THE EFFECT OF BASE OIL COMPOSITION ON PRESSURE SENSITIVE ADHESIVE PROPERTIES

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Abstract

Hot-melt pressure-sensitive adhesives (PSAs) are typically composed of an elastomeric styrenic block copolymer, tackifying resin and oil. Given that the oil, which acts as a plasticizer, is a major component of the adhesive formulation, it is important to understand how the properties of the oil can affect adhesive performance. In this study, we demonstrate how the chemical composition and viscosity of oils impact adhesive properties. Thirteen different base oils, selected from iso-paraffinic, paraffinic, naphthenic and aromatic types, were tested. We attempted to bring a new perspective to this technology by bringing together researchers from the fields of petroleum and adhesion.

Background

Petroleum base stocks are hydrocarbon based liquids, containing thousands of different hydrocarbon molecules, as well as sulfur and nitrogen containing compounds. Separation and identification of each structure in a base stock is therefore impractical; instead, relative quantities of similar molecules are measured. Molecules are generally classified as paraffins, cycloparaffins (or naphthenes), aromatics, sulfur-containing molecules (thiophenes) or nitrogen-containing molecules. Examples of typical molecules are depicted in Figure 1 through Figure 5. It is important to understand the underlying composition of these base stocks, as it determines properties such as compatibility or solubility with other compounds, such as polymers and tackifiers in adhesives.

Paraffinic molecules are straight aliphatic chains and are considered to be non-polar. Iso-paraffinic molecules contain branched chains. Naphthenic oils contain saturated hydrocarbon rings that are slightly more polar than the straight or branched alkane chains found in paraffinic and iso-paraffinic oils. This slightly higher polarity of the naphthenic oils results in a lower aniline point and greater compatibility with different elastomeric polymers and tackifying resins used in adhesives. Aromatic molecules contain the six carbon, aromatic benzene ring. The polarity provided by this ring gives these molecules a greater ability to solubilize other components in an adhesive formulation. Further discussion of oil interactions in adhesives can be found in references 1-3. Galán (1) found that the paraffinic content of an oil affected PSA tape performance, while Neau (2) and Tsaur (3) found the naphthenic content of an oil to affect adhesive properties.

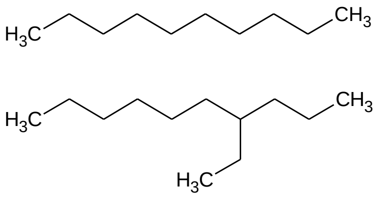

Figure 1. Typical Paraffinic Molecules.

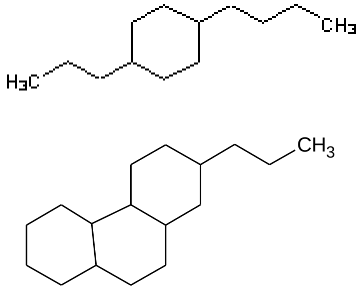

Figure 2. Typical Naphthenic Molecules

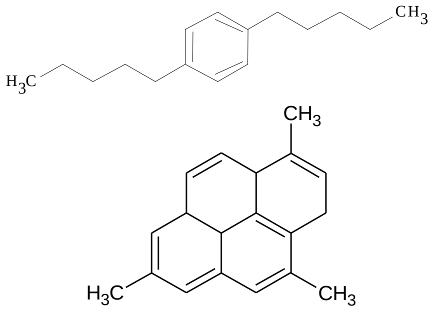

Figure 3. Typical Aromatic Molecules

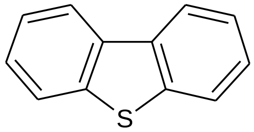

Figure 4. Typical Sulfur-containing Molecule

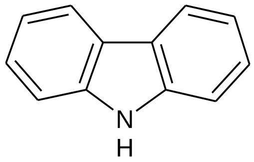

Figure 5. Typical Nitrogen-containing Molecule

Base stocks are classified into two broad types – naphthenic and paraffinic – depending on the crude types they are derived from. (4) Naphthenic crudes and the base stocks refined from them are mainly naphthenic and aromatic in composition. Paraffinic crudes and the base stocks refined from them contain much higher levels of paraffinic molecules. Refining can alter the relative compositions further. For example, severe hydrotreating of paraffinic oils can reduce the aromatic content to essentially zero. Dewaxing can remove significant proportions of normal paraffinic molecules, or convert them to iso-paraffinic molecules.

There are several methods used to determine paraffinic, naphthenic and aromatic carbon content of base stocks. Two empirical methods were developed using solvent refined basestocks. The American Society for Testing and Materials (ASTM) D3238 (5) uses refractive index, density and molecular weight to calculate per cent paraffinic, naphthenic and aromatic carbons. Similarly, ASTM D2140 (6) uses density, specific gravity and refractive index to determine carbon-type composition of insulating oils. Carbon content was also analyzed by high resolution mass spectrometry (HRMS) using an internal method (PCM). The HRMS quantitative analysis uses intensity summations of characteristic fragment ions to determine hydrocarbon types. Standard materials with known cyclic and paraffinic (linear) content are used to calibrate the instrument.

The carbon content analysis and other key properties of the baseoils used in the study are shown in Table 1 and Table 2. The oils are referenced by the Saybolt Universal Viscosity (SUV) and base stock type. A wide viscosity range of paraffinic oils was investigated, including three iso-paraffinic oils and two paraffinic oils with high-aromatic content. Three naphthenic oils were also investigated, one with no aromatics and lower viscosity than the other two oils. Since oil viscosity can have a significant impact on properties of formulated adhesives, five oils with approximately the same viscosity, but very different carbon compositions, were investigated. The key properties of these oils are shown in Table 2.

Table 1. Physical Properties of Iso-paraffinic and Paraffinic Oils.

Physical Property	**Method**	Iso-paraffinic 60N	Iso-paraffinic 100N	Iso-paraffinic 250N	Paraffinic 60N	Paraffinic 220N	Paraffinic 350N
Density @ 15°C	D4052	0.827	0.832	0.846	0.858	0.863	0.867
Specific gravity @ 20°C, Kg/L	D4052	0.826	0.830	0.845	0.857	0.862	0.865
Specific gravity @ 25°C, Kg/L	D4052	0.824	0.828	0.843	0.852	0.860	0.863
Refractive Index @ 25°C	D1218	1.455	1.458	1.465	1.466	1.469	1.473
Viscosity @ 40°C, cSt	D445	10	19	50	10	41	68
Viscosity @ 100°C, cSt	D445	2.6	4.2	8.0	2.5	6.3	8.9
SUV @ 100^{o}F, SUS	D2161	61	102	254	61	213	354
Viscosity Index	D2270	103	120	132	79	101	104
Aniline Point, °C	D0611	106	115	127	94	114	121
Glass transition, °C	DSC	-97.4	-97.4	-87.0	-96.1	-81.9	-78.1
Compositional,%	D3238/ D2140						
Paraffins		73.4	79.8	79.5	54.6	65.4	69.0
Cycloparaffins		26.6	20.2	20.5	45.4	34.6	31.0
Aromatics		0	0	0	0	0	0
Compositional,% (HRMS)	PCM 528						
Paraffins		63.7	62.9	55	25.5	23.6	21.7
Cycloparaffins		36.2	36.9	44.8	74.4	76.3	78.3
Aromatics		0.1	0.2	0.2	0	0	0
Thiophenes		0	0	0	0	0	0
GC Distillation, °C	D2887						
5%		314.5	375	428.5	302	383	367
10%		324	385	447.5	310	395	387
50%		367.5	422	499	343	441	488
95%		415.5	472.5	557	390	506	565
FBP		443	496	589.5	473	561	600

Table 2. Physical Properties of Paraffinic and Naphthenic Mineral Oils.

Physical Property	Method	Paraffinic 550N-A	Paraffinic 550N-B	Paraffinic 550N-C	Naphthenic 550N-A	Naphthenic 550N-B	Naphthenic 100N	Naphthenic 350N
Density @ 15°C	D4052	0.869	0.883	0.874	0.892	0.904	0.886	0.873
Specific gravity @ 20°C, Kg/L	D4052	0.867	0.882	0.873	0.890	0.902	0.885	0.872
Specific gravity @ 25°C, Kg/L	D4052	0.865	0.880	0.870	0.888	0.900	0.883	0.870
Refractive Index @ 25°C	D1218	1.474	1.484	1.479	1.485	1.491	1.478	1.476
Viscosity @ 40°C, cSt	D445	101	90	98	101	98	19	69
Viscosity @ 100°C, cSt	D445	11.5	10.3	10.9	9.1	9.0	3.6	8.7
SUV @ 100°F, SUS	D2161	525	469	511	538	517	101	360
Viscosity Index	D2270	101	96	96	45	50	41	97
Aniline Point, °C	D0611	124	110	118	104	99	91	118
Glass transition, °C	DSC	-74.4	-74.9	-74.2	-67.3	-69.4	-83.6	-76.9
Compositional,%	D3238/ D2140							
Paraffins		69.5	69	65	58		46.6	65.6
Cycloparaffins		31.5	24	32	41		53.4	34.4
Aromatics		0	7	3	<1		0	0
Compositional,% (HRMS)	PCM 528							
Paraffins		21.8	17.3	22.7	7.4	8.5	6.3	17.7
Cycloparaffins		78.2	54.1	64.6	77.1	64.2	92.4	82.3
Aromatics		0	26.1	12.6	15.5	26.9	1.3	0
Thiophenes		0	2.6	0.2	0	0.2	0	0
GC Distillation, °C	D2887							
5%		442	417.5	421.5	366.5	372.5	282	378
10%		456	435.5	441.5	383.5	387.5	297	395
50%		501.5	488	495.5	436	432.5	357	464.5
95%		570.5	556	556	505.5	505.5	441	554
FBP		603	585.5	586.5	544	550.5	504.5	593.5

Discussion – Oil Properties

Pearson's correlation coefficient (r) and accompanying P-values were used to indicate whether there was a linear relationship between two continuous variables. The closer the absolute value of the coefficient was to 1, the stronger the linear relationship between the two variables. A coefficient of 0 indicated that there was no linear relationship between the variables. Coefficients with a P-value of 0.05 or less were considered to be significant.

The Pearson's correlation coefficients and their P-values for the various oil properties were calculated using MiniTab® and are listed in Table 3. Highlighted squares indicate a significant correlation. Interestingly, the paraffinic (linear) and naphthenic (cyclic) carbon content as measured by ASTM D3238 (%Cp and %Cn) and by high resolution mass spectroscopy (HRMS para and HRMS cyclo) were not correlated; however, the D3238 aromatic content (%Ca) was correlated with the HRMS aromatic and HRMS thio (sulfur containing) values. The lack of correlation between HRMS carbon content and D3238 (and D2140) carbon content was attributed to the development of D3238 using American Petroleum Institute (API) Group I, solvent refined base stocks with less than 90% saturates. (See Appendix for API base stock Group classification criteria.) When D3238 is used with Group II or III oils such as those included in this study, a negative number is obtained for aromatics. For the oils in this study, negative %Ca values were set equal to 0 before continuing with the calculations. Compounds relevant to Group II and III analysis are included in the calibration of the HRMS method.

Table 3. Pearson's coefficients and associated P-values for oil properties.

	oil visc	Oil DSC Tg (°C)	%Cn	%Cp	%Ca	HRMS cyclo	HRMS para	HRMS arom	HRMS thio	aniline point (°C)	oil Mw
Oil DSC Tg (°C)	**0.895**										
P-Value	**0**										
%Cn	0.248	0.412									
P-Value	0.413	0.162									
%Cp	-0.292	-0.44	**-0.995**								
P-Value	0.333	0.132	**0**								
%Ca	0.487	0.437	0.512	**-0.594**							
P-Value	0.092	0.135	0.074	**0.032**							
HRMS cyclo	0.421	**0.592**	0.147	-0.124	-0.14						
P-Value	0.151	**0.033**	0.632	0.687	0.648						
HRMS para	**-0.708**	**-0.833**	-0.386	0.412	-0.38	**-0.833**					
P-Value	**0.007**	**0**	0.192	0.162	0.2	**0**					
HRMS arom	**0.652**	**0.621**	0.47	-0.55	**0.884**	0.002	**-0.555**				
P-Value	**0.016**	**0.023**	0.105	0.052	**0**	0.995	**0.049**				
HRMS thio	0.302	0.234	0.436	-0.503	**0.81**	-0.166	-0.234	**0.639**			
P-Value	0.316	0.441	0.136	0.08	**0.001**	0.588	0.441	**0.019**			
aniline point (°C)	0.302	0.113	-0.547	0.538	-0.208	0.048	0.103	-0.263	-0.039		
P-Value	0.316	0.714	0.053	0.058	0.495	0.877	0.739	0.385	0.899		
oil Mw	0.408	0.172	-0.417	0.389	0.018	-0.111	0.116	-0.051	0.174	**0.942**	
P-Value	0.166	0.575	0.157	0.189	0.953	0.717	0.705	0.868	0.57	**0**	
oil Mz	0.463	0.247	-0.388	0.359	0.047	-0.043	0.042	-0.02	0.187	**0.943**	**0.995**
P-Value	0.111	0.417	0.191	0.229	0.878	0.889	0.891	0.947	0.541	**0**	**0**

The Pearson’s correlation coefficients and their P-values show that the oil viscosity (visc) and glass transition temperature (Tg) as measured by differential scanning calorimetry (DSC) were highly, positively correlated with each other. The oil viscosity was moderately correlated with HRMS para (negatively) and HRMS aromatic (positively) content. The oil molecular weight (Mw) was correlated to the oil aniline point. These relationships could be visualized with a matrix plot. The cell where a row and column intersect displays a plot of the two parameters, and the fitted line indicates any apparent relationship between the two parameters, Figure 6. A horizontal line indicates no apparent correlation. Significant interactions are indicated by stars and can be summarized as:

- Oil viscosity correlated strongly with Tg, HRMS para, HRMS arom
- Oil viscosity and Tg did not correlate with %Cn, %Cp or %Ca from D3238
- Oil Tg correlated with HRMS cyclo, para and arom
- HRMS cyclo and HRMS para did not correlate with %Cn and %Cp
- HRMS arom did correlate with %Ca
- %Cn and %Cp were negatively correlated; HRMS cyclo and para were negatively correlated
- Aniline point correlated with molecular weight but not with carbon content

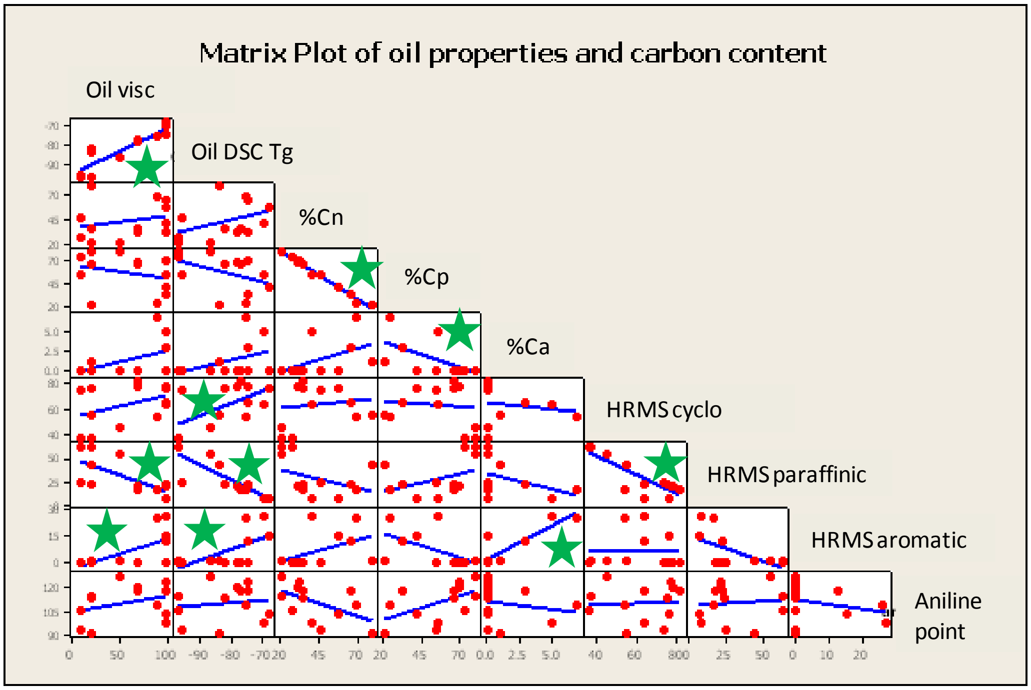

Figure 6. Matrix plot of interactions between oil properties for oils with a wide range of viscosity. Significant interactions are indicated by stars.

When only the 550N oils, with 40°C viscosity about 100 cSt, are considered, slightly different relationships are seen. It is still observed that:

- %Cn and %Cp were correlated
- Tg correlated with HRMS para

Additionally,

- Oil Tg correlated negatively with molecular weight
- HRMS para correlated with aniline point and molecular weight
- HRMS cyclo correlated negatively with %Ca

Hot Melt Pressure Sensitive Adhesive (PSA)

Hot melt adhesives were prepared using a styrene-isoprene-styrene (SIS) block copolymer containing 15% styrene, 19% diblock with a melt index (grams/10 min at 200°C, 5 Kg) of 12. This polymer was blended using sigma blades in a Brabender Plasticorder mixer at 150°C with an aromatic-modified C5 tackifier resin, oil and antioxidant in the ratio 100/140/40/2. The adhesives were coated onto PET film at 150°C at a target weight of 22 ± 2 g/m^2.

PSA Dynamic Mechanical Analysis (DMA)

The adhesives were characterized by dynamic mechanical analysis (DMA), and Pearson’s correlation coefficients were calculated for DMA properties and oil properties. In general, addition of oil to an adhesive reduces the adhesive modulus (G’), Tg and third crossover (3rd cross) temperatures, producing a softer adhesive. It was expected that higher naphthenic carbon (%Cn, HRMS cyclo) and aromatic carbon (%Ca, HRMS arom) content would result in lower third crossover temperatures due to increased compatibility and softening effect of these more polar molecules with the styrenic end blocks of the block copolymer.

Visual examination of the DMA profiles of the prepared adhesives (Figure 7) showed that there were significant differences in adhesive Tg, third crossover temperature and G' at room temperature. Although it was expected that DMA properties would fall into separate groups for each oil type, the range of values obtained using paraffinic oils included the ranges obtained when iso-paraffinic and naphthenic oils were used, Table 4. It was noted that use of iso-paraffinic oils resulted in lower adhesive Tg than did use of naphthenic oils. This correlates with the Tg of the oils.

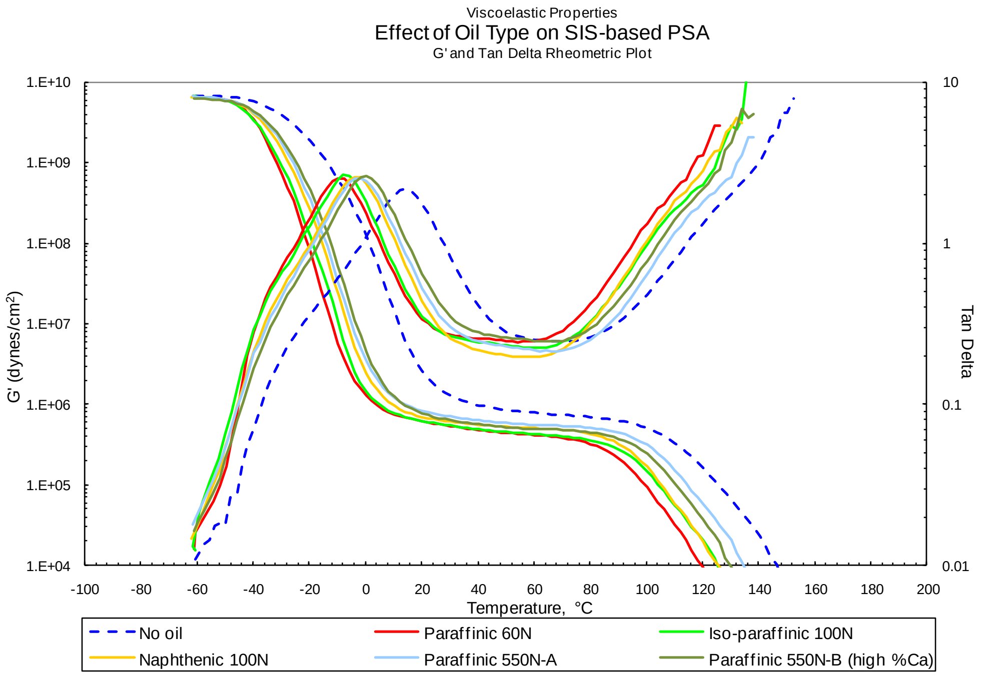

Figure 7. DMA curves for representative pressure sensitive adhesives prepared with paraffinic, iso-paraffinic and naphthenic oils. A control formulation prepared without oil is included for reference.

Table 4. Range of DMA properties obtained for each type of oil tested.

Oil type	**Tg min (°C)**	**Tg max (°C)**	**3rd crossover min (°C)**	**3rd crossover max (°C)**	**G' (25°C) min (x10^5 dynes/cm^2)**	**G' (25°C) max (x10^5 dynes/cm^2)**
Paraffinic	-9.7	0.3	96	106	4.2	7.0
Iso-paraffinic	-7.9	-5.7	100	106	4.2	6.6
Naphthenic	-3.7	0.3	100	106	6.2	6.5
No oil	14.3		114		17.9	

Considering all 13 oils, it was found that the adhesive Tg increased with oil viscosity, oil Tg, and oil aromatic content; and the adhesive Tg decreased with HRMS para content, Table 5. The third crossover temperature, where the adhesive begins to flow, also increased with oil viscosity, oil Tg and aniline point, Figure 8. Surprisingly, no correlations of third crossover temperature with carbon content type were found. Additionally, no correlations were observed between oil properties and the adhesive modulus (G') at room temperature.

Table 5. Pearson's correlation coefficients for oil properties and adhesive DMA properties. Highlighted squares indicate a significant correlation.

	oil visc	Oil DSC Tg (°C)	%Cn	%Cp	%Ca	HRMS cyclo	HRMS para	HRMS arom	HRMS thio	aniline point (°C)
Adh Tg	**0.898**	**0.952**	0.466	-0.505	**0.576**	0.388	**-0.714**	**0.709**	0.4	0.08
P-value	**0**	**0**	0.109	0.078	**0.039**	0.19	**0.006**	**0.007**	0.176	0.794
G (25°C) x 10^5	0.457	0.505	0.384	-0.384	0.279	0.302	-0.392	0.244	0.302	-0.006
P-value	0.117	0.078	0.195	0.195	0.355	0.316	0.185	0.421	0.315	0.984
3rd cross	**0.741**	**0.653**	-0.096	0.083	0.07	0.331	-0.334	0.105	0.094	**0.782**
P-value	**0.004**	**0.015**	0.755	0.787	0.82	0.269	0.264	0.733	0.761	**0.002**

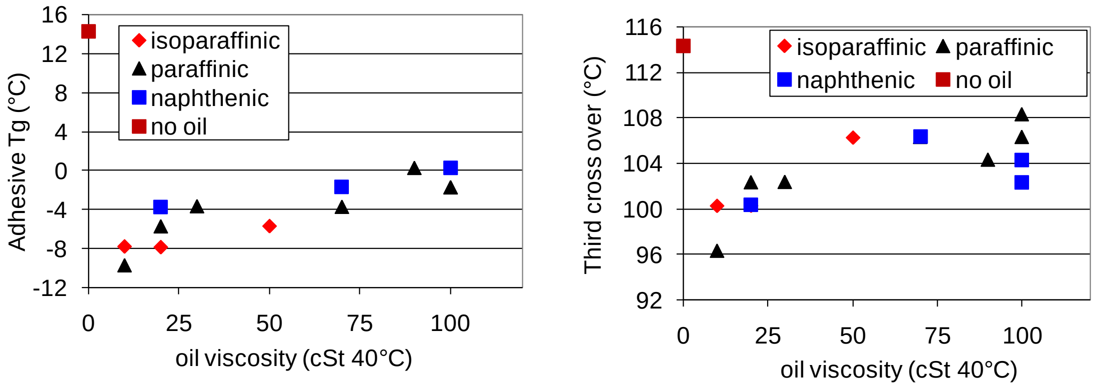

Figure 8. Oil viscosity strongly affected adhesive Tg and third crossover temperature.

It had been previously observed (3) that a higher %Cn reduced oil compatibility with the isoprene rubber phase of SIS block copolymers, resulting in a higher adhesive modulus (G') and Tg. The deGennes' Equation was used to explain this phenomenon:

$$G_n^{o} = v_2^{x} * G_n^{oo}$$

where G_n^{o} = G' at tan delta minimum, G_n^{oo} = neat polymer G' at tan delta minimum,
v_2 = volume fraction of the polymer, and x = exponent which depends on the compatibility of the polymer diluents system.

The deGennes' exponent (x) for these oils in the SIS polymer tested varied from 2.09-2.34, and it did not show a correlation with oil carbon content, Figure 9. As expected. the deGennes' exponent did have a significant negative correlation (-0.8, P-value = 0.001) with adhesive G' at 25°C, indicating that the more compatible oils (higher x) more effectively softened the adhesive, Figure 10.

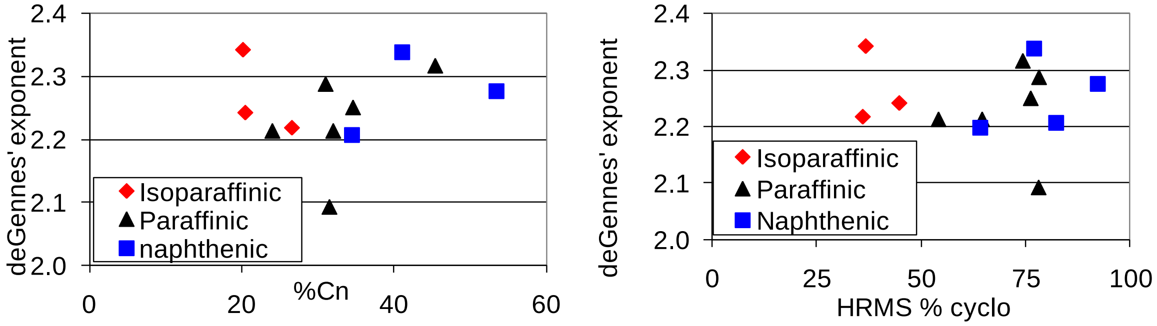

Figure 9. No correlations were observed between deGennes' exponent and oil carbon composition.

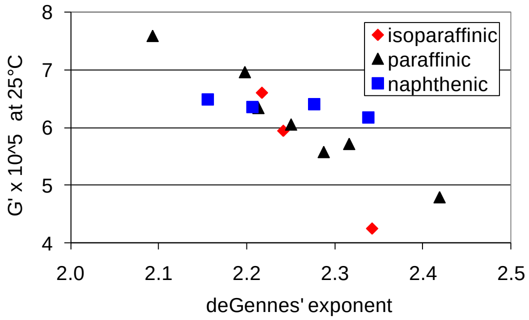

Figure 10. Adhesive modulus at 25°C and deGennes' exponent were strongly related.

When considering the properties and composition of all 13 oils tested, the oils had the following correlations with properties of the prepared adhesives:

- Adhesive Tg increased with oil viscosity, oil Tg, and oil aromatic content
- Adhesive Tg decreased with HRMS para content
- Adhesive Tg and softening point increased with HRMS arom
- Iso-paraffinic oils resulted in lower adhesive Tg than use of naphthenic oils, probably due to the lower Tg of the iso-paraffinic oils
- Third crossover temperature increased with oil viscosity, oil Tg and aniline point
- Increased aromatic or naphthenic content did not result in endblock softening and lower 3^{rd} crossover
- deGennes' coefficient (x) correlated positively with adhesive modulus (G') and negatively with adhesive viscosity, but did not correlate with oil carbon content

When only the approximately 100 cSt viscosity 550N oils were considered, some different relationships between adhesive properties and oil properties were seen.

- Adhesive third crossover temperature increased with aniline point
- Adhesive third crossover temperature and viscosity were negatively correlated with oil HRMS arom, as originally expected
- Adhesive third crossover temperature was correlated negatively with deGennes' x
- Adhesive Tg correlated negatively with oil aniline point

These observations indicate that oil viscosity dominates adhesive properties, but the oil carbon composition does affect adhesive viscosity and flow (3^{rd} crossover temperature) when oils of similar viscosity are compared. Previous results (1) linking PSA tape performance to the paraffinic content of an oil may also be explained by the oil viscosity since the viscosity and paraffinic content of the oils used in that study were correlated with each other.

Tape Performance

Tape performance was measured following PSTC methods for 180° peel and loop tack on stainless steel, room temperature hold power (0.5"x0.5", 1Kg, stainless steel), shear adhesion failure temperature (SAFT), and rolling ball tack (RBT). Aged tape performance was measured after conditioning tape at 40°C and 50% relative humidity for two weeks. Testing details can be found in previous publications. (7) Data is presented in the Appendix.

The influence of oil viscosity on PSA initial peel, loop tack and hold power was evident in Figure 11, while SAFT and RBT do not appear to be affected by oil viscosity.

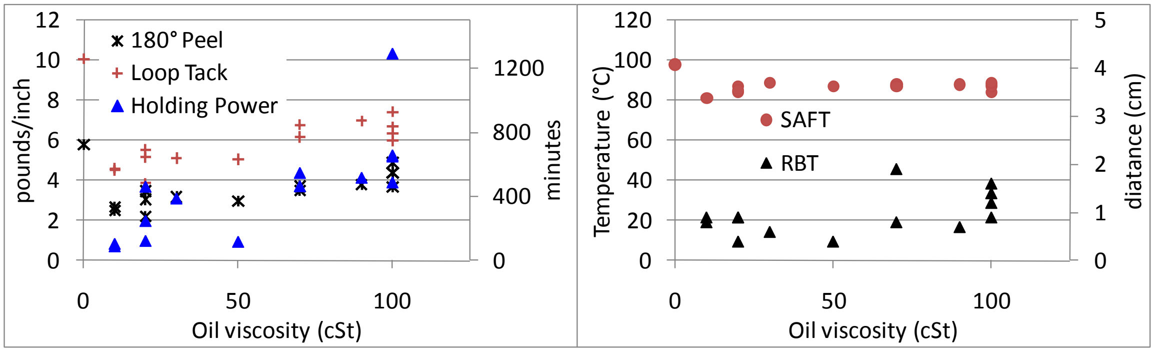

Figure 11. Effect of oil viscosity on initial tape performance. Error bars were omitted for clarity.

Plots of oil viscosity versus initial tape performance, grouped by oil type, showed the effect of oil viscosity on tape performance, Figure 12.and Figure 13. The influence of oil viscosity was reduced when aged tape performance was evaluated. It was not clear from these plots if there were interactions between the oil type and the measured performance.

Pearson's correlation coefficients and their P-values were calculated for the oil properties, adhesive properties, initial tape performance and aged tape performance. Correlations between oil properties and adhesive or PSA tape performance are indicated in Table 6. Oil viscosity and Tg, which are highly correlated with each other, affected almost all measurements of adhesive properties and tape performance. After oil viscosity and Tg, the initial tape performance was most highly influenced by the HRMS paraffinic carbon content, as evidenced by the highly negative correlation coefficients. The oil aromatic content was correlated with the initial hold power of the PSA. Interestingly, when viscosity is removed as a variable (550N oils), the SAFT and RBT are correlated with the oil carbon content.

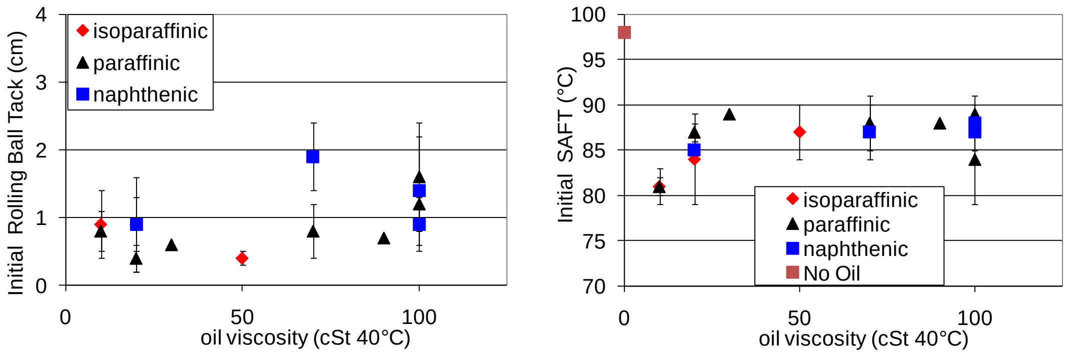

Figure 12. Oil viscosity was not strongly correlated to rolling ball tack or SAFT.

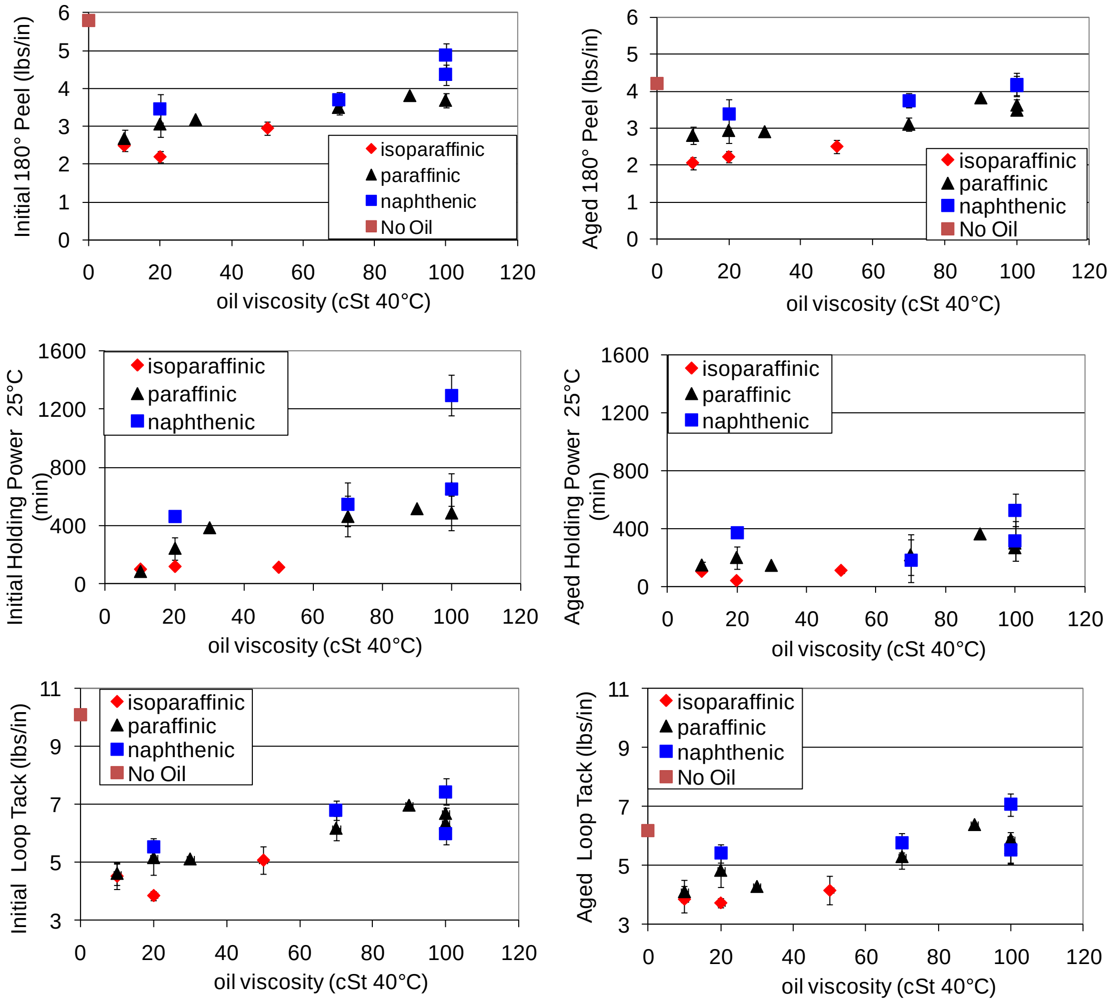

Figure 13. The effect of oil viscosity on tape performance was reduced after tape aging.

Table 6. Oil parameters that positively or negatively influenced PSA properties and performance. Oil viscosity varied from 10 cSt to 101 cSt at 40°C. 550N oils had viscosity ~ 100cSt. "X" indicates an effect on initial tape values. "A" indicates an effect on aged tape values. Underlining indicates a negative correlation.

Correlations	Bulk Adhesive Properties - all oils					Tape Performance - all oils				
	Adhesive Tg	3rd Xover	G' at 25°C	RBSP	Viscosity	180° Peel	Loop tack	Hold power	SAFT	RBT
Oil viscosity	X	X		X	X	X A	X A	X	X A	
Oil Tg	X	X		X	X	X A	X A	X	X A	A
HRMS cyclo						A	X			
%Cn						A		A		
HRMS para	$\underline{X}$					$\underline{X}$ $\underline{A}$	$\underline{X}$ $\underline{A}$	$\underline{X}$ $\underline{A}$		
%Cp						$\underline{X}$ $\underline{A}$	$\underline{A}$	$\underline{A}$		
HRMS aromatic	X			X		X A	A	X A		
%Ca	X						A	X		
Aniline point		X						X		

Correlations	Bulk Adhesive Properties - 550N oils					Tape Performance - 550N oils				
	Adhesive Tg	3rd Xover	G' at 25°C	RBSP	Viscosity	180° Peel	Loop tack	Hold power	SAFT	RBT
Oil viscosity	Not applicable					Not applicable				
Oil Tg						A				
HRMS cyclo										X
%Cn									X	
HRMS para						$\underline{A}$				
%Cp									$\underline{X}$	
HRMS aromatic		$\underline{X}$			$\underline{X}$					$\underline{X}$
%Ca										$\underline{X}$
Aniline point	$\underline{X}$	X				$\underline{A}$				

Visual examination of a matrix plot of the HRMS carbon content versus the initial tape performance, Figure 14, indicates that the type of oil affected the PSA tape response to the amount of each carbon type present in the oil. For example, HRMS cyclo iso-paraffinic oil has a weak positive correlation with initial loop tack, HRMS cyclo naphthenic oil has a strong positive correlation with loop tack, and HRMS cyclo paraffinic oil had no correlation with initial loop tack.

The interaction of carbon content and oil type with PSA properties was seen more clearly with the series of 550N oils that have about 100 cSt viscosity at 40°C but different carbon composition, Figure 15.

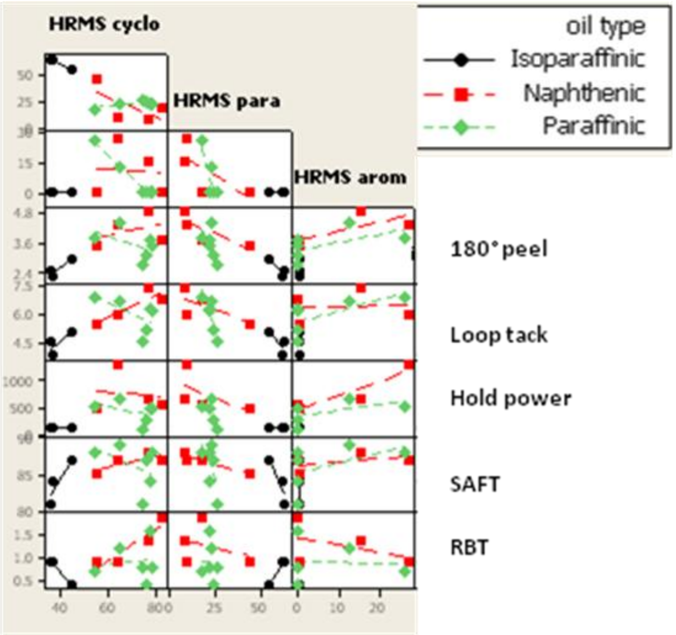

Figure 14. Matrix plot of HRMS carbon content vs. initial PSA performance shows interaction between oil type and carbon content.

Although the trends were similar for both oil types, there were clear differences between the two types. One example is highlighted by the lines added to the interaction plot for adhesive RBSP with HRMS cyclo content. Caution must be used interpreting these results since differences may be due to the differences in oil Tg: about -74°C isoparaffinic 550N oils versus about -68°C naphthenic 550N oils.

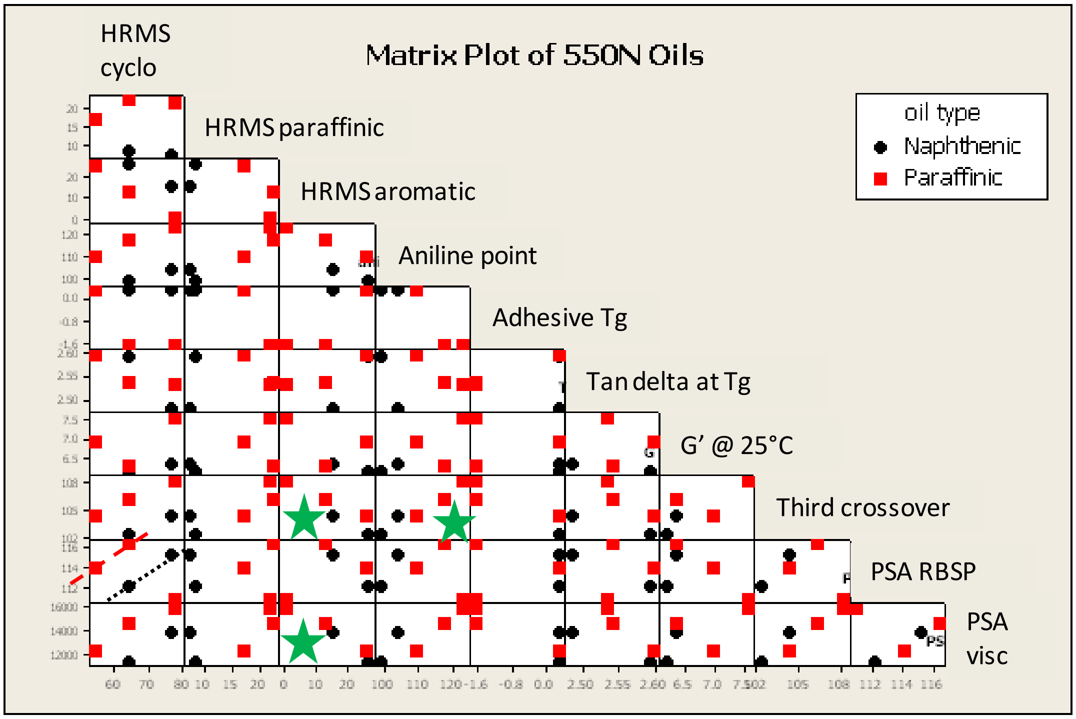

Figure 15. Matrix plot showing 550N oil carbon content correlations with adhesive properties. Significant interactions are indicated by stars

Attempts to model the influence of oil carbon composition on tape performance were not successful due to the high degree of correlation between the various oil properties (Figure 6 and Table 3).

Oil properties and composition had the following correlations with pressure sensitive tape performance:

- Increased oil viscosity increased PSA initial 180° peel, loop tack and room temperature hold power
- The effect of oil viscosity on tape performance was reduced after tape aging
- Initial RBT was not affected by oil viscosity, SAFT was weakly affected
- Paraffinic carbon content (%Cp and HRMS para) negatively correlated with PSA tape 180° peel, loop tack and hold power at room temperature
- Oil aromatic content correlated positively with PSA initial hold power (%Ca and HRMS arom) and with 180° peel (HRMS arom)
- HRMS paraffinic carbon content had a large negative correlation with initial tape performance
- Oil type (paraffinic, iso-paraffinic, naphthenic) appeared to changed the response of the PSA tape to the amount of each carbon type present in the oil
- When oil viscosity was held constant (550N oils),
    - RBT correlated with HRMS cyclo, and negatively correlated with HRMS arom, %Ca
    - SAFT correlated with %Cn (negative correlation with %Cp)
    - Aged peel correlated with oil Tg, and negatively correlated with HRMS para and aniline point

Conclusions

Oil viscosity and oil glass transition temperature are strongly correlated with each other and strongly influence almost all adhesive properties and tape performance measures of the SIS-based pressure sensitive adhesives tested. This influence was greater than any effects from oil base stock type, aniline point or carbon composition. This suggests that the adhesive formulator can modify adhesive performance by adjusting oil viscosity and Tg.

The carbon composition of iso-paraffinic and naphthenic oils appeared to affect tape performance differently, but performance differences may be due to the oil Tg and not the base oil type. Oil carbon content as measured by high resolution mass spectroscopy (HRMS) was correlated to tape performance, and adoption of this method as a standard should be considered. HRMS paraffinic carbon content correlated with initial and aged PSA tape 180° peel, loop tack and hold power at room temperature. HRMS aromatic carbon content correlated with the adhesive glass transition temperature and softening point. This suggests that minor adjustments to adhesive performance can be accomplished by selecting oils with similar viscosity but different carbon composition.

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Appendix

Table 7. The American Petroleum Institute (API) developed base stock categories to differentiate base stocks. Sulfur, saturates and viscosity index are used to classify base stocks.

Base Stock Group	**Sulphur, wt.%**	**Saturates, wt.%**	**Viscosity Index**
Group I	> 0.03	< 90	80 - 120
Group II	≤ 0.03	≥ 90	80 - 120
Group III	≤ 0.03	≥ 90	> 120
Group IV	All Poly-alpha-olephins (PAO)		
Group V	All base stocks not included in Groups I - IV		

Table 8. DMA properties of adhesives prepared.

	Control - no oil	**Iso-paraffinic 60N**	**Iso-paraffinic 100N**	**Iso-paraffinic 250N**	**Paraffinic 60N**	**Paraffinic 220N**	**Paraffinic 350N**	**Paraffinic 550N-A**	**Paraffinic 550N-B**	**Paraffinic 550N-C**	**Naphthenic 100N**	**Naphthenic 350N**	**Naphthenic 550N-A**	**Naphthenic 550N-B**
Tg (°C)	14.3	-7.8	-7.9	-5.7	-9.7	-5.7	-3.7	-1.7	0.3	-1.7	-3.7	-1.7	0.3	0.3
Tan delta max	2.2	2.6	2.6	2.5	2.5	2.5	2.5	2.5	2.6	2.5	2.6	2.5	2.5	2.6
G' (25°C) x 10^5	17.9	6.6	4.2	5.9	5.7	6.1	5.6	7.6	7.0	6.3	6.5	6.4	6.4	6.2
3rd cross	114	100	100	106	96	102	106	108	104	106	100	106	104	102
T @ Tan delta min	70	62	62	66	54	62	62	68	66	66	58	60	62	58
G'no (25°C) x 10^5	7.3	4.8	4.2	4.6	4.3	4.6	4.4	5.4	4.9	4.8	5.1	4.5	4.8	4.2
adhesive deGennes' x	2.1	2.2	2.3	2.2	2.3	2.3	2.3	2.1	2.2	2.2	2.2	2.3	2.2	2.3
G'no D1161	47.5													

Table 9. Pearson’s coefficients and p-values for adhesive and oil properties.

	oil visc	Oil DSC Tg (°C)	%Cn	%Cp	%Ca	HRMS cyclo	HRMS para	HRMS arom	HRMS thio	aniline point (°C)	oil Mw	oil Mz	deGennes' x
Adh Tg	**0.898**	**0.952**	0.466	-0.505	**0.576**	0.388	**-0.714**	**0.709**	0.4	0.08	0.199	0.271	-0.339
P-value	**0**	**0**	0.109	0.078	**0.039**	0.19	**0.006**	**0.007**	0.176	0.794	0.515	0.371	0.257
G (25°C) x 10^5	0.457	0.505	0.384	-0.384	0.279	0.302	-0.392	0.244	0.302	-0.006	0.161	0.189	**0.782**
P-value	0.117	0.078	0.195	0.195	0.355	0.316	0.185	0.421	0.315	0.984	0.599	0.536	**0.002**
3rd cross	**0.741**	**0.653**	-0.096	0.083	0.07	0.331	-0.334	0.105	0.094	**0.782**	**0.805**	**0.85**	-0.429
P-value	**0.004**	**0.015**	0.755	0.787	0.82	0.269	0.264	0.733	0.761	**0.002**	**0.001**	**0**	0.144
PSA RBSP	**0.869**	**0.715**	0.27	-0.32	0.53	0.06	-0.43	**0.704**	0.39	0.31	0.49	0.52	-0.26
P-value	**0**	**0.006**	0.38	0.29	0.06	0.85	0.14	**0.007**	0.19	0.30	0.09	0.07	0.40
PSA viscosity	**0.775**	**0.731**	0.17	-0.17	0.08	0.40	-0.41	0.15	0.05	0.53	**0.6**	**0.643**	**-0.613**
P-value	**0.002**	**0.005**	0.57	0.58	0.79	0.18	0.16	0.62	0.88	0.06	**0.030**	**0.018**	**0.026**

Table 10. Initial tape performance.

Initial tape performance	No oil	Iso-paraffinic 60N	Iso-paraffinic 100N	Iso-paraffinic 250N	Paraffinic 60N	Paraffinic 220N	Paraffinic 350N	Paraffinic 550N-A	Paraffinic 550N-B	Paraffinic 550N-C	Naphthenic 100N	Naphthenic 350N	Naphthenic 550N-A	Naphthenic 550N-B
180° Peel (lb/in)	5.8	2.5	2.2	3.0	2.7	3.1	3.5	3.7	3.8	4.4	3.5	3.7	4.9	4.4
standard deviation	0.7	0.2	0.1	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.4	0.2	0.3	0.3
Loop Tack (lb/in)	10	4.5	3.9	5.1	4.6	5.2	6.2	6.3	7.0	6.7	5.5	6.8	7.4	6.0
standard deviation	2	0.4	0.2	0.5	0.4	0.6	0.4	0.5	0.5	0.3	0.3	0.3	0.5	0.4
Holding Power (min)	5046	103	122	116	88	246	464	488	517	658	461	547	650	1294
standard deviation	374	10	16	12	21	77	139	120	66	74	19	148	111	137
SAFT (°C)	98	81	84	87	81	87	88	84	88	89	85	87	88	87
standard deviation	4	1	5	3	2	1	3	5	3	2	1	3	3	3
Rolling Ball Tack (cm)	>30	0.9	0.9	0.4	0.8	0.4	0.8	1.6	0.7	1.2	0.9	1.9	1.4	0.9
standard deviation	0.0	0.5	0.7	0.1	0.3	0.2	0.4	0.8	0.4	0.8	0.4	0.5	0.8	0.4

Table 11. Aged tape performance.

Aged tape performance	No oil	Iso-paraffinic 60N	Iso-paraffinic 100N	Iso-paraffinic 250N	Paraffinic 60N	Paraffinic 220N	Paraffinic 350N	Paraffinic 550N-A	Paraffinic 550N-B	Paraffinic 550N-C	Naphthenic 100N	Naphthenic 350N	Naphthenic 550N-A	Naphthenic 550N-B
180° Peel (lb/in)	4.2	2.1	2.2	2.5	2.8	2.9	3.1	3.6	3.8	3.5	3.4	3.8	4.2	4.2
standard deviation	0.3	0.2	0.1	0.2	0.3	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.4	0.3
Loop Tack (lb/in)	6.2	3.9	3.7	4.2	4.1	4.8	5.3	5.6	6.4	5.9	5.4	5.8	5.5	7.1
standard deviation	0.7	0.4	0.2	0.3	0.1	0.4	0.4	0.3	0.3	0.2	0.3	0.5	0.6	0.6
Holding Power (min)	3693	100	37	108	148	200	218	299	362	267	371	179	527	312
standard deviation	719	14	27	31	33	75	142	102	56	73	111	66	151	40
SAFT (°C)	98	83	84	89	83	87	90	90	88	91	89	89	90	88
standard deviation	2	3	3	3	3	3	3	1	2	2	1	3	3	2
Rolling Ball Tack (cm)	>30	0.7	0.7	0.7	0.4	0.9	1.2	0.9	0.9	1.0	0.9	1.1	3.3	1.1
standard deviation	0.0	0.6	0.4	0.5	0.2	0.6	0.5	0.5	2.0	0.2	0.3	0.2	2.0	0.6

Table 12. Pearson's coefficients and p-values for initial tape performance.

	oil visc	Oil DSC Tg (°C)	aniline point (°C)	%Cn	%Cp	%Ca	HRMS cyclo	HRMS para	HRMS arom	PSA RBSP (°C)	PSA viscosity (cP)	Adh Tg	3rd cross
init 180 Peel	**0.87**	**0.95**	-0.06	0.55	**-0.57**	0.43	0.53	**-0.8**	**0.67**	**0.752**	**0.669**	**0.911**	0.51
P-value	**0**	**0**	0.84	0.05	**0.041**	0.14	0.07	**0.001**	**0.013**	**0.003**	**0.012**	**0**	0.07
init Loop Tack	**0.86**	**0.91**	0.12	0.52	-0.53	0.39	**0.59**	**-0.792**	0.54	**0.719**	**0.748**	**0.906**	**0.659**
P-value	**0**	**0**	0.69	0.07	0.06	0.18	**0.034**	**0.001**	0.06	**0.006**	**0.003**	**0**	**0.014**
init Hold Power	**0.75**	**0.82**	-0.19	0.36	-0.40	**0.59**	0.36	**-0.70**	**0.74**	**0.580**	0.39	**0.827**	0.32
P-value	**0.003**	**0.001**	0.52	0.23	0.17	**0.034**	0.23	**0.008**	**0.004**	**0.038**	0.19	**0**	0.30
init SAFT	**0.68**	**0.77**	0.37	0.30	-0.34	0.40	0.33	-0.54	0.49	**0.658**	**0.609**	**0.732**	**0.665**
P-value	**0.011**	**0.002**	0.21	0.32	0.26	0.17	0.28	0.06	0.09	**0.015**	**0.027**	**0.004**	**0.013**
init RBT	0.47	0.40	0.10	0.09	-0.07	-0.15	0.45	-0.36	-0.01	0.30	0.40	0.44	0.39
P-value	0.10	0.18	0.74	0.77	0.83	0.62	0.12	0.22	0.97	0.32	0.18	0.13	0.19

Table 13. Pearson's coefficients and p-values for aged tape performance.

	oil visc	Oil DSC Tg (°C)	aniline point (°C)	%Cn	%Cp	%Ca	HRMS cyclo	HRMS para	HRMS arom	PSA RBSP (°C)	PSA viscosity (cP)	Adh Tg	3rd cross
aged 180 Peel	**0.80**	**0.92**	-0.18	**0.56**	**-0.59**	0.50	**0.62**	**-0.88**	**0.66**	**0.56**	0.53	**0.91**	0.41
P-value	**0.001**	**0**	0.56	**0.045**	**0.035**	0.09	**0.024**	**0**	**0.014**	**0.046**	0.06	**0**	0.17
aged Loop Tack	**0.80**	**0.89**	-0.11	0.52	**-0.57**	**0.71**	0.45	**-0.79**	**0.75**	**0.59**	0.51	**0.91**	0.44
P-value	**0.001**	**0**	0.73	0.07	**0.044**	**0.007**	0.12	**0.001**	**0.003**	**0.03**	0.08	**0**	0.13
aged Hold Power	**0.62**	**0.80**	-0.34	**0.73**	**-0.74**	0.38	0.43	**-0.68**	**0.59**	0.53	0.50	**0.78**	0.25
P-value	**0.024**	**0.001**	0.25	**0.004**	**0.004**	0.20	0.15	**0.011**	**0.035**	0.07	0.08	**0.002**	0.41
aged SAFT	**0.76**	**0.84**	0.39	0.35	-0.35	0.18	0.48	-0.53	0.25	**0.60**	**0.91**	**0.78**	**0.83**
P-value	**0.002**	**0**	0.19	0.24	0.24	0.56	0.10	0.06	0.40	**0.030**	**0**	**0.002**	**0**
aged RBT	0.50	**0.61**	-0.09	0.27	-0.26	-0.07	0.37	-0.49	0.35	0.53	0.39	**0.56**	0.27
P-value	0.08	**0.026**	0.76	0.37	0.39	0.83	0.22	0.09	0.24	0.06	0.19	**0.046**	0.37