**SILICONE PSAs: TRENDS IN THE EAST AND WEST**

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**Abstract**

Silicone PSA users in Asia will be significantly increasing the use of platinum curing PSAs. In the Americas and Europe, however, use of platinum cure PSA is projected to remain flat, while use of peroxide cure silicone PSAs continue to grow. This paper analyzes this trend and suggests reasons for the shift in preference in Asia. It summarizes the range of commercially available materials and recent innovations. The technical, physical and performance properties of platinum cure silicone PSAs are compared with those of traditional peroxide cure materials. The benefits of platinum cure systems as well as potential issues are explored along with suggestions on how to achieve higher line speeds, avoid contamination and alter performance properties. The paper also describes novel applications that are improved or enabled through the use of platinum-cure silicone PSAs.

**Introduction**

Market research suggests that less than 1% of all tape produced globally is formulated using silicone adhesives. Silicone PSAs (Pressure Sensitive Adhesives) fill a small but important niche in the world of adhesives. Their properties, which stem from the flexibility and stability of their silicon-oxygen bonds, give them unique performance capabilities.

**High- and low-temperature performance**: Often, silicone PSAs are used in specialized tapes for high-temperature applications – above 150°C (300°F) – where organic adhesives fail. Such applications include electrical insulation or bonding, flexible printed circuit laminates, high-temperature masking, plasma spray tapes and release wraps for heat seal bars. Silicone PSAs can also retain adhesive properties at very low temperatures – as low as -73°C (-100°F) – and are used in freezer, aerospace and cold-weather tapes.

**Surface energy**: Silicone PSAs have a relatively low surface energy and can adhere to low-surface-energy substrates, such as etched PTFE, silicone, polyester, polyolefin and fluorohalocarbon films. This ability to adhere to low-surface-energy materials leads to the use of silicone PSAs in splicing tapes for release liners; silicone rubber tape constructions, such as flame spray tapes; and tapes requiring a PTFE backing.

**Resistance**: Silicone PSAs are resistant to chemical attack from acids and bases and will remove cleanly from surfaces. This combination of attributes makes silicone PSAs an excellent choice for masking applications and the production of printed circuit boards. Silicone PSAs are also resistant to moisture, UV radiation and biological attack.

This basic understanding of how silicone PSAs are used in tape applications provides a context for understanding the silicone PSA market.
Market Dynamics

The global market for all types of self-adhesive (or pressure sensitive) tapes is estimated to be slightly more than 24 billion square meters.\(^3\) In terms of sales, Asia leads with 42% of total sales volume, followed by the Americas with 34% and Europe with 24%.\(^4\)

![Figure 1. Total global sales of pressure sensitive tapes by geographic area](image1)

From a market segmentation standpoint, packaging tapes, like those used to seal boxed shipments, account for 66% of the global total; while the remaining 34% are classified as non-packaging tapes.\(^5\) This non-packaging segment is where tapes manufactured with silicone PSAs reside.

![Figure 2. Pressure sensitive tape market segmentation](image2)

Within the non-packaging tapes segment, the global demand for tapes made with silicone PSAs is estimated at 63 million square meters.\(^6\) This is less than 1% of this segment’s total tape production.
Figure 3. Non-packaging segment – global demand for silicone PSA vs. non-silicone tapes

Asia is the largest consumer of silicone PSAs using 51% of the total global demand. The Americas follow with 31% of the global demand with the vast majority sold in the United States and Canada. The market for PSAs in Europe and Japan are smaller at 8% and 10% of global demand respectively.

Figure 4. Silicone PSA demand by region

Demand for silicone PSAs continues to grow faster than the US gross domestic product (GDP). There are several trends driving this growth. Most notable is the increased global demand for electronic devices, which has fuelled the Asia market for tapes used within and to produce these devices. As electronic devices become increasingly smaller and running hotter, silicone PSAs play a vital role, offering adhesion at high temperatures. The excellent electrical properties of silicone PSAs – such as dielectric strength, arc and corona resistance – make them a logical choice for electronics applications. Increased production of printed circuit boards also leverages silicone adhesive tape demand, because masking tapes are used during plating, wave soldering, chemical etching and treating operations. Silicone offers excellent temperature and chemical resistance and removes cleanly from surfaces once the processing is complete. Novel applications within the apparel sector are also contributing to an increase in demand.

U.S. and European markets for silicone PSAs are also growing at higher than GDP rates, as well. Growth in these regions is driven by the tendency to replace mechanical fasteners with adhesives,
growth in the aerospace sector, an increasing need for chemical resistance, and rising operating

Platinum catalyzed PSAs are a niche market within a niche market, and offer exciting possibilities for

The remainder of this paper will focus on the chemistry, capabilities and

Silicone PSA Cure Chemistries

Silicone PSAs are formulated with two main components – a linear high-molecular-weight siloxane

Commercially available silicones PSAs utilize a polydimethylsiloxane (PDMS) or

The condensation reaction between available silanol functionality on the resin and polymer enhance the

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development of other industries, such as automotive, electronics, and medical devices. As these markets

Two curing systems encompass most of the silicone PSAs currently sold into the tapes market: peroxide catalyzed free radical cure (BPO) and platinum-catalyzed silicon hydride to vinyl addition cure.

Peroxide Cure
The BPO cure system requires a multi-zoned (or staged) oven. The first stage is for solvent removal, which occurs at lower temperatures (60 to 90°C [140 to 195°F]) to ensure the peroxide does not inadvertently cure solvent into the PSA matrix, which results in reduced performance and poor temperature stability. The second stage (130 to 200°C [265 to 390°F]) decomposes the catalyst, forming free radicals that complete the crosslinking reaction.\(^9\) The primary benefit of the peroxide-catalyzed system is the ability to control PSA properties by changing the catalyst addition level. The tape producer has the flexibility to use 0 to 4% peroxide. The additional curing with peroxide increases crosslink density, resulting in a more tightly cured PSA. Some of the disadvantages of peroxide-cure PSAs include the handling of volatile solvents, generation of peroxide by-products, the need for more sophisticated curing ovens and the need to prime certain substrates to improve adhesive anchorage.

Platinum Cure
An alternative curing mechanism – platinum-catalyzed addition cure – is commercially available for silicone PSAs. These adhesives are cured by a platinum-catalyzed reaction of silicon hydride to vinyl. Even though platinum-curing systems are supplied in hydrocarbon solvents, they can be cured in a single-zone oven at lower overall temperatures (100 to 150°C [212 to 300°F]). As shown in Figure 8, the platinum-catalyzed reaction occurs as the solvent evaporates, without the generation of by-products.\(^10\)
The platinum (Pt) cured system has other benefits over peroxide cure systems. These benefits include faster line/cure speeds, reduced sensitivity to temperature variation within the oven, no generation of volatile by products and the ability to use more thermally sensitive substrates (polyethylene, polypropylene, etc.)

Another benefit of the platinum catalyzed silicone system is the fact that it does not inherently need the hydrocarbon solvent for anything other than viscosity control. Additionally, a solventless silicone PSA with the tack, adhesion and high-temperature shear of a typical solvent-based silicone PSA is commercially available. Solventless silicone PSA users can reduce their Hazardous Air Pollutant (HAP) emissions, potentially to below the Maximum Achievable Control Technology (MACT) limits. A solventless silicone PSA also benefits those who seek silicone PSA performance, but do not have or cannot afford the equipment and facilities to handle solvent-based adhesives.

**Platinum-Cure Silicone PSA Properties**

Platinum-curing silicone PSAs can be formulated with different silicon hydride-to-vinyl ratios to obtain specific performance characteristics. Table 1 provides typical properties for a platinum-curing silicone PSA.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent Solids</td>
<td>50 - 100%</td>
</tr>
<tr>
<td>Viscosity (cps)</td>
<td>20,000 – 50,000</td>
</tr>
<tr>
<td>Appearance</td>
<td>Clear</td>
</tr>
<tr>
<td>Service Temperature</td>
<td>- 73 to 280°C (-100 to 535°F)</td>
</tr>
<tr>
<td>Functionality</td>
<td>Dimethyl</td>
</tr>
</tbody>
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Table 1. Typical physical properties of a platinum curing PSA
To compare the performance of commercially available platinum-cure PSAs with commercially available peroxide-cure PSAs, four adhesives were evaluated:
1) A solvent based, peroxide-cure, dimethyl silicone PSA,
2) A solvent based, peroxide-cure, diphenyl silicone PSA,
3) A solvent based, Pt-cure, dimethyl silicone PSA, and
4) A solventless, Pt-cure, dimethyl silicone PSA.

The peroxide catalyzed adhesives were prepared at 50 wt. % solids in solvent using 2% benzoyl peroxide based on silicone solids. Figures 9 & 10 show the peel adhesion (PSTC-1) and the Polyken probe tack performance (ASTM D-2979) for each PSA on polyester and polyimide substrates.13

![180 Degree Peel Adhesion](image)

**Figure 9.** 180 Degree peel adhesion
Comparison of these four adhesives illustrates two important points. First, a commercially available solvent-based platinum-cure PSA has tack and adhesion properties comparable to, or in some cases better than, peroxide-cure PSAs. Second, platinum-cure PSA benefits, such as low-temperature cure, clean removability and no formation of peroxide by-products, are available without sacrificing the performance attributes expected of a silicone PSA.

A second important point is that platinum cure PSA offer formulation customization that can be used to expand the range of tack and adhesion options for silicone PSAs. For example, platinum cure PSAs can be formulated as high adhesion “permanent” adhesives or as very low adhesion self supporting adhesive films. Platinum cure PSAs can be formulated without solvent and still exhibit similar performance to solvent based dimethyl adhesives.

**Market Growth/Platinum-Cure Benefit Links**

Why is the demand for platinum-curing silicone PSAs growing in Asia? The answers are strongly linked to the benefits inherent to platinum-cure PSA systems and the ability of those systems to overcome some of the known limitations of peroxide-cure systems.

**Single oven cure** – As stated earlier, curing the peroxide-catalyzed silicone PSA is a two-stage process requiring a multi-zoned oven. A platinum-catalyzed PSA, on the other hand, can be cured in a single-zone oven at lower temperatures. Employing a platinum-cure silicone PSA allows for higher line speeds with less initial capital investment. Coaters in Asia typically operate at speeds ranging from 3 to 10 m/min for most silicone adhesives. Platinum-curing silicone PSA coaters typically operate at speeds ranging from 10 to 30 m/min, and have demonstrated speeds up to 100 m/min – **A 10X increase over the top speed of a BPO cure system!** The ultimate speed was not limited by the adhesive curing, rather was limited by the supporting equipment, dryers and winding equipment. Initial capital investment can
be further reduced by using a solventless PSA and avoiding the costs associated with solvent collection, incineration and handling. Investment costs can be reduced as the oven residence time is used for curing rather than solvent evaporation, and the ovens do not need to be engineered for flammable vapor service.

**Lower temperature cure** – As stated above, platinum PSAs can be cured at lower temperatures than peroxide cure silicone PSAs. Typically, silicones are used in high temperature services requiring heat resistant materials like PET or polyimide (PI). Curing these tapes at lower temperatures can result in less shrinkage of the PET or PI substrate, minimizing shrinkage is important in LCD or plasma display applications. Platinum cure PSAs are the only option for coating low temperature substrates like polyethylene (PE) and polypropylene (OPP). Use of PE and OPP with silicone PSAs is limited, but several inquiries have been made for coating silicone on OPP or PE for low surface energy adhesion or masking applications where temperature resistance is not required. Solventless silicone PSAs can also be used to avoid damaging the OPP and PE during tape production, as can happen when these substrates are exposed to solvents at higher temperatures.

**No generation of peroxide by products** – At temperatures below 150°C (300°F) benzoyl peroxide can volatilize in the second oven, and without proper ventilation can condense in confined spaces potentially building to explosive levels. Adequate oven temperature, good manufacturing practice, and alternative peroxide catalysts can prevent safety incidents from ever occurring. Asian tape producers who try platinum curing PSAs for their performance benefits are also pleased to avoid peroxide volatility and supply problems.

**Wet lamination on a fluoro-silicone release liner** – Silicone adhesive double sided and self supporting transfer tape applications have grown in Asia. These applications require adhesion between dissimilar components operating at elevated temperatures, with the minimum thickness of tape. Making these complex tape constructions with silicone PSA typically requires wet lamination (casting) the adhesive onto a fluoro-silicone coated release liner.

Only a few peroxide cure silicone PSAs that can release easily from a fluoro liner after wet lamination; whereas most platinum curing PSAs will release easily when wet laminated onto a fluoro liner. This allows tape producers more flexibility in adhesive properties and more opportunities for product innovation.

**Coater compatibility** – The demand for silicone adhesive tapes in Asia is growing at more than 10% per year. The demand for acrylic adhesive tapes in Asia is also growing fast, and long lead times are often not tolerated. Production flexibility is vital to the Asian tape producer. Because platinum catalyzed
silicone PSAs cure at temperatures similar to acrylic adhesive systems, delays due to oven temperature adjustment are avoided. Use of platinum-cure silicone PSA also may eliminate the need to chemically treat or prime certain substrates prior to adhesive coating. No priming, and no oven adjustment allow greater operational flexibility and shorter lead times.

Low migration (remove cleanly with very low residue) – This attribute is this strongest driver for the growth of platinum-cure silicone PSAs in Asia. New innovations in platinum-curing silicone PSAs function as well as BPO-cure adhesives at temperatures above 260°C (500°F) with very little residual silicone left on the surface after removal. Low migration is a valuable capability in printed circuit board (PCB) applications. Some tape customers in Asia have been able to use low migration masking tapes to eliminate washing steps in the PCB production process.

Solventless – Another benefit of the platinum catalyzed silicone system is the fact that it does not inherently need the hydrocarbon solvent for anything other than viscosity control. Solventless silicone PSA users can reduce their Hazardous Air Pollutant (HAPs) emissions, potentially reducing them to below the Maximum Achievable Control Technology limits. Most of those seeking solventless PSAs desire the performance properties of silicone PSAs, but do not have the investment in equipment and facilities to handle solvent based adhesives. Sales of solventless silicone PSAs have significantly increased over the past year. This growth has been relatively balanced among the three geographic regions. It is conceivable that a new entrant to silicone tape production could enter the market with a much lower initial investment in equipment and facilities and produce silicone tape at high speeds using a solventless silicone PSA. Such an operation could be developed in any geographic region, but the pressure sensitive markets in China or India are more fragmented, and more likely to have new entrants.

Addition Cure System Requirements

Every new technology ever commercialized involves trade offs, and so this is also true for platinum catalyzed silicone PSA technology. To optimize the benefits of Pt curing silicone PSAs, it is important to pay attention to the following factors.

Supplier Involvement – Peroxide cure silicone PSAs offer users the flexibility to alter the properties by increasing or decreasing the catalyst concentration in the formulated adhesive. For platinum cure PSA systems changing the catalyst level has little to no effect on tack or adhesion properties of the cured adhesive. The formulation, itself, must be altered. From a robust manufacturing perspective, formulation insensitivity is a benefit. With platinum-cure PSA systems, open and honest communication between the tape producer and the adhesive supplier is the key to success. By sharing their application needs and performance requirements, producers can obtain the optimum product for their intended application and ensure that minor reformulations can be completed within the window of opportunity. For the silicone supplier, this means developing customized products, which requires a flexible and nimble supply chain.

Proper Equipment Cleaning Procedures – In an ideal world, the tape producer would be able to move seamlessly between peroxide- and addition-curing silicones. Unfortunately, for both the silicone supplier and tape producer this is not the case, as platinum catalyst can be contaminated by residual peroxides and left unable to complete the curing reaction. Good manufacturing practice and thorough cleaning procedures are required to effectively switch between silicone systems. The tape producer can manage campaigns to minimize cleaning frequency or avoid it altogether by utilizing multiple, dedicated adhesive coaters.
**Platinum catalyst is expensive** – Platinum metal prices have reached record highs over the last few months. Increasing demand in the automobile catalyst sector is driving up the price of platinum metal and, hence the price of silicone formulated platinum catalysts. The impact of platinum on the bath cost of a silicone PSA has the effect of a 5-15% increase in bath cost when compared to BPO systems. The added cost is certainly a factor to consider before adopting a Pt cure silicone PSA; however the value captured by novel tape solutions, such as the lead free soldering application, typically outweighs the additional adhesive costs.

Asian tape producers are adhering to these requirements, and as a result, platinum curing silicone PSAs continue to grow in Asia, delivering the innovative solutions the market demands.

**Novel Applications Made Possible with Silicone PSAs**

**Lead free soldering masking tapes** - Masking tapes made with silicone PSAs are used to protect surfaces during soldering operations. The Restriction of Hazardous Substances (RoHS) directive passed in Europe places limits on certain hazardous chemicals and effectively forces electronics producers to move away from lead soldering. Lead replacement materials have increased the temperature of the soldering operations from 250-260°C (480 to 500°F) to 270-280°C (518 to 536°F). At these higher temperatures, BPO cure silicone tapes retain their adhesives properties and protect the temperature sensitive components, but tend to leave silicone residue upon removal. New innovations in platinum curing silicone PSAs complete the protective function just as well as BPO cure adhesives with very little residual silicone left on the surface after removal. Figure 12 shows how the platinum cured PSA leaves behind much less silicone. In this particular case, the tapes were placed on the SUS plate, heating to 280°C (536°F) and then held for 2 hours. The tape was then removed at 180°C (356°F) at a peel speed of 300 mm/min.

![Figure 12. Demonstrating clean removal of platinum cured silicone PSA](image)
Very low adhesion films – Platinum-curing silicone PSAs can be formulated to achieve moderate tack with very low adhesion allowing for easy peel. Figure 13 below illustrates this concept for a portable gaming device. This particular unit utilizes an acrylic type PSA. However, this same concept can also be used in high temperature environments, like a kitchen range top, using platinum-curing silicone PSAs. Such silicone PSA films could be cut into patterns and be used for masking applications. The clarity and temperature resistance of silicone PSA films could also be useful in the diffusion film within back light unit assemblies, as depicted in Figure 14. Back light assemblies are commonly used in notebook computer monitors and LCD screen televisions.

Figure 13. A low-tack protective film for a portable gaming device

Figure 14. Composition of a back-light unit.

Summary

Largely driven by the electronics industry, markets in Asia continue to demonstrate rapid annual growth rates for specialty pressure-sensitive tapes. The temperature and chemical resistance attributes of
silicone PSAs make them an excellent fit to many new applications. A special variety of silicone PSAs catalyzed by an addition-curing mechanism expands the capabilities of silicone PSAs to include single-oven, lower-temperature cure; flexibility in release; solventless delivery and very low migration. The use of platinum-cure silicone PSAs continues to increase in Asia through innovations in lead-free solder, low-adhesion films and alternative film substrates. The benefits of platinum-cure silicone PSAs can also help North American and European tape producers create innovative new products and applications.

Literature citations

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