

9. Silicone Release Coatings for the Pressure Sensitive Adhesive Industry

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In today's modern environment there is a wide range of applications for silicone release liners with pressure sensitive adhesives, ranging from release labels to diaper closures, medical applications (e.g., wound dressings), building insulation and health and beauty products [1-2-3].

Release liners are part of a composite made of a label with its own adhesive on a release liner or carrier with its own release coating. The label comprises either a synthetic face stock such as polypropylene or paper. The adhesive is usually an organic material such as a polyacrylate or polyisoprene based rubber. The release liner can be made from various substrates treated with a suitable product, the release coating. Such release liners allow transporting labels with their adhesives from the point of manufacture to the point of label application (e.g., a filling station of some sort). The release coating allows easy delamination or easy label transfer from their liners onto the object to be labeled.

The use of release liners began before World War II but really took off with the development of silicone release coatings in the early 1950s. There are several chemical types of release materials. However, many are migratory types; that is, significant amounts of the release material contaminate the surface of the released material. Those that do not migrate or transfer to the released material to any significant degree include polyacrylates, carbamates, polyolefins, fluorocarbons, chromium stearate complexes and silicones. Silicones enjoy a unique position because they can be applied and cured into a polydimethylsiloxane (PDMS) network on various backing substrates so limiting migration, but also because they allow substantially lower release forces than other materials. Silicone-coated substrates are sometimes referred to as siliconized release liners.

The choice and combination of backing substrate, silicone release coating and adhesive needs to be carefully selected.

Silicone Release Characteristics

One of the key properties of silicone is its low surface tension, and in particular, its low critical surface tension of wetting or low surface energy. This is a consequence of low intermolecular forces and high chain flexibility [4]. Unlike more rigid carbon-carbon backbones, PDMS polymers because of their backbone flexibility, and as they are at room temperature substantially above their T_g, can easily expose their low interacting/surface active methyl groups to provide low adhesion; or in other words, low release forces against adhesives they are exposed to.

Organic adhesives as used on labels cannot easily wet such a low energy silicone surface as there are no groups to interact, which results in ease of delamination and ease of transfer of the label from the liner to its point of use.

But low surface energy is not the only aspect to consider. Even fluorocarbons, despite a lower surface energy than silicones, do not match silicone release performance. Another key

component is the rheological behaviour of the cured PDMS network applied onto the backing substrate [5]. Recent work has shown that interfacial slippage also plays a role in the low release values observed on the release of pressure sensitive adhesives from silicone release coated liners [6-7-8]. A mechanism has been proposed for cured PDMS network/release coatings in which interfacial slippage minimizes the bulk shear deformation experienced by the organic adhesive [8].

Commercially cured PDMS release coatings can exhibit significant interfacial slippage. Sometimes silicone resins known in the paper industry as release modifiers need to be added to a silicone formulation to increase release forces. This may be necessary for processing reasons to convert the laminate construction to the label, or it may depend on the release force required for particular dispensing application. It is believed that these release modifiers “freeze out” interfacial slippage, resulting in increased adhesive deformation upon delamination and higher release forces. The release modifier reduces the segmental mobility of the PDMS chains within the cured coating network. If the PDMS is constrained by a rigid backing, there is still slippage at the interface due to bending of the PDMS at the crack tip at finite peel angles. It has become clear that the great advantage of PDMS in release applications is its low coefficient of friction under shear, compared to lower surface energy but higher shear friction (more rigid) fluorocarbons.

Factors to Consider for Silicone Release Coatings

Many other factors influence the selection of coating technologies and materials for liners and laminates. These include end-user requirements like converting, die-cutting and printing requirements and environmental concerns. If using silicones, some factors are related to them, some not (see Table 1).

The equipment used may drive the choice of release coating material. Most commonly used are either based on a three roll differential offset gravure or a five or six smooth roll coating head. Environmental and regulatory pressure may play a role as well, encouraging the selection of solventless or emulsion systems to deliver the required performance.

Substrate type, cure temperature, dwell time and humidity can affect cure and anchorage of the silicone coating to the substrate. The selection of adhesive required for the application also has a major bearing on release and anchorage characteristics.

In recent years, the use of plastic liners such as polyethylene, polypropylene or polyester films has increased. Siliconizing such substrates is a challenge because of their low resistance to high temperatures and their variability as they may contain additives such as antiblocking agents or stabilizers. Some of these are detrimental to the cross-linking of the silicone release coating. But overall these thermoplastic films are difficult substrates as they show poor adhesion and sometimes poor silicone cure to the applied coating. Special grades of film have been developed to improve adhesion, but they are more expensive. UV-cured silicone release coatings have been developed to avoid exposure to high curing temperatures, but overall the penetration of such UV-cured systems is low compared to heat-cured systems, which remain the preferred system.

If using silicone release coating materials, there is an array of silicone chemistries to select from. UV cure is sometimes used when applying a release coating on a low melting

temperature substrate such as low density polyethylene [9], but the most widely used cured chemistry for silicone release liner preparation is thermal cure.

To achieve a cured network, there are solvent-based, emulsion-based and solventless silicone systems [10]. Whereas the coating of the first two types is relatively straightforward, the coating of 100% solids materials is highly specialized and needs sophisticated coating equipment.

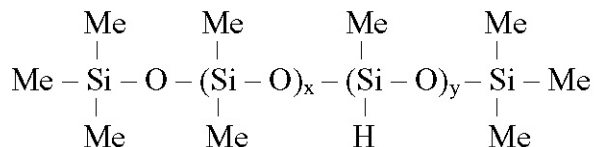
Table 1. Factors to Consider When Using Silicone Release Coatings

<i>Non silicone related factors</i>	<i>Silicone related factors</i>
Equipment Substrate Cure temperature Dwell time Humidity Adhesive type	Silicone cure chemistry Composition: <ul style="list-style-type: none"> • polymer architecture • modifier architecture • cross-linker architecture • additives

Cure Chemistry

To avoid migration, the PDMS release coating is applied and then heat cured onto the substrate to give a cross-linked silicone. To achieve cross-linking of the silicone release coating, the most predominantly used chemistry is cure via a hydrosilylation reaction. The composition of such silicone release coating consists of vinyl-functional PDMS, a hydrogen-functional PDMS and a platinum catalyst (see Figure 1). These can be reacted together using a hydrosilylation reaction. Additives used include inhibitors to provide for long bath life at room temperature and release modifiers. These silicone coatings are

a) hydrogen-functional siloxane



b) vinyl-functional siloxane

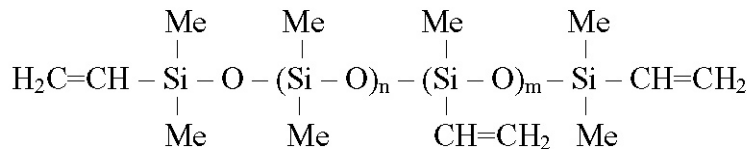


Figure 1. Structures of the silicone polymers used in release coatings.

The hydrosilylation reaction, especially of carbon-carbon multiple bonds, is one of the most important reactions in organosilicon chemistry and has been extensively studied for half a century [11-12-13]. This reaction is used to produce many organosilicon compounds. However, one of its primary uses is as a fast cross-linking or cure chemistry reaction as here to cure silicone release coatings.

Hydrosilylation is the addition reaction of a silane group (SiH) on a vinyl group (SiCH=CH₂) catalyzed by a noble metal such as rhodium or most often platinum. A general model has been proposed to explain how the platinum is involved in the reaction (see Figure 2) [14]. There are basically two different forms of this cure chemistry used industrially, both catalyzed by platinum. In one, a SiH-functional polymer reacts with a vinyl-functional polymer carrying Si-CH=CH₂ groups. In the other, a SiH functional polymer reacts with a hexenyl functional polymer carrying Si-CH₂-CH₂-CH₂-CH₂CH=CH₂ groups (see Figure 2). This simplified proposed mechanism does not explain the difference between vinyl- and hexenyl-based systems. In the hexenyl-based system, the unsaturation has been distanced from the polymer backbone and is therefore less sterically hindered. This allows a release coating material with a slightly faster cure upon application.

Associated with these two different forms of cure chemistry (vinyl or hexenyl), various inhibitors can be used to ensure sufficient bath life and prevent premature cure at room temperature of the coating mixture prior to use and curing. Inhibitors compete with the initial step of the hydrosilylation reaction and the addition of the unsaturated group from the polymer on the platinum catalyst (see Figure 2). So the selection of the platinum inhibitor has a major impact on cure speed [15-16]. An inhibitor strongly bound to the platinum catalyst forms essentially a very high barrier of access for the unsaturated group from the polymer to the active platinum catalyst center during stage one of the reaction mechanism above. Typical inhibitors employed here are acetylenic alcohols such as 1ethynyl,1-cyclohexanol or fumarate- or maleate-based inhibitors.

As the price of platinum increases (it has doubled in recent years), new polymer/crosslinker structures have been developed to reduce costs, in particular for solventless coating. Today rapid cure can be achieved with lower levels of platinum (i.e., 50 instead of 100 ppm).

As line speeds increase, the silicone is submitted between applicators at the nip of the coating equipment and the substrate to shear rates of the order of 10⁶ sec⁻¹. At these high shear rates, the silicone behaves very differently than expectations based on rheological measurements, which are usually made under relatively low shear. Silicone misting is one such manifestation [17-18]. So additives have been developed that will greatly reduce the volume of mist produced, even at 1600 m/min [19].

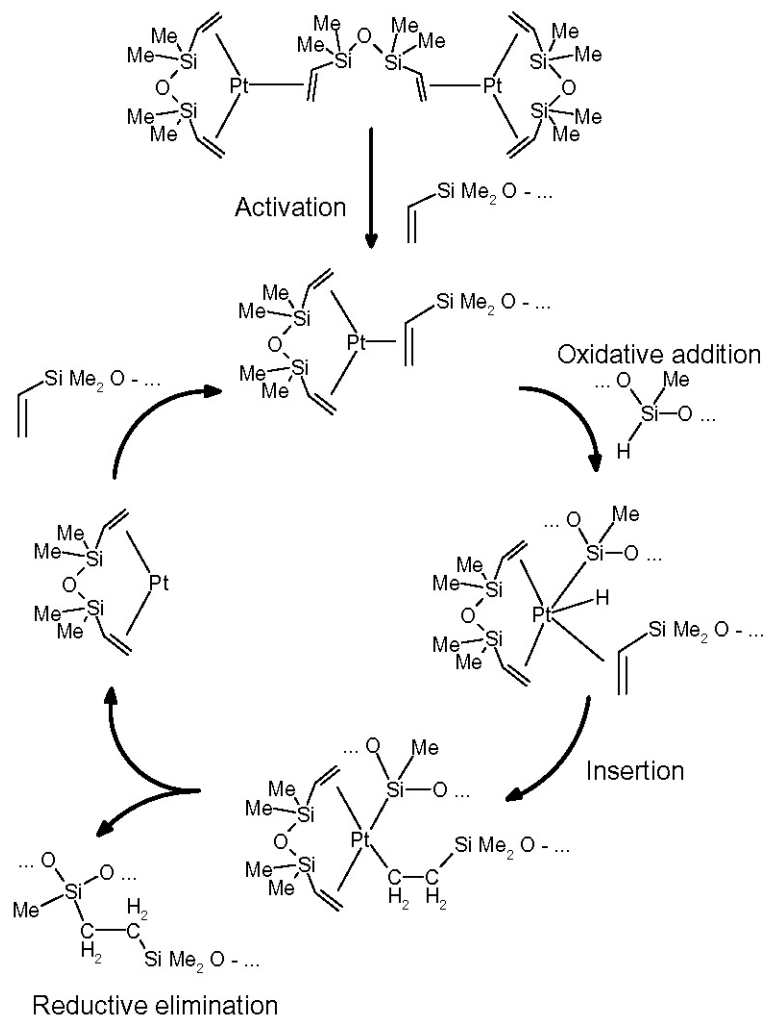


Figure 2. Hydrosilylation/addition cross-linking and cure mechanism

. Greater Use of Plastic Release Liners

In recent years, the use of plastic release liners such as polypropylene, polyethylene and polyester has increased, fueled in part by an increase in premium applications such as no-label-look beverage labels for aesthetic appeal and brand enhancement.

The siliconising of plastic films has a number of associated problems. These include the requirement of low curing temperature for polyolefin films, amongst others. Further, there is difficulty in adhering silicones to plastic films and maintaining anchorage of the silicone to the plastic film over time. This problem is particularly prevalent with polyester films. In addition, plastic films are quite variable. For example, several additives can be used in film production including antiblocking agents, heat stabilizers and plasticisers. These additives can affect cure and anchorage. This variability adds to the design complexity for a robust universal thermally-cured silicone system.

Some of the cure and anchorage issues associated with some plastic films can be overcome by using special grades of film. For example, co-extruded or primed polyester is used to ensure that there is no adhesion failure of the silicone to the film over time. However, these special grades of film are generally more expensive than standard grades. Consequently, the widespread use of these “treated” films has been limited.

The challenges to the silicone supplier are to develop robust silicone release coating systems for general grades of film that overcome the problems discussed above. The first attempts to overcome some of the challenges of coating films were made with the introduction of UV-curing silicone systems. UV-curing silicone systems met the low temperature constraints for polyolefin films. However, due to customer preferences and all-round release performance, thermally-curing silicone release coating systems that provide robust performance to films have been sought.

References

- ⁸⁵ Botts, J.; Philofsky, H. US Patent 2,601,243, June 24, 1952.
- ⁸⁶ Berridge, C. US Patent 2,843,555, July 15, 1958.
- ⁸⁷ Stalet, G. private communication, 2005.
- ⁸⁸ Yammanishi, A.; Sato, K. US Patent 4,518,031, May 21, 1985.
- ⁸⁹ Rhone Poulenc, *Guide de l'utilisateur*, data sheet ML09-7j.
- ⁹⁰ Dow Corning World, 1983, (January-February), 4.
- ⁹¹ Haenig, U. and Sauer D. 1500 Jahre Kultur der Osterinsel, 152, Philip von Zabern: Mainz, Germany 1989.

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