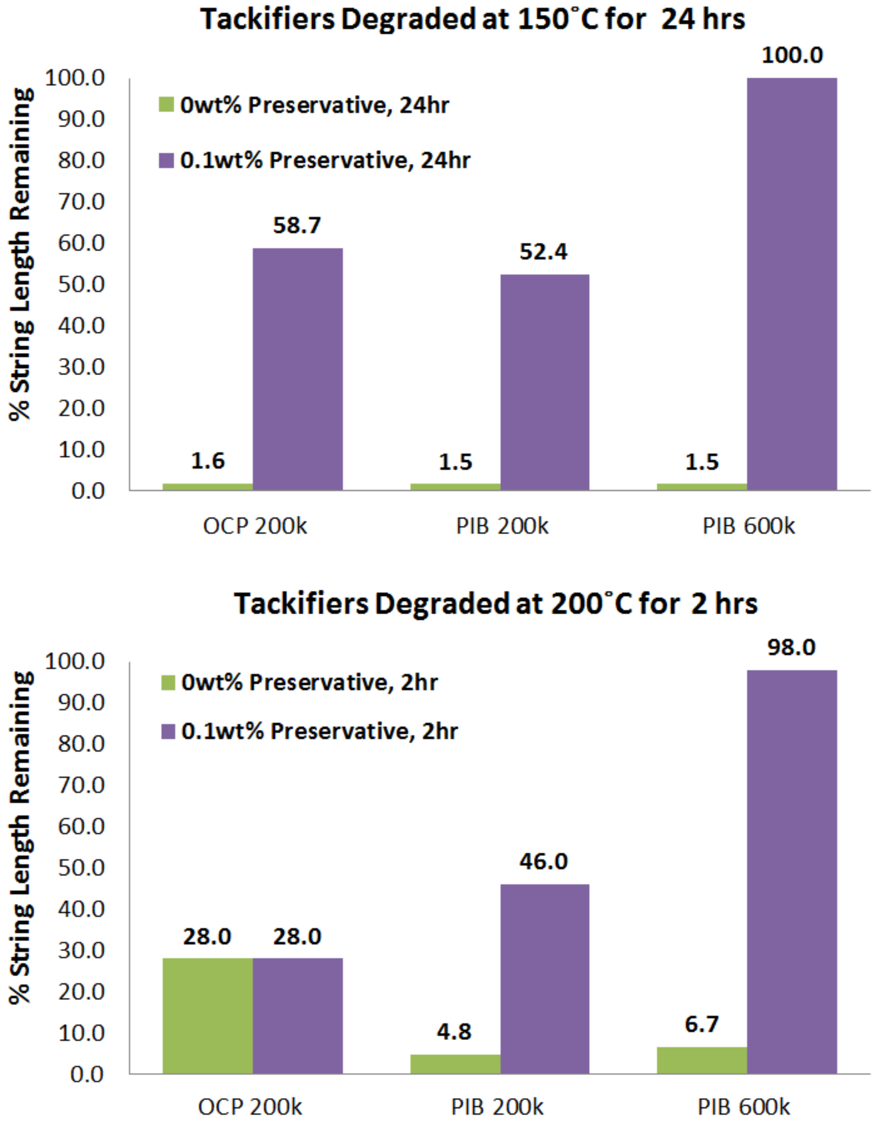
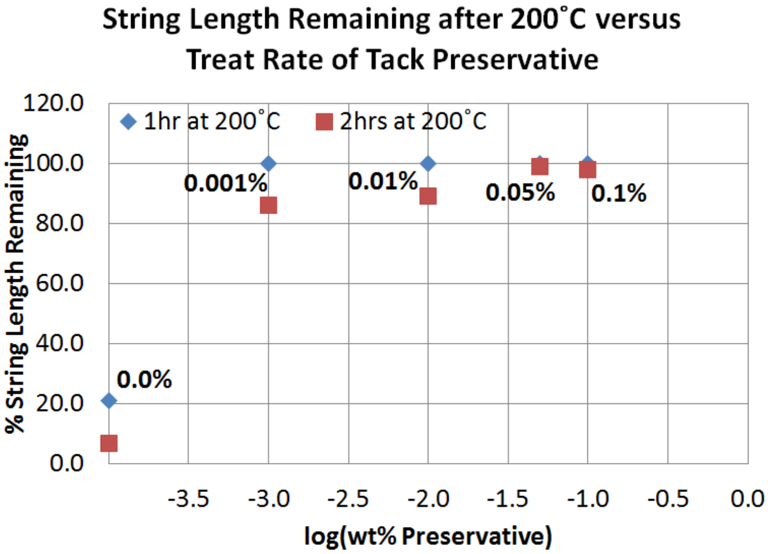


Figure 6: The tack preservative provided high temperature resistance to the tackifiers which allowed high retention of string length after 24hrs at 150˚C and 2hrs at 200˚C. PIB-based tackifiers exhibit the most dramatic improvement suggesting that the tack preservative is specific to PIB. The behavior of OCP between 150˚C and 200˚C suggests an antioxidant effect over long-term, lower temperature heating for OCP tackifiers.

Initial treat rates for the tack preservative were based on the 0.1wt% treat rate from the base oil impurity study. A series of varying treat rates in 0.8wt% PIB 600k in Group III oil were prepared. PIB 600k was chosen since it provides the highest tack and had the best performance with the new additive. The results in Figure 7 show the robust performance of this additive from high to low concentrations. No string length loss was observed for any concentration of the additive from 0.001 to 0.1wt% at 200˚C for 1hr. A concentration of ~0.05wt% is required to also resist string length loss over 2hrs. This concentration regime is possible even at low treat rates in a finish lubricant through a tackifier modified by this additive. While high treat rates provide better heat resistance to the tack the extra tack preservative content contributes additional color after degradation. 0% preservative gives an ASTM D1500 color of <0.5 after 2hrs at 200˚C; <u><</u>0.01% is 0.5 – 1.0 in color; 0.05% is 1.5 in color; and 0.1% is 2.0.



<u>Figure 7</u>: The tack preservative is effective in the PIB 600k tackifier over a very wide range of treat rates from 0.001wt% (10 ppm) to 0.1wt%. No improvement was observed at >0.05wt%.

The tackifiers discussed thus far have only been two-component solutions of PIB or OCP polymer and Group III oil. A lubricant often includes polyolefin viscosity modifiers to improve the viscosity index and achieve a more stable viscosity across a large temperature range. A series of tests were performed to show the robustness of the tack preservative with mixed PIB and OCP polymer chemistries in a finish lubricant.

The PIB 600k polymer and tack preservative were added to Group III-based oil with an OCP-based viscosity modifier. As shown in Figure 6, olefin copolymers are not affected by the tack preservative due to the difference in chemical structure between PIB and OCP. It is important to note that increasing the viscosity of a tackified oil multiplies the string length though no additional tackifier is added.[6] Obviously the addition of the OCP viscosity modifier will improve the initial string length of the finish lubricant but it will also dilute the concentration of tackifier and tack preservative and physically block the interaction between those two components. An excess of this OCP-based viscosity modifier was included (25wt%). The oil in this modifier was Group II to further demonstrate the improved performance above simply adding BHT. As previously shown, BHT greatly reduces string length loss at high temperature when only Group III oil is used with PIB.[13] Impurities from less refined oils compromised the effect of BHT.

In short, the lubricant using the tack preservative was formulated in Group III oil with a Group II-based commercial OCP viscosity modifier to test the operation of the tack preservative in a sample lubricant. A series of these lubricants with viscosities from 26-30 cSt at 100˚C and initial string lengths of 75-80 were prepared to optimize the content of tackifier polymer and tack preservative for a sample high temperature tackifier product. These sample formulations are described in Table 3. They do not specify the wt% Group II oil in the OCP viscosity index improver ("OCP VII").

Table 3: Formulations prepared to test and optimize the performance of the novel tack preservative in a realistic lubricant containing OCP viscosity modifier, Group II oil, and diluted tackifier. Performance was maximized by doubling the tackifier polymer content and raising the level of preservative by an order of magnitude.

Sample	**A0**	**A1**	**A2**	**B0**	**B1**	**B2**
Note	1x PIB **Control**	1x PIB 1x TP	1x PIB 10x TP	2x PIB **Control**	2x PIB 1x TP	2x PIB 10x TP
wt% PIB 600k	0.08	0.08	0.08	0.17	0.17	0.17
wt% OCP VII	25.00	25.00	25.00	25.00	25.00	25.00
wt% Preservative	0.00	0.02	0.17	0.00	0.02	0.17
wt% Group III Oil	74.92	74.90	74.75	74.83	74.82	74.67
%String, 1hr at 200˚C	90	82	100	91	100	100
%String, 2hr at 200˚C	71	82	60	81	94	100

Sample A0 is the control group: a Group III lubricant with PIB tackifier and OCP viscosity modifier. The % string length after 2hrs at 200˚C is 71% which is greatly improved over the simple 0.8wt% PIB 600k tackifier with 0% additive in Figure 6. This is due to the contribution of larger percentages of shorter OCP polymer to provide viscosity in addition to the small percentage of long PIB tackifier. As the PIB tackifier degrades due to thermal instability the viscosity of the degraded lubricant is maintained by the more stable OCP viscosity modifier. When the PIB tackifier is used as the sole source of viscosity improvement (without an OCP viscosity modifier) then viscosity will decay exponentially under heating as the small concentration of highly effective tackifier chains break down into a small concentration of short pieces that do not provide tack or viscosity. The oxidation-prone nature of the OCP viscosity modifier may also help prevent oxidation of the PIB.

When the tack preservative was added at a treat rate based on Figure 7 (Sample A1) it reduced 1hr % string length and increased 2hr % string length versus the initial string length. The string length was stabilized between the two measurements but an 18% loss of string was still observed. In prior samples from Figure 6 and 7 no string length loss was observed. It was hypothesized that the preservative required some minimum concentration in the oil to affect the PIB and survive radicals generated by the oil. The treat rate of tack preservative was increased by an order of magnitude to produce Sample A2. This increase in additive improved

1hr heat resistance but greatly reduced 2hr heat resistance versus samples A0 and A1. Higher preservative to PIB ratios appear to accelerate degradation of string length. The initial improvement at 1hr may have been the preservative acting as an antioxidant prior to accelerating degradation.

The hypothesis guiding formulation was adjusted to consider both the ratio of tack preservative and PIB and their overall concentration in the lubricant. Sample B0 was produced as the control group for the B series of samples with double the PIB content versus the A0-A2 samples. This gave the same 1hr % string length remaining value as sample A0 with half the PIB. B0 had better 2hr % string length remaining as A0 but not better than additized A1. Tack preservative was added to the control, B0, to produce additized sample B1. This was an improvement on string length stability at high temperature versus the A0-A2 series. However string length stability remained lower than the results with the simple PIB 600k tackifier in Figure 6. Sample B2 was prepared using an order of magnitude more tack preservative to achieve no string loss after 1hr and 2hr at 200˚C.

In summary, we have demonstrated a novel tack preservative which prevents the measurable loss of tack during long-term (16-24hrs at 150˚C) and short-term (1-2hrs at 200˚C) thermal degradation experiments. This new additive is capable of operating in Group III base oil with an OCP viscosity modifier. Additionally, less pure Group II diluent oils do not prevent the tack preservative from functioning, unlike BHT in prior studies.

III.d. Preliminary Investigation of High Temperature Polymers

OCP and PIB polymers are only a small part of the commercial polymer sector. There are roughly thirty polymers common in industrial applications and these are separated into four tiers.[22] Several inherently high temperature polymers with working temperatures ranging up to above 200˚C were obtained to prepare high temperature polymer-oil solutions. Polyethylene terephthalate (PET) is an engineering polymer with very low cost containing aromatic terephthalate in its backbone. Polysulfone (PSU) is known for its relatively weak solvent resistance. Polyphenylsulfone (PPSU) was chosen due to its lower polarity and higher hydrocarbon content than polysulfone. Polyetherimide (PEI) is a high performance polymer with high polarity which is attractive for ester-based Group V oils. Standardly available extrusion grades of polymer were obtained to avoid the cost of specialized formulations.

Engineering and high performance polymers are typically polar with ether, amide, or ketone linkages between subunits of benzene. These linkages have positively and negatively charged bonds which cause a strong attraction between chains to neutralize these charges.[23] ‘Pi-pi stacking’ occurs between the non-polar benzene units and further strengths that attraction.[23] Solvents and oils to dissolve the high polymers must then interact with both the polar linkages and non-polar benzene backbone to disrupt the attraction between chains.

The most effective solvent was a mixture of toluene and methyl ethyl ketone (MEK). The two components of this co-solvent system contribute both the polar and aromatic solvency required. This solvent system produced a range of effects on the polymers. PET was dissolved in toluene:MEK at room temperature to concentrations as high as 10wt% to form a gel. PSU with toluene:MEK formed an interesting free-flowing latex phase. PEI gave a similar effect with much greater viscosity with toluene:MEK. PPSU turned from clear to white from the toluene:MEK but did not flow.

While the toluene:MEK blend is effective in some cases it has a low boiling point (90˚C) that limits its application and creates the issue of flammable vapors. Elevated temperatures used in lube oil (~80˚C, 180˚F) and grease (~200˚C, 400˚F) production would not be compatible with this method. Dissolution of the polymers in high solvency base oils like Group I, naphthenic, bright stock, and esters near the flash point of the oil (150-200˚C) was not successful.

Based on this initial inquiry there are several recommendations for future work. Most high performance polymers only begin to melt above 200˚C and though many high solvency base oils can approach this temperature the oils will become oxidized. Nitrogen blanketing or autoclaving is necessary. Another consideration is the initial form of the polymer. Extruded polymer may be ground down but powdered grades for applications like rotomodeling offer high surface areas to accelerate the rate of dissolution. Greater solubility may also be accomplished by selecting special grades of polymer with some fraction of the benzene backbone replaced by more soluble C4-C6 alkyl units.[23] For example, nylon, polyphthalimide, and Kevlar are all polyamides which differ primarily by aromatic content from 0-100%.

IV. Conclusions

Lubricant additives are most often needed in extreme, high temperature conditions when they are most likely to be degraded. Tackifiers based on polyisobutylene chemistry are especially sensitive to long- and short-term periods of heating due to their chemical structure. Improving the state-of-the-art for high temperature tackifier stability was approached from three areas in this investigation. Conventional wisdom guides high temperature lubricant formulation toward Group III oils due to lower impurities like aromatics and heteroatoms.

We have demonstrated, through studying individual impurity species added to Group III oil, that base oil composition versus thermal stability of PIB is more complicated than originally thought. Some ‘bad actors’ exhibit a stabilizing effect for PIB at 0.1wt% (1000 ppm) concentration. More work is needed to tell if this trend continues for high or lower concentrations of impurity. Lessons learned from the base oil impurity study helped develop a novel tack preservative which greatly stabilized string length in PIB-based tackifiers over 2-24hrs of high temperature treatment. This new additive can correct for the thermal instability of PIB and serve as the active ingredient in new high temperature tackifier formulations

Preliminary work on expanding the library of polymers suitable for tackifier products did not identify a promising candidate from the high performance polymer family. Polymer physics predicted effective viscosity modification and tack if such polymers could be dissolved. Based on this work it appears that PIB modified with the tack preservative is the most cost-effective and readily available way to advance the current performance of tackifiers at high temperature.

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