

# TACKIFIERS FOR HIGH TEMPERATURE LUBRICANTS

Victor Levin, Ph.D. and Fredric Litt, Ph.D.



## FUNCTIONAL PRODUCTS INC.

8282 Bavaria Road, Macedonia, Ohio 44056, USA

Tel: 330-963-3060 Fax: 330-963-3322

[www.functionalproducts.com](http://www.functionalproducts.com)

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### SUMMARY

It has long been observed that polyisobutylene (PIB) -based tackifiers are thermally unstable at temperatures well below their ceiling temperatures, temperatures that may be encountered in both service and manufacturing of high-temperature greases. We have found that degradation of the polymer occurs as a consequence of the oxidation of the base oil and, in API Group I lubricants, will respond to antioxidants. However, the oxidative breakdown of even the small amount of Group I oil introduced with conventional additives negates any added stability of tackifier-containing lubricants made with Group III base oils, the performance being limited to the Group I level. Antioxidants alone will not recover the Group III performance, but Group III performance can be attained if the tackifier additive itself is reformulated to use a Group III diluent.

### INTRODUCTION

Tackifiers are solutions of polymers in oil, and through most of their history they were limited to polyisobutylene dissolved in petroleum oil. More recently, however, other polymer types with molecular weights from about 200,000 to 6,000,000 have been used to make petroleum oil tacky [1]. The tackiness of oil solutions depends upon several parameters, including the chemical structure of the polymer (coiled vs. uncoiled for polymers with small Kuhn segment length [2] or the orientation of chains in the direction of extension for more rigid polymer chains), the molecular weight of the polymer and the viscosity of the base oil. For a given polymer, increasing the base oil viscosity is accompanied by an increase in tackiness. For the same oil, increasing the polymer molecular weight is accompanied by an increase in tackiness. For example, the string length of a PIB solution in oil at the same polymer treatment level, increases ten fold with an increase in PIB molecular weight from 2,000,000 to 4,000,000. (note: All string lengths refer to the "ductless siphon" test; see Appendix.) It therefore seems that by simply increasing the polymer molecular weight, it is possible to substantially increase the tackiness. Increasing the polymer molecular weight, however, is coupled with a decrease in both thermal/oxidative stability and shear stability.

Conventional tackifiers based on polyisobutylene are not thermally stable and tackiness and viscosity are lost at temperatures above about 90°C. It will be shown below that the thermal stability of the polymer solution is strongly dependent on the polymer molecular weight. Presently manufactured tackifier solutions based on polyisobutylene are prepared with Group I oils and, as mentioned above, are not stable 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 and IV base oils. We have now seen requests for thermally stable tackifiers for use in Group III and IV greases.

The reason for the instability of polyisobutylene (and even ethylene-propylene copolymers) in Group I oil is not fully clear at this time. The comparison of the high temperature performance of these polymers

in Group I-II oils with the high temperature performance in Group III-IV oils (which are themselves much more thermally stable than Group I-II oils) could help to understand the thermal stability of polymers in Group I-II oils.

## EXPERIMENTAL

We verified thermal stability or instability of polymer solutions in the oil by viscosity measurements and by ductless siphon method (see Appendix and Fig.1)

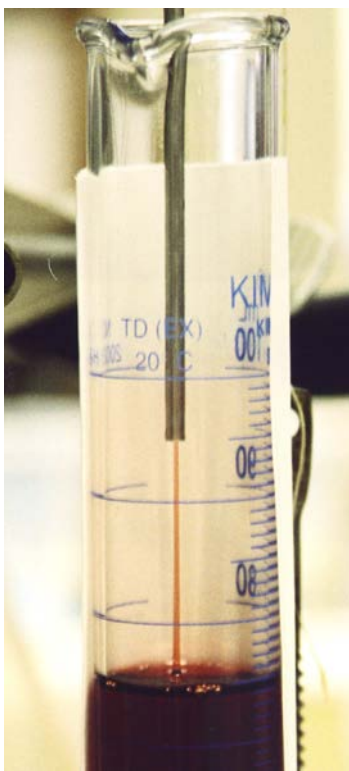


Figure 1 Ductless Siphon Apparatus

Three polymers that produce tackiness in petroleum oil were studied: ethylene-propylene copolymer with a molecular weight about 200,000 and two polyisobutylenes with molecular weight 2,000,000 and 4,000,000. The diluents used in making the tackifier additives were Group I through Group III base oils. The antioxidant was 2,6-di-t-butyl-p-cresol.

Polymers were granulated and then dissolved in oil at 85°C in a glass container on hot plate with low-shear agitation. The time of dissolution was approximately 48 hours. The kinematic viscosities of the initial solutions were measured at 100°C according to ASTM D445. The resulting polymer solutions were stored in an oil bath at 100-150° C ( $\pm 0.5^\circ\text{C}$ ). Kinematic viscosities at 100°C (ASTM D445) were measured periodically during the storage time to monitor the change in viscosity. Tackiness was measured periodically during storage using the "ductless siphon".

## RESULTS AND DISCUSSION

For a polymer solution to be tacky, the polymer chain should be capable of full extension. One property that encourages chain extension is steric hindrance between monomer segments. Frequently, this steric hindrance requires that the monomer be 1,1-disubstituted, an example being isobutylene.

Polymers of 1,1-disubstituted monomers, however, tend to be thermally unstable. Unlike other polymers which can not exist in equilibrium with their monomers, these exhibit a "ceiling" temperature where the polymer and monomer can exist in equilibrium [3]. At higher temperatures, the polymer simply depolymerizes. In practice, these polymers are not commercially useful at temperatures close to their ceiling temperature, since evaporation of the monomer drives the equilibrium toward depolymerization. A typical technical data sheet [4] on a polyisobutylene -based tackifier warns that "Viscosity stability is lost at temperatures in excess of 92°C", which is a temperature well within the limits of the tackifier's manufacturing process, the manufacturing and blending temperatures of many greases, and the service expectations of high temperature lubricants.

Olefin copolymer-based tackifiers, however, lack the 1,1 substitution pattern and are therefore more thermally stable than those based on polymers with this substitution, as confirmed by our experimental data.

Viscosity loss of two polyisobutylene-based tackifiers in 70 SEN paraffinic oil at 100°C is demonstrated in Fig 2.

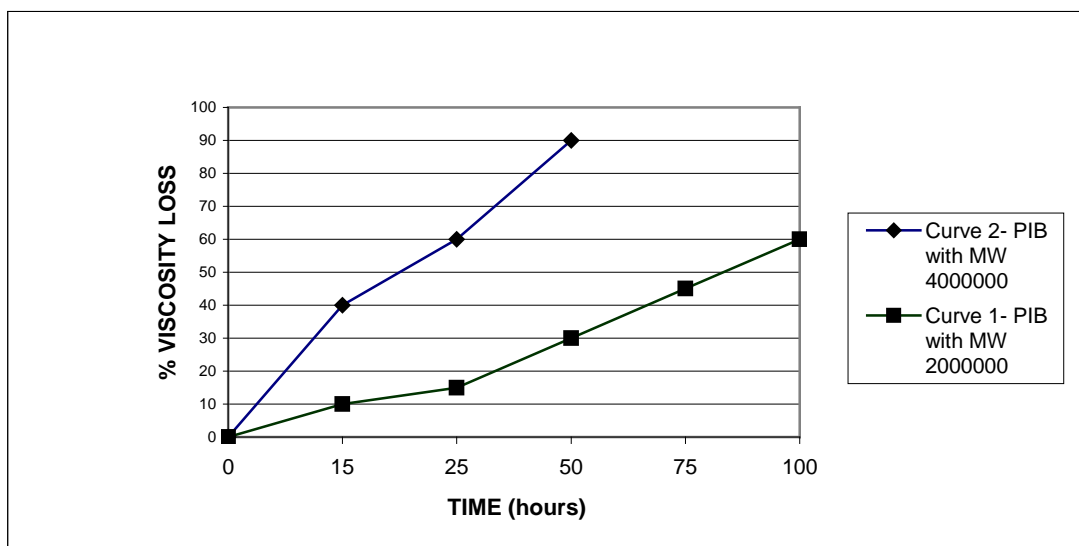


Figure 2. Viscosity loss of PIB solution in API Group I paraffinic oil at 100°C w/o antioxidant.

Curve no. 1 corresponds to the solution of polyisobutylene with molecular weight 2,000,000 (Viscosity Average Molecular Weight, Flory); curve no. 2 corresponds to a solution of polyisobutylene with molecular weight 4,000,000. In both cases we see a dramatic loss of viscosity and a dramatic loss of tackiness. Some loss is also found with olefin copolymer based tackifiers. For example, the viscosity of an olefin copolymer solution in Group I oil drops from 1000 cSt to 960 cSt after only 5 hours at 100°C.

There are two possible processes which could explain such a dramatic decrease in the solution viscosity of different polymers in oil: degradation of the polymer itself or oxidation of oil with the subsequent degradation of polymers as result of the oil oxidation.

A well-documented auto-oxidation mechanism for oil involves a free-radical chain reaction [5-7]. In an initiation step, alkyl free radicals are formed by unspecified thermal processes. These radicals will react easily with oxygen forming peroxy radicals. The reaction is propagated by the reaction of the peroxy radical with a new hydrocarbon oil molecule forming both a hydroperoxide and another alkyl radical. This new radical will also react with oxygen forming a new peroxy radical. The initial reaction products are generally hydroperoxides.

The reaction is branched by a hydroperoxide splitting into two new radicals, each of which can form new alkyl radicals by reacting with oil. This process is termed secondary initiation and becomes the predominant initiation mechanism. Reaction of these alkyl radicals with oxygen makes new peroxy radicals and the oxidation reactions continue.

In a polymer in oil solution, the peroxy radicals formed in oil oxidation can attack the polymer chains as easily as they attack the oil, each polymer molecule being surrounded by oil molecules. The propagation and branching stages for the polymer molecules occur simultaneously with those for the oil molecules.

It has been described in the literature that polyisobutylene is a very stable polymer under normal condition of use. There are some data that indicate that polyisobutylene in bulk is thermally stable at 100°C. The viscosity change of low molecular weight polyisobutylene at a storage temperature below 120°C is negligible during a one month period. A low molecular weight neat polyisobutylene polymer loses only 9% of its viscosity at a temperature as high as 177°C [8].

According to [9], medium and high molecular weight polyisobutylene polymers begin to degrade at 160-180°C. As shown above, olefin copolymers in bulk should be more stable than polyisobutylene polymers but they are also thermally unstable in oil solution. It should be noted that the test temperature (100°C) was well below polyisobutylene's ceiling temperature. On the basis of this data, it can be proposed that the degradation of polyisobutylene polymers and olefin copolymers in oil solution can be caused by the oxidation of the oil itself.

It is very well known that antioxidants can be used to prevent the deterioration of oil. If the oxidation of oil is the main cause of polymer degradation, the inhibition of oil oxidation can prevent the polymer degradation in solution.

Fig.3 illustrates the viscosity loss of solutions of polyisobutylene with various molecular weights in Group I oil at 100°C, with and without antioxidant. It is clear from this data that the addition of an antioxidant to oil substantially increases the thermal stability of the polymer solution in Group I oil.

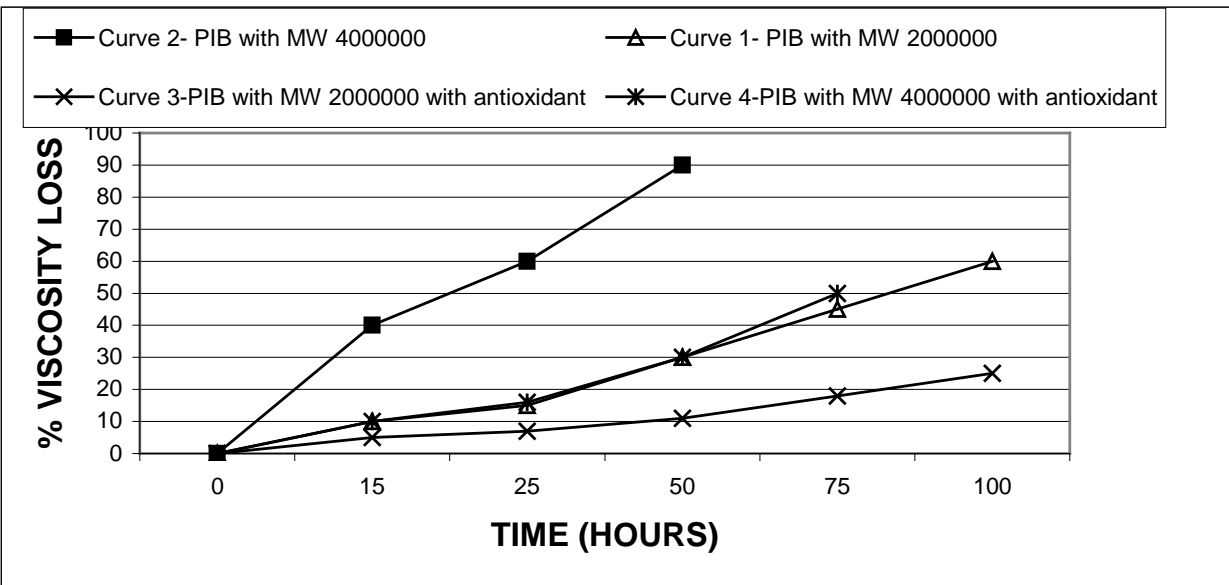


Figure 3. Comparison of Viscosity loss of PIB solution in API Group I paraffinic oil at 100°C w/o antioxidant and with the antioxidant.

The polymer solutions, however, lost viscosity during storage at 100°C, even in the presence of an antioxidant. This viscosity loss was accompanied by a considerable decrease in tackiness. As an example, the string length for a polyisobutylene solution dropped from 65 for the initial solution to a final value of 15 without the presence of an antioxidant. The string length dropped to 49 for the solution with an antioxidant after storage at 100°C. Increasing the amount of antioxidant had almost no effect on this value. We can conclude that antioxidants are helpful but insufficient in Group I oil at temperatures as low as 100°C.

The conventionally used Group I base oils are gradually being replaced by base oils that are produced by hydro-treating or hydro-treating and catalytic dewaxing (Groups II and III). Group IV base stocks synthetic and generally more costly. Polyalphaolefins have been the dominant synthetic lubricant base stock since the 1970s because of their excellent physical properties including superior oxidative and thermal stabilities [10]. We can expect that the thermal stability of polymer solutions in Group II-IV oils should be higher than the thermal stability of these same polymers dissolved in Group I oils.

Fig.4 represents the viscosity loss at 100°C of a polyisobutylene (molecular weight 2,000,000) solution in a Group II oil and, for comparison purposes, in a Group I base oil, both solutions having 0.1% antioxidant. It is evident that the thermal stability of polyisobutylene in Group II base oil is much greater than the thermal stability in Group I base oil. The viscosity loss after 100 hours of storage at 100°C is about 8% for the Group II solution versus about 25% for the Group I solution.

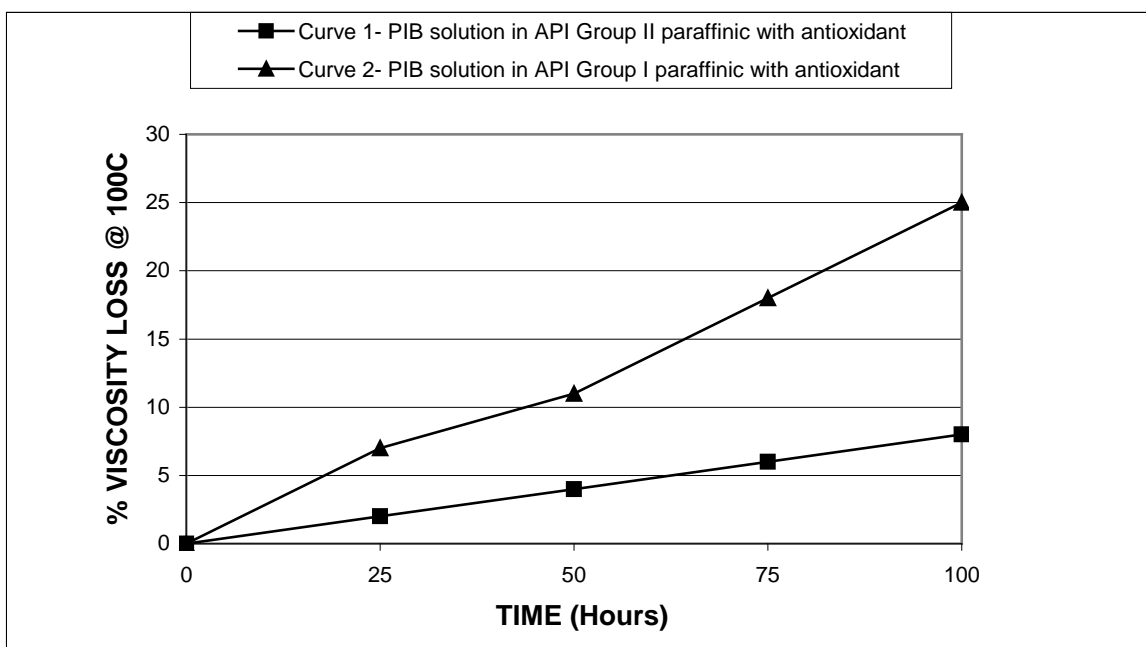


Figure 4. Viscosity loss of PIB in API Group I and Group II paraffinic oils with antioxidant.

Increasing the storage temperature of the polymer solutions in both Group I and II oil to above 100°C resulted in a dramatic decrease in thermal stability. None of these polymer solutions can be used at sustained operating temperatures of 140-150°C.

We investigated the breakdown of antioxidant-treated blends of tackifier in Group III oil. Despite the antioxidant, the viscosity of 5% PIB tackifier (made using Group I oil) in Group III oil drops from 6.8 cSt to 4.6 cSt after 48 hours storage at 120°C. This final viscosity is close to the initial viscosity of the Group III base oil (4.4 cSt); after these storage conditions the additive contributed neither tackiness nor thickening. This observation surprised us, since we expected the Group III oil's superior oxidative stability to extend the tackifier lifetime.

To eliminate a variable from the study, we dissolved the PIB in the same Group III base oil that was to be used in making the grease. We then used this tackifier, with antioxidant, in making Group III oil blends that we tested for viscosity and tackiness retention. The results are shown in Table 1; we found the tackifier made using Group III base oil to be remarkably more stable than the conventional additive in the same base oil.

Encouraged by these results we tested this same additive in a Group IV (PAO) and found stability similar to that in the Group III. We also tested a non-PIB tackifier polymer additive and found similar results. Even at 150°C, we found no particular advantage for PAO over Group III as diluent for manufacturing the additive.

Raising the test temperature to 170°C, Table 1 showed a useful level of stability even at that high temperature. While this result is not too unexpected for the non-PIB tackifier, it is more surprising for the PIB tackifier, since that temperature is approaching the ceiling temperature for polyisobutylene.

Tackifier Polymer		2M PIB	200K OCP
Tackifier Diluent		Group III	Group III
Test Base Oil		Group III	Group III
Test Temperature	Deg C	150	150
Viscosity Loss @ Hours			
0		0	0
24		1.2	0.9
48		0.6	0.4
Test Temperature	Deg C	150/170	150/170
Hours		48/24	48/24
Viscosity Loss		1.2	1.1

Table 1. Viscosity Change of Lubricants with Group III Oil

To confirm that the small amount of base oil introduced with the additive was responsible for the large difference in thermal stability, we tested the Group III PIB tackifier / antioxidant / Group III base oil combination with 5% and 10% added Group I paraffinic base oil, Table 2. Again, we found the thermal / oxidative performance to degrade to the level of a Group I combination.

As Table 2 shows, if 5-10% of Group 1 oil is added to the finished lubricant, the viscosity drops substantially even with a test temperature as low as 120°C. This means that small amount of Group 1 oil has poisoned the stability of the Group III oil. This data confirms our hypothesis regarding the dominant role of base oil oxidation in the degradation of polymer-in-oil solutions. We can conclude that conventional tackifiers manufactured using Group I oil will cause the loss of the thermal and oxidative stability that would otherwise be expected of Group III-IV oils.

Tackifier Polymer	2M PIB	2M PIB	2M PIB
Tackifier Diluent	Group III	Group III	Group III
Added Group I Oil	0	0.05	0.1
Test Temperature	120 deg C	120 deg C	120 deg C
Hours			
0	0	0	0
24	1.2	26	23
48	0.8	49	42

Table 2. Viscosity Loss with Group I Oil Added to Group III Lubricants

The viscosity loss of polyisobutylene with molecular weight 2,000,000 and 4,000,000 dissolved in Group III and IV base oils, each treated with either 0 or 0.1% antioxidant, during storage at 100°C, is illustrated in Tables 3A and 3B. String length using these additives were identical at the beginning and at the end of storage test (100 hours). These tests were repeated using olefin copolymer and yielded the same results.



Tackifier Polymer	2M PIB	2M PIB	4M PIB	4M PIB
Tackifier Diluent	Group III	Group III	Group III	Group III
Antioxidant	0.001	0	0.001	0
Temperature	100 deg C	100 deg C	100 deg C	100 deg C
Hours				
0	0	0	0	0
24	0.4	0.6	0.2	0.8
48	0.3	0.4	1	1.6
72	1.2	0.1	1	1.2
96	0.2	0.3	0.4	1.5

Table 3A. Viscosity Loss of Tackifier in Group III Oil with and without Antioxidant

Tackifier Polymer	2M PIB	2M PIB	4M PIB	4M PIB
Tackifier Diluent	Group IV	Group IV	Group IV	Group IV
Antioxidant	0.001	0	0.001	0
Temperature	100 deg C	100 deg C	100 deg C	100 deg C
Hours				
0	0	0	0	0
24	0.8	1	0.8	0.8
48	1.2	0.9	1	1.6
72	0.9	0.9	1.6	1.2
96	0.7	1.5	0.2	0.3

Table 3B. Viscosity Loss in Group IV Lubricants with Tackifiers with and without Antioxidants

We decided, based upon the superior thermal stability of polymer solutions based on Group III and IV oils, to experimentally look at higher temperatures close to the temperature of polymer de-polymerization.

Table 4 shows the viscosity of solutions of polyisobutylene (molecular weight 4,000,000) and olefin copolymer (molecular weight about 200,000) in PAO with 0.1% of antioxidant at 150°C. The viscosity loss was zero. The string length using these additives was practically the same at the beginning and at the end of storage period.

Tackifier Polymer	4M PIB	200K OCP
Tackifier Diluent	Group IV	Group IV
Antioxidant	0.001	0.001
Temperature	150 deg C	150 deg C
Hours		
0	0	0
24	0.8	1.3
48	0.4	1.1
72	1.8	0.8
96	0.9	1.5

Table 4. Viscosity Loss of Tackifiers in Group IV Oil with Antioxidants

Polyisobutylene with molecular weight 4,000,000 is an excellent polymer additive for providing tackiness to oil. The main disadvantage of this polymer, as for all polymers with very high molecular weight, is low shear stability. Polyisobutylene polymer with molecular weight 2,000,000 is also very effective as a tackifier and is much more shear stable.

Due to their lower molecular weight, olefin copolymer-based tackifiers produce shorter strings than polyisobutylenes but the lower molecular weight makes them much more shear stable. Table 5 illustrates the change in viscosity of solutions of polyisobutylene in a Group III base oil and an olefin copolymer in the same oil during storage at 150°C. The viscosity loss after 96 hours of storage did not exceed 10%.

Tackifier Polymer	4M PIB	200K OCP
Tackifier Diluent	Group III	Group III
Antioxidant	0.001	0.001
Temperature	150 deg C	150 deg C
Hours		
0	0	0
24	2	1
48	5	3
72	8	6
96	10	7

Table 5. Viscosity Loss of Tackifiers in Group III Oil with Antioxidants

Table 1 represents the thermal stability of finished lubricants with the same polyisobutylene tackifier in different Group III oils (test for 48 hours at 150°C and, after that, for 24 hours at 170°C). These finished lubricants were completely stable under these very severe conditions. (The temperature of 170°C is very close to the polyisobutylene ceiling temperature).

Most of the above summarizes the stability of the blends in terms of viscosity, which is easier to measure than tackiness but not really the objective of the additive. Table 6 summarizes the thermal stability of tackifiers based on Group III oil in Group III base oil both in terms of viscosity and tackiness, as measured by the ductless siphon procedure. The table shows that these tackifiers fulfill the objective of providing the required high-temperature stability in tackiness stability as well as in viscosity stability.

	<b>V-378</b>		<b>V-388</b>	
Tackifier Polymer	2M PIB	2M PIB	200K OCP	200K OCP
Tackifier Diluent	Group III	Group I	Group III	Group I
Test Base Oil	Group III	Group III	Group III	Group III
Antioxidant	0.001	0.001	0.001	0.001
Temperature	100 deg C	100 deg C	100 deg C	100 deg C
Hours	96	96	96	96
Additive Viscosity Loss (%)	0	37	0	5
Lubricant String Length Loss (%)	0	31	0	25
Temperature	120 deg C	120 deg C	120 deg C	120 deg C
Hours	96	96	96	96
Additive Viscosity Loss (%)	0.2	33	0	5
Lubricant String Length Loss (%)	7.7	83	0	25
Temperature	150 deg C	150 deg C	150 deg C	150 deg C
Hours	72	72	72	72
Additive Viscosity Loss (%)	0.1	97	1	--
Lubricant String Length Loss (%)	7.7	100	9.1	--

Table 6. Group III Lubricants with Tackifiers and Antioxidants  
Tackiness Loss and Viscosity Loss

## CONCLUSIONS

- The oxidation of polymer-containing lubricants can be monitored by viscosity changes that are due to polymer breakdown.
- The breakdown of PIB at temperatures below its ceiling temperature, about 180-200°C, is driven by oxidation of the base oil.
- Antioxidants can be used to protect tackifier - containing lubricants at temperatures up to about 120°C.
- In a thermal / oxidatively stable Group III or IV base oil, PIB can be used at temperatures approaching its ceiling temperature.
- As little as 5% Group I oil, which could enter unintentionally as the diluent oil of additives, will degrade the performance of a Group III lubricant to the Group I level.

- Both PIB and non-PIB additives can be tailored for high temperature performance by manufacture using a Group III diluent oil.

## APPENDIX

A vacuum is drawn on a capillary under the liquid surface, and the liquid level is lowered so that the capillary is above the surface. The suction pulls the tacky liquid up even through airspace. Tackier solutions will draw a longer filament than less tacky solutions; nontacky solutions are not drawn across the airspace at all. A graduated cylinder is used as the container; the siphon draws the level down until the filament breaks (fig.1). The maximum height of the filament supported by the vacuum is recorded as the string length.

It is convenient to run the test in a 100-ml graduated cylinder. Fill the cylinder with about 105 ml of the oil, then position the capillary so that the bottom of the capillary is at the 100-ml mark. After the vacuum is applied, the level will drop to the 100-ml mark and, for a tacky oil, below the mark until the flow rate decreases to where the string breaks. The cylinder graduations (milliliters) provide a simple way to report the final liquid level.

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## BIOGRAPHIES

Victor Levin received his BS and MS degrees in Chemistry and Physics of Polymers from Mendeleev University, and his PhD and ScD from the Moscow Academy of Sciences. He was formerly the Deputy Director of the Polymer Institute. He is now Laboratory Director at Functional Products Inc. and an Adjunct Professor of Polymer Science at the University of Akron.

