INTRODUCTION:

Silicone release liners for pressure sensitive adhesives use a wide variety of substrate and silicone chemistries in order to be customized for different industries such as tape, label, graphic arts, industrial, medical, automotive and electronics. The release liner design depends on the subsequent converting processes the liner must survive and the final customer end use.

Low silicone transfer release liners for electronics applications need both good release to aggressive adhesives and low silicone transfer to the adhesive and other surfaces. Loparex has developed a patented process to manufacture low silicone transfer release liners trademarked LO-EX™. Some of the testing and properties of this product line will be discussed. Before we discuss low silicone release liners for the electronics market, we must consider all the factors in designing release liners including substrate, coating process and silicone chemistry.

SUBSTRATES

The selection of the release liner substrate is often based on main physical properties such as caliper, smoothness, stiffness, tensile, heat resistance, color, cleanliness, die cuttability and dimensional stability. There are other considerations such as COF, ability to be thermoformed, FDA considerations, etc. Some of the more common substrates used for release liners are:

Glassine – hard, smooth, light weight, caliper consistent

Super calendered kraft (SCK) – hard, smooth, caliper consistent

Machine finished kraft (MFK) – not as dense or smooth as SCK

Poly coated kraft (PEK) – 1 side or 2 sides coated with excellent silicone hold out

The dimensional stability of the base sheet is enhanced with 2 side poly coating. Base sheets can be selected that provide a superior layflat poly coated liner. Temperature resistance improves when moving from low density to high density PE to polypropylene. The harder surface of polypropylene provides the best die cutting.

Clay coated paper – less expensive than PE coated paper, but less curl resistant.

Saturated Kraft – chemically treated with high tear strength for specialized applications.

Films – Many types are available in a wide range or calipers, both natural and colors.

Low and High density polyethylene (LDPE & HDPE), coextruded versions of polyolefins
Polypropylene (PP) (cast and biaxially oriented), polyester (PET) and polystyrene and others.

Of all these substrates, polyester is often preferred for the electronics release liner applications due to its cleanliness (no paper fibers), dimensional stability, and heat resistance. The polyester base chosen must also meet minimum requirements for contaminants such as phosphates, chlorides, sulfates, etc. that could contaminate other surfaces.
COATING METHODS

There are several common methods of applying silicone coatings. Each has their advantages and limitations. The cure mechanisms are thermal using tin (Sn), platinum (Pt) and rhodium (Rh) catalysts and radiation curing by ultraviolet (UV) and electron beam (EB). The heat sensitivity of the substrate is a bigger factor with thermal curing. Radiation curing has the advantage of a more cure off the coater. Maximizing the degree of cure before rewinding during the coating operation helps avoid silicone transfer to the backside of the release liner. Radiation cured coatings have an advantage in this respect.

Solvent borne formulations can be applied with rod or direct gravure. Solventless formulations are higher viscosity and are applied with multi-roll coaters that may require higher silicone coat weights to obtain uniform complete coverage. Low coat weights using rod or direct gravure can be used for low silicone transfer systems.

<table>
<thead>
<tr>
<th>METHOD</th>
<th>ADVANTAGES</th>
<th>LIMITATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROD</td>
<td>Low cost, easy set up for rod size changes, useful for solvent borne formulations so lower coat weights achievable, good coverage.</td>
<td>Not useful for solventless coatings which are higher in viscosity. More prone to scratching films.</td>
</tr>
<tr>
<td>DIRECT GRAVURE</td>
<td>Meters consistently, useful for solvent blends for lower coat weights, less speed sensitive for papers</td>
<td>May cause “silicone skips” if gravure cells are plugged.</td>
</tr>
<tr>
<td>OFFSET GRAVURE</td>
<td>Useful for solventless, less gravure patterning</td>
<td>Not for solvent borne so higher coat weights may be required.</td>
</tr>
<tr>
<td>MULTI-ROLL COATER</td>
<td>Useful for solventless, can achieve lower coat weights than offset gravure</td>
<td>Not for solvent borne so higher coat weights may be required.</td>
</tr>
</tbody>
</table>

CURE METHODS & CHEMISTRY

There are several different common silicone chemistries available to produce a wide range of release properties to pressure sensitive adhesives from easy to medium to tight (highest). Each type of chemistry has different properties and many varieties of polymers (chain length, location of functional groups) are available. With the addition of the many additives and formula combinations, there is an endless selection of possibilities. In each case, selection of the release system must be made after careful consideration of all the variables including the customer’s adhesive, processing conditions, substrate, coating method, etc. There may be up to several dozen major variables to consider in each design. First, let’s consider the major advantages and limitations of each type of chemistry.

Sn catalyzed solvent borne systems are compatible with most adhesives but are not as well cured off the coater. This means there is the possibility of transfer of silicone to the back side of the release liner. Sn catalyzed systems, also known as condensation systems, are more susceptible to humidity conditions and have a longer post curing time. Compared to other thermal systems, the Sn systems can be coated at lower temperatures and therefore have an advantage when coating temperature sensitive substrates like low density polyethylene coated paper. They are also available as environmentally friendly emulsions to eliminate the need for solvents.
**Pt catalyzed** thermal systems are generally more completely cured thermal systems than Sn immediately off the silicone coater. A wide variety of release from premium (very easy) to much tighter are available in solvent borne and solventless systems. They tend to have easier release at faster stripping speeds than Sn systems. One disadvantage is that they require higher curing temperatures than Sn so they have a disadvantage on temperature sensitive substrates. They may be more likely to interact with adhesives upon aging so it is best to check compatibility before use. Pt systems are also available as water-based emulsions.

**Rhodium catalyzed** silicone systems require very high temperatures for curing making them suitable only for papers. The high temperatures tend to dry out light papers making them more brittle. An advantage is that they are generally compatible with many adhesives.

**Electron Beam** radiation curable silicones have the advantage of a fast cure, however they are generally not compatible with acrylic adhesives. As a non-thermal curing system, EB is useful for temperature sensitive substrates and can be used on paper as well as films and PE coated paper.

**UV (ultraviolet)** cationic cured silicone systems have the advantage of a fast cure and also relatively good aging with a wide variety of adhesive systems. While UV lamps do give off heat, temperature sensitive substrates such as films and PE coated papers can be coated with excellent cure.

UV cure is essentially complete coming into the rewind off the coater. This makes UV one of the best silicone systems for complete cure that is well suited for many acrylic adhesives. UV cationic cure silicone system when applied at low coat weights is an excellent choice for consistently manufacturing low silicone transfer release liners for aggressive acrylic adhesives. A graph comparing LO-EXT™ grades with other commercially available silicone systems will be shown in a later section.

**ELECTRONICS MARKET**

The electronics market demands a product with a **high degree of cleanliness and minimal silicone transfer to electronic components**. For example, labels used in computer hard disk drives must not contaminate any electronic circuits which are progressively becoming smaller in size and more sensitive to very minor amounts of contamination.

**Cleanliness**

The substrate most often used for this end use is polyester. It is clean and has a hard surface for die cutting. Polyester is also relatively temperature resistant compared to polyethylene or polypropylene films making it able to withstand higher adhesive cure temperatures. Paper or poly coated papers are generally not used since they have the inherent problem of fiber dust from cut edges.

**Extractables**

Silicone coatings are applied as oligomers of polydimethyl siloxanes of various chain length and functionality. Thermal and radiation cured coatings are formulated with various additives for fast cure, good bath life, anchorage, etc. for the base sheet to be coated.

In each curing method, there is always some migratory species that are not polymerized into the system. Unpolymerized silicone can be extracted from the liner with a suitable solvent such as toluene, heptane or MIBK (methyl isobutyl ketone). The amount of silicone extracted in the solvent can be analytically measured with instrumentation such as an Atomic Absorption Spectrophotometer also
known as AA. Known analytical standards are used for comparison. After measuring the silicon atom concentration, the quantity of silicon can be converted in poly dimethyl siloxane to compute the total amount of silicone per unit area. The unit of measurement often mentioned for total silicone extractables is \( \mu g/cm^2 \).

The extractables test used at Loparex immerses the sample in heptane or toluene solvent for 30 minutes with rapid agitation on a vibration table. There are also other different test methods. For example, Idema, the Trade Association for the National Data Storage Industry, has a test method, Idema Method M7-98, which uses hexane wash and analyzes the residue for silicone and other contaminants. This is a quick five minute soak of the sample in solvent, collecting the residue and solvent, evaporating the solvent and weighing the residue gravimetrically. Its purpose is to primarily to check for organic surface contamination and not necessarily to measure total extractables of a silicone release liner by solvent extraction.

Although the percent extractables number is often used in the release liner industry, it should be pointed out that the \% extractables and total extractables are different numbers. The \% extractables is a measurement of the \% of unreacted silicone as a percent of the coat weight. Total extractables is a measurement of the total amount of silicone per unit area. The \% extractables and the coat weight will both influence the total extractables. Total extractables measures the maximum amount of unreacted silicone available per unit area and is one of the criteria used in the electronics industry to determine the suitability of the release liner.

After extraction, a converter will often factor in the coat weight and then determine the \% of uncured silicone or \% extractables. For the end user, however, it is not the \% extractables but the more encompassing total extractables that determines the release liner quality.

This graph shows how a combination of low \% extractables and low coat weight influences the total extractables. For example, if 1.0#/ream of dry coating has 2\% extractables, the total extractables would be 3.24 \( \mu g/cm^2 \). In this case a coating with relatively good cure is too high in total extractables to meet a specification of <1.0 \( \mu g/cm^2 \). By combining a radiation cured system with a low coat weight, the total extractables can be kept to a minimum while still providing the necessary release for acrylic adhesives. For this reason, LO-EXT™ process radiation cured coatings are selected for this market.

\[
\text{#/ream} \times \% \text{ extractables} \times 1.62 \text{ Factor} = \text{Total Extractables (}\mu g/cm^2\text{)}.
\]
TOTAL Extractables (~tg/cm²) of Various Silicone Systems Compared

TOTAL Extractables (μg/cm²) of Various Silicone Systems Compared

LO-EX™ Total Extractables Consistently below 1.0 μg/cm².
Outgas

Outgas is a measurement of the total volatiles in ng/cm², including polydimethyl siloxanes and other organic compounds which volatilize when a sample is heated to a certain temperature over a given time period. Outgas must be kept to a minimum to prevent volatile organic components from contaminating head/disk assemblies and causing interference in the manufacture of hard disk drives. The test is designed to mimic what might happen when heating takes place in electronic components such as a computer disk drive assembly. Manufacturers will measure the outgas of various components including parts, assemblies, tapes, adhesives, etc.

Samples are exposed to various temperatures and time periods such as 85C/24 hours or 100C/30 minutes and then analyzed by GC/MS. Idema M11-99, “General Outgas Test Procedure by Dynamic Headspace Analysis”, qualitatively and quantitatively measures the volatile organic components at 85C for 16 hours.

Both the time and especially the temperature at which this test is done will affect results generally given in ng/cm². Both time and temperature should be noted when determining specifications.

Generally a good number is <5 ng/cm² at 85C/24 hours.

When we compare a number of formulas for outgas, we find that UV cured coatings without thermal heating can be quite high. Low coat weights of UV curable coatings with the addition of thermal heat will dramatically reduce the total outgas.

![Graph](image)

Outgassing 85C/24 hrs. (ng/cm²)

<table>
<thead>
<tr>
<th>UV</th>
<th>UV/Thermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Volatiles (ng/cm²)</td>
<td>111.5</td>
</tr>
<tr>
<td>Total Siloxanes (ng/cm²)</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Outgas of UV/Thermal systems can be much lower than UV.
ESCA or XPS Surface Analysis

The amount of migratory silicones in a release liner can be characterized by analyzing the surface of an adhesive for silicon after contact with the liner. X-ray photoelectron spectroscopy (XPS) is the analytical technique often used for this study. XPS is also referred to as ESCA (Electron Spectroscopy for Chemical Analysis). The test characterizes the adhesive surface by determining the percentage of certain elements. Elemental silicon is quantified and reported as the atom percentage of all the relevant elements in the adhesive. Generally, some transfer is seen from all silicone release liners, but the goal is to reduce this as much as possible. Results under 5% silicon are generally considered as low migration or transfer of silicone.

Samples are prepared by casting 5 mils wet of a solvent acrylic adhesive to the release liner, allowing it to air dry 5 minutes and oven dry 10 minutes at 158°F. The adhesive surface is then laminated to plain 92 gauge polyester with a 4.5 lb. roller. Alternatively, the adhesive may be sandwiched between two release liners.

After 24 hrs. of more under lamination at room temperature, the release liner is slowly peeled away exposing the adhesive surface. The adhesive surface is then tested immediately for elemental silicon by XPS to determine the presence of silicone or poly dimethyl siloxane [CH3CH3SiO]n. Results are reported in % of silicon on the adhesive surface at a specified angle.

The angle at which the test is done significantly affects results. For example a 20 degree angle will yield higher amounts of silicon than a 40 degree angle. The 20 degree angle is a shallower penetration into the surface. Silicone is present at higher concentrations on the surface. Various formulas used at the beginning of our research into low silicone transfer were tested at both angles to show a comparison.
The ESCA test angle will change the value of the % silicon on the test surface.

Range of Release Available
The LO-EXTM product line is available in a wide range of release from easy to tight. Due to the lower coat weights, the easy release may not be as easy as some other silicone coatings. As always, testing before use is recommended.

Differential liners with easy/medium or easy/tight combinations in 3:1 and 4:1 ratios and even higher ratios have been manufactured. Medium and tight release coatings have slightly higher total extractables but are generally below 1.5 μg/cm² on the tighter release coating.

Conclusion
A new patented process makes possible the manufacture of release liners with low silicone transfer to address the needs of a growing market in high technology products.

Acknowledgement
I would like to thank my colleagues, Kevin Cunningham and Dan Thompson, for their counsel in preparing this presentation.