1. Introduction
Terpene-based resins constitute a major portion of tackifiers, besides rosin esters, derived from renewable resources. The diverse chemistry along with their compatibility with various polymers used in the adhesive industry makes terpene resins suitable for a variety of adhesive applications. Pressure sensitive adhesives are one such class of adhesives where terpene resins find utility and deliver performance. Terpenes used to manufacture these resins belong to the class of terpenoids called mono-terpenes (C\textsubscript{10}H\textsubscript{16}). Typically, the terpenes used in tackifier industry are obtained from turpentine, which in turn is obtained from pine trees as either gum turpentine or crude sulfate turpentine (CST). The two major terpenes obtained from turpentine are alpha pinene and beta pinene (Figure 1). Another very commonly used terpene for tackifiers that is not derived from turpentine is d-limonene, which is obtained from citrus sources, i.e. orange peels.

![Figure 1: Terpenes for tackifiers](image1)

Terpene resins are primarily synthesized by a cationic polymerization process where a suitable solvent and a Lewis acid catalyst are employed. The three major classes of terpene resins (Figure 2) in the tackifier industry are polyterpene resins, phenol-modified polyterpene resins (terpene-phenol resins) and styrene-modified polyterpene resins (styrenated terpene resins).

![Figure 2: Three types of terpene resins](image2)

2. Evaluating Terpene Resins in Pressure Sensitive Adhesives (PSA)
The tackifier resins evaluated in this study were polyterpene, styrenated terpene, and terpene-phenol resins. The softening point for all tackifiers was between 95 and 105°C, except for the limonene resin at 115°C. Resins were evaluated in styrenic
block co-polymer adhesives – SIS (styrene-isoprene-styrene) and SBS (styrene-butadiene-styrene) – and in solvent acrylic PSA. The following systems were studied:

- Various terpene resins in SIS and SBS adhesives
- Polyterpene co-tackifier in SIS-SBS blends in adhesives
- Terpene Phenol resins as co-tackifiers in SIS, SBS adhesives
- Terpene Phenol resins in solvent acrylic PSA
- Polyterpene resin in label adhesive (SIS)

3. SIS Adhesives

The formulation, types of terpene tackifiers studied, and the evaluation criteria were as follows:

Formulation (weight %)

- SIS (15% styrene content) 36.6%
- Antioxidant 0.4%
- Naphthenic Oil 10%
- Tackifier 53.0%

Terpene Tackifiers studied

- Alpha-beta resin (AB)
- Limonene resin (LIMO)
- Beta pinene resin (Beta) / Rosin Ester (RE)
- Styrenated Terpene resin (ST)
- Terpene Phenol resin (TP)

Properties Evaluated

- 180° Peel stainless steel (SS), polypropylene (PP) and LDPE (all 30 minute dwell)
- Shear Adhesion Failure Temperature (SAFT) – 1” x 1” with 500 g
- Rheology- G’/G” crossover temperature
- Room Temperature Static Shear

The overall performance of the terpene tackifiers was compared with some select types of hydrocarbon resins. Figures 3, 4, and 5 show the results of the evaluations.
4. SIS Adhesives – Overall conclusions

- Overall non-polar nature and compatibility of terpene resins with mid-block can offer an adhesive that has good adhesion to a variety of substrates including Low Surface Energy (PP, PE).
- The non-polar beta pinene resins appear to deliver the best balance of adhesion and heat resistance when used in combination with a low level of a polar tackifier such as RE.
- Limonene-based resins have very good thermal stability, and with their compatibility with the mid-block they can afford an adhesive with overall very good heat resistance.
5. SBS Adhesives

The formulation, types of terpene tackifiers studied, and the evaluation criteria were as follows:

Formulation (weight %)

- SBS (25% styrene content) 33.3%
- SBS-radial (23% styrene content) 3.3%
- Antioxidant 0.4%
- Naphthenic Oil 10%
- Tackifier 53.0%

Tackifiers studied

- Beta pinene resin (Beta) / Rosin Ester (RE)
- Styrenated Terpene resin (ST)
- Terpene Phenol resin (TP)

Properties Evaluated

- 180° Peel SS, PP, LDPE (all 30 minute dwell)
- SAFT – 1” x 1” with 500 g
- Room Temperature Static Shear

Figures 6, 7 and 8 show the results of the evaluations.

6. SBS Adhesives – Overall conclusions

- Terpene resins with some degree of polarity (TP, styrenated terpenes) are useful tackifiers for SBS adhesives and deliver adhesion to multiple substrates including LSE (PP, PE).
- The non-polar nature and the high molecular weights of beta pinene resins necessitates the need to incorporate a polar resin (RE) to make an adhesive that affords good adhesion.
- The high molecular weight of the beta pinene resins facilitates improved heat resistance of final adhesive relative to other types of terpene resins.
Figure 7: SAFT - SBS adhesive

Figure 8: Static Shear - SBS adhesive
7. Adhesives with blends of SIS and SBS
Two formulations (Table 1) were evaluated using an alpha-beta polyterpene resin. The properties evaluated were as follows: 180° Peel, SS, Loop Tack, SS, and SAFT. The overall performance of the terpene tackifier was compared with a hydrocarbon resin. Figures 9, 10 and 11 show the results of the evaluations.

<table>
<thead>
<tr>
<th></th>
<th>F1</th>
<th>F2</th>
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</thead>
<tbody>
<tr>
<td>SIS</td>
<td>24%</td>
<td>16%</td>
</tr>
<tr>
<td>SBS</td>
<td>8%</td>
<td>16%</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>0.5%</td>
<td>0.5%</td>
</tr>
<tr>
<td>Naphthenic oil</td>
<td>10%</td>
<td>10%</td>
</tr>
<tr>
<td>Tackifier</td>
<td>57.5%</td>
<td>57.5%</td>
</tr>
</tbody>
</table>

**Table 1**: Adhesive formulations using blends of SIS and SBS

**Figure 9**: 180° Peel, SS- SIS+SBS blend

**Figure 10**: Loop Tack, SS- SIS+SBS blend
8. Terpene-Phenol (TP) Resins in SIS and SBS Adhesives

TP resins are very useful tackifiers for SIS or SBS adhesives where they can impart enhanced peel and tack. Figures 12 and 13 show the influence of a TP resin when used as a co-tackifier with a hydrocarbon resin.

It is important, however, to balance the loading level of a TP resin in order to minimize impact on high temperature resistance of the PSA (Figure 14).
Figure 13: Loop Tack on SS with TP

Figure 14: SAFT (°C) with TP
9. Terpene-Phenol (TP) Resins in Solvent Acrylic PSA

Terpene Phenol resins can impart enhanced adhesion to solvent acrylic PSA. When used at a 30% loading, an overall enhancement in adhesion (tack and peel) was observed (Figures 15 and 16).

**Figure 15**: Loop Tack on SS and HDPE with TP in Acrylic PSA

<table>
<thead>
<tr>
<th></th>
<th>Neat Polymer</th>
<th>With TP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loop Tack (SS) N/25mm*25mm</td>
<td>11.2</td>
<td>17.7</td>
</tr>
<tr>
<td>Loop Tack (HDPE) N/25mm*25mm</td>
<td>5.6</td>
<td>11.2</td>
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</tbody>
</table>

**Figure 16**: Peel on SS and HDPE with TP in Acrylic PSA

<table>
<thead>
<tr>
<th></th>
<th>Neat Polymer</th>
<th>With TP</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 deg. Peel (SS) N/25mm</td>
<td>10.7</td>
<td>25.2</td>
</tr>
<tr>
<td>180 deg. Peel (HDPE) N/25mm</td>
<td>2.7</td>
<td>8.8</td>
</tr>
</tbody>
</table>
10. Polyterpene Resin in Label Adhesive (SIS)

In a basic SIS-based label adhesive formulation where no oil was incorporated, a liquid polyterpene resin delivered good adhesion. Figures 17 and 18 show the performance comparison of the liquid terpene resin with a liquid hydrocarbon resin. The formulation studied was as follows:

- SIS: 36%
- Antioxidant: 1%
- Liquid Resin: 20%
- RE (100°C s.p.): 43%

![180° Peel, SS (N/25mm)](image)

**Figure 17:** Peel on SS with SIS label adhesive

![Loop Tack, SS (N/25mm*25mm)](image)

**Figure 18:** Loop Tack on SS with SIS label adhesive
The SAFT values for the two adhesives made with the two liquid resins were very close: 75°C with the HC and 73°C with the PT.

11. Terpene Resins in PSA – Summary
Terpene resins are effective tackifiers for PSAs (e.g. SIS, SBS, Acrylics). The resins provide good adhesion to low surface energy substrates, and can be used either as the only tackifiers or as co-tackifiers in a PSA. Terpene resins with moderate polarity (terpene phenol, styrenated terpene) can impart enhanced adhesion with SBS adhesives.

12. Test Conditions and Methods
- Coated adhesives on 2 mil PET.
- Coating thickness of 1 mil.
- Peel measurements on Thwing-Albert Materials Tester.
- Loop Tack measurements on Thwing-Albert Materials Tester.
- SAFT on SS (1” x 1”; 500 g) with 1°C/min ramp.
- Rheology on Ares G2 rheometer: from -60 to 180°C sweep at 6°C/min, using 10 rad/sec.

13. Acknowledgments
All the adhesive formulating and evaluations were conducted at the Arizona Chemical Company Science & Technology center in Savannah, GA, and the efforts and contributions of the following members of the Adhesives Applications Team are especially recognized –
- Mr. Michael Moran
- Mr. Thomas Reffle
- Ms. Carmen York
- Mr. Richard Kosakowski

The information presented in this paper was generated based upon in-house knowledge and experience, and is being offered for consideration only. The data and results presented should be treated as a general guideline and not as a guarantee or predictor of performance of a formulated adhesive using the type of resins studied.