LOW TEMPERATURE SILICONE RELEASE COATINGS FOR TEMPERATURE SENSITIVE FILMS

John Kilgour, Chemist, Momentive Performance Materials, Waterford, NY

Introduction

The fastest growing area for silicone release coatings is in film substrates for release liners. The film based liners provide the label maker with a variety advantages including flatter adhesive surfaces for clear on clear labels, better die cuttability, better dimensional stability for film labels, and better line strength for automated labeling. While PET has been used for making release liners, in part because it can withstand the higher temperature needed for current silicone coating technology, a variety of temperature sensitive films including PE, BOPP, PE/PP laminates and PEK are waiting to grow into these performance opportunities.

The original response to the need for coating on temperature sensitive films was the discovery and development of UV cured silicone coating. Several UV silicone release coatings are available using based on both cationic and radical cure. While these are capable of coating temperature sensitive films, they are relatively expensive and require specialized coating equipment. In addition, there are some release performance limitations due to the large concentration of organic functional groups needed for adequate cure.

Thermally cured silicone release coatings have lagged behind the UV counterparts in coating at low temperatures. Occasionally a thermal silicone release formulation will be offered to the industry, most usually for PEK, which is the most thermally stable of the low temperature film substrates. But until now, only small “tweaks” to existing thermal formulations have been attempted. This paper describes the first successful concentrated effort to discover and design a silicone release coating aimed solely at low temperature cure on films with Tg’s at less than 120C.

Low Temperature Cure

Designing a new low temperature coating formulation meant discovering the kinetics controlling and defining cure. There are several methods of speeding up the high temperature reaction rates for the hydrosilylation reaction, which is the key reaction for curing thermal silicone coatings. But simply making the reaction go faster is not the same as lowering the activation temperature for the reaction. For the new low temperature system, every component was evaluated specifically for performance in the desired temperature range of 80 to 110C. Achieving success and curing at low temperature required new compositional discoveries in each silicone component. Thus, while the new systems will perform in any temperature range, they display their optimal advantage at low temperature. The results shown in Figure 1 below demonstrate exceptional cure at low temperature on commercial coating equipment under real coating conditions.

The graph in Figure 1 shows cure for two new low temperature formulations, designed for different release performance levels, and coated at two speeds and temperatures. They demonstrate the ability to
use the system to gain productivity through fast coating (lower dwell times), or further economic advantage by using thinner gauge films (lower temperature).

Thermal silicone release coatings are formulated using a vinyl containing siloxane polymer (base polymer), a hydride containing siloxane polymer (crosslinker), a platinum catalyst in silicone fluid, and an organic inhibitor:

\[
\begin{align*}
\text{Catalyst} & \quad \text{Hydride Siloxane Polymer} & \quad \text{Vinyl Siloxane Polymer} \\
\text{“Pt”} + \begin{cases} R_1 \\ R_2 \end{cases} & \quad \begin{cases} \text{HSiO}_{2/2} \\ \text{Me}_2\text{SiO}_{2/2} \end{cases} & \quad \begin{cases} \text{CH}_2=\text{CHSiO}_{2/2} \\ \text{R} \end{cases}
\end{align*}
\]

A variety of X’s and Y’s, R’s and S’s and concentrations of platinum have been developed to work at high temperatures (250 to 325F).

**Vinylsiloxane Polymer**

Most vinylsiloxane polymers in use today are linear silicones with vinyl groups on the terminal silicones. Attempts to speed the reaction in these vinylsiloxane polymers by shortening the polymer length (increasing the vinyl concentration) have been successful until a lower limit is reached and lower release properties are observed. Vinylsiloxane polymers that have both terminal and pendant vinyl groups are also used. They have advantages in providing unique release performance due to further
control of polymer formation and coating modulus. But adding more pendant groups to increase the reaction kinetics actually slows the reaction rate due to the lower reactivity of pendant vinyl groups. The solution was to redesign the siloxane to incorporate more terminal vinyl groups while controlling molecular weight and defining the crosslink density of the final silicone coating.

The cure reaction in silicone release coatings is due to the formation of a three-dimensional silicone polymer network. Figure 2 shows a comparison of cure for a conventional vinylsiloxane with several low temperature vinylsiloxane structures. As the web temperature drops below 240°F, the conventional vinylsiloxane increases in extractables (less cure) while the low temperature structures continue to cure completely below 220°F. The kinetic advantage as shown by the better cure is the result of faster network formation.

![Cure vs. SiVi Structure](image)

**Figure 2.** Extractable results (cure) for low temperature vinyl siloxane polymers vs. a conventional control polymer. New vinyl siloxane polymers show better cure as temperature declines below 220°F.

Figure 3 shows the results of Delta E measurements on a paper substrate. Stain was applied to the paper after coating at 0.7 lb/ream. The amount of color observed is an indication of how completely the silicone covers the substrate. In this case the lower Delta E’s for the low temperature polymers indicate better coverage, and better network formation. Although the change in vinyl siloxane polymer structure aided our low temperature kinetics, it is the better network formation and coverage that dictated the final choice of structure. More dramatic control of the reaction kinetics is found in the crosslinker and catalyst discoveries.
SilylHydride Crosslinker

Current crosslinkers consist of hydridomethylsilox (DH) units and dimethylsilox (D) units. An empirical understanding has evolved relating the cure performance to the relative amounts of D and DH. As the ratio of D to DH increases from zero to one, the cure time of the reaction time decreases and then starts to increases as the ratio is increased. Although the reaction reaches completion faster, the initiation temperature does not decrease. The discovery of SiH structures with a low activation energy, which could be incorporated into the crosslinking structure, was the key to the creation of low temperature cure formulations. The structure was then designed for premium release coating performance. Figure 4 shows the comparison of a conventional silicone hydride crosslinker and a silylhydride crosslinker developed for low temperature cure. At high temperatures of 275F or above both types crosslinkers provide similar cure. But as the temperature declines, particularly below 240F, the more reactive SiH crosslinker shows continued complete cure while the one used in the current technology is no longer fast enough to provide complete cure.

As illustrated in Figure 4, when the new silylhydride is paired with first a conventional vinylsiloxane, and then with two low temperature vinylsiloxanes, the results show that the kinetics are dominated by the silylhydride crosslinker. The two new vinylsiloxane formulations cure better than the conventional vinylsiloxane as the temperature decreases to 225F, with potential for further advantage at lower temperatures. But the most dramatic kinetic improvement is the use of the new silylhydride crosslinker in comparison to the conventional crosslinker.
Platinum Catalyst

The catalyst is a second key component in reducing the reaction cure temperature. Karstedt’s catalyst, discovered years ago by GE, has become the industry standard for thermal release coating. Although Karstedt’s can be used as low as 25°C, the initiation of the hydrosilylation reaction is not fast enough for complete cure in the time required for high speed release coating until temperatures in the range above 240°F. Where cure is desired at lower temperature applications, a dramatic increase in the amount of catalyst is required. In developing the low temperature system, the discovery of a lower activating platinum catalyst was critical.

The activity of the platinum catalyst is determined by the oxidation state and ligands associated with the platinum metal. Slower catalysts such as chloroplatinic acid (Speir’s catalyst) have a significant “lag time” between when they are introduced into the reaction solution and when the reaction starts. Karstedt’s catalyst uses divinyldisiloxane as a ligand, and enters the hydrosilylation reaction faster, but performs best at higher temperature. The discovery of a new platinum catalyst complex with a lower activation energy for initiating the hydrosilylation reaction allows the curing to take place at the desired temperature.

Evidence for the lower activation temperature of the new platinum catalyst is provided by DSC experiments. The DSC follows the reactivity of the catalyst by following the course of the hydrosilylation reaction. A formulated solution is slowly heated from ambient temperature through the

![Figure 4. Extractable results (cure) for low temperature silylhydrides in conjunction with control vinylsiloxanes and low temperature vinylsiloxanes with conventional catalyst. The kinetics are dominated by the silylhydride reaction speed.](image-url)
reactive temperature range until complete reaction has been attained. The DSC follows the reaction by measuring heat generated by the reaction, and there are three critical temperature measurements. The first is the temperature at which the reaction is initiated. The second is the temperature peak seen at the fastest part of the reaction. The third is the 95% completion temperature at which the reaction is considered complete. It should be noted that there is no direct relation between temperatures observed in DSC and curing release coatings. However, the use of the DSC for predicting reactivity trends for the reaction components has been well documented.

Figure 5 shows a typical DSC and the points for each measurement. The insert shows the comparative results for a formulation made with Karstedt’s catalyst and several versions of the new catalyst. The measurements in the insert show that the new catalyst initiates the hydrosilylation reaction at ten degrees lower than Karstedt’s. Similarly, the new catalyst reaches the peak reaction at ten degrees lower than Karstedt’s catalyst. Finally, the new catalyst reaches completion ten to twelve degrees lower than the currently used formulation. While the absolute temperatures do not translate to coating, the ten degree temperature advantage of the new catalyst demonstrates a very significant kinetic advantage. Along with the faster hydride crosslinker and better vinylsiloxyane polymer, the new catalyst defines a complete formulation with a synergistically lower temperature requirement for activation and reaction of silicone release coating.

**DSC Analysis of Low Temperature Cure Catalyst**

![DSC Analysis](image)

**Figure 5.** DSC comparison of Karstedt’s catalyst with new Platinum Catalyst. The graph shows typical DSC. The insert shows the results for the reaction onset, peak reactivity and 95% completion for silicone coating formulations. The new Platinum Complex maintains a 10+ degree temperature advantage.
Inhibitor

Numerous classes of organic inhibitors have been developed for silicone release coatings, among these maleate esters, such as diallyl maleate, and alkynyl alcohols, such as Surfynol-61, have proven to be the most effective. They are used as “reaction switches” to keep the reaction from starting before the silicone formulation is on the substrate, and then allowing the reaction to rapidly reach full speed. As inhibitors, they are chosen for a combination of both bulk bath life in the silicone reservoir and thin film bath life on the rollers. The inhibitor’s volatility at coating temperatures is also one factor considered in controlling the initiation of the hydrosilylation reaction required for curing. In low temperature coating, it may be desirable for the inhibitor to evaporate from the surface at oven temperatures of 175 to 220°F. A low boiling alkynol alcohol was used to provide a combination of inhibition and rapid evaporation.

Silicone Coated PEK

With the kinetics of each component chosen for low temperature cure, the system was formulated and the design tested. Figure 6 shows results of low temperature release coating on polyethylene coated kraft paper (PEK) on a pilot coating. The web temperature was set at 194°F (90°C), and the PEK was coated at three different coating speeds, resulting in dwell times of 5, 3 and 2 seconds. Samples of the PEK were then extracted with MIBK for 24 hours, and then analyzed for silicone. The results are reported as “extractables,” the amount of silicone that can be extracted from the coating. Comparing the amount of silicone extracted with the coatweight of silicone on the substrate gives a measure of the extent of

![Cure for PEK Coated at 90C](image)

**Figure 6.** Extractable results (cure) for two examples of the new platinum complex formulated with the complete low temperature formulation on PEK at 90°C. The low level of extractables demonstrates complete silicone cure at fast coating speeds.
reaction. The lower the extractables, the more complete the reaction. Normally a target of less than 5% extractables is considered acceptable for silicone release coating. Figure 5 shows that coating PEK at 194 F (90C) with the new low temperature formulation gives very low extractable levels between 2 and 3% even at coating swell times of 2 seconds.

To this point the project focused on achieving rapid cure at low temperatures. But a silicone coating must provide the desired release characteristics, or the effort is of little commercial value. Figure 7 shows the initial release results for TESA 7475 acrylic tapes. The x-axis shows several different formulations of varying vinylsiloxane polymers and silylhydride crosslinkers. As both the vinyl siloxane and hydride siloxane structures and ratios change, the release values change from relatively high to low release. The current work is focused on developing the low release formulations on different substrates. Ultimately the high release formulations will be developed for applications where high release is needed. This might occur for example where lower release adhesives are being used, or in dual release liners where release ratios of three to one are desired.

**Initial Release TESA 7475**

![Graph showing initial release results for TESA 7475 acrylic tape from PEK coated with low temperature formulations. The x-axis shows formulations containing different structures of vinylsiloxane and silylhydride crosslinkers. The control is a standard vinylsiloxane and crosslinker heated until complete cure was attained. The release values vary with the composition of the silicone polymers defining a wide range of performance.](image)

**Figure 7.** Release results for TESA 7475 acrylic tape from PEK coated with low temperature formulations containing different structures of vinylsiloxane and silylhydride crosslinkers. The control is a standard vinylsiloxane and crosslinker heated until complete cure was attained. The release values vary with the composition of the silicone polymers defining a wide range of performance.

Dynamic release is a second measure of release performance. Figure 8 shows the release results for TESA 7475 tapes pulled at different speeds from 0.04 to 4 m/sec. Two different formulations of vinylsiloxane polymer and silylhydride crosslinker are shown. One shows a dynamic release profile and the second a flat release profile. Control of both the release force and the dynamic profile are due to the nature and density of the crosslinking in the final polymer network. The new functional groups developed for low temperature cure have the added benefit of increasing the control of network formation and release performance. Selection of the appropriate components can be used to define both the desired release force and profile.
Figure 8. Dynamic release for TESA7475 acrylic tapes from PEK coated with the low temperature release coatings with different compositions of vinylsiloxane and silylhydride crosslinker. The results demonstrate the ability to control dynamic and flat release profiles.

Figure 9 shows the same formulations with TESA 4651 tape applied. The hot melt tapes have typically low release values. As the adhesive becomes less aggressive, and the release values become lower, the release force responds to the low surface energy supplied by the silicone polymer. At low release levels there is less impact on release from the modulus of the silicone polymer and the values tend to compress.

Figure 9. Release results for TESA4651 tape from PEK coated with low temperature formulations containing different structures of vinylsiloxane and silylhydride crosslinkers. The control is a standard vinylsiloxane and crosslinker heated until complete cure was attained. The low release values represent a sensitivity to the silicone polymer coating.
Silicone Coated Polypropylene

As a temperature sensitive film, polypropylene is a greater challenge for low temperature coating. Polypropylene has a low Tg, and is not supported on paper as the polyethylene coating on paper is. Thus PP is more sensitive to dimensional stability under the coating conditions of temperature and pulling tension. With this in mind, polypropylene was coated using the new low temperature formulation at 175F (80C) on the pilot coater at Black Clawson. The formulation employed the low temperature platinum catalyst and vinylsiloxane. Several of the new crosslinkers were tested, and the fastest current silylhidride crosslinker was used as a control for comparison. The results shown in Figure 10 show that excellent cure was obtained at slower line speeds. However as the line speed was increased, the new crosslinker structures give continued excellent cure at less than 2% extractables while the conventional crosslinker provides less complete cure.

![Cure on Polypropylene at 175F](image)

**Figure 10.** Cure on polypropylene film at 175F on a pilot coating line. The low temperature catalyst and vinylsiloxane were formulated with a fast conventional silylhidride crosslinker and three low temperature crosslinkers. As the coating speed is increased to low temperature crosslinkers continue to provide excellent cure (low extractables) while the conventional crosslinker starts to fail.

The silicone coated polypropylene films were also tested for their release properties. TESA 7475 tapes were applied at pulled at intervals from 1 to 28 days. The results are shown in Figure 11. The formulations all used the new platinum catalyst and the vinylsiloxane polymer. The current crosslinker was used as a reference sample, and several new crosslinkers were used. As with the PEK films above, a range of release values were found. The results show that release can be controlled from a premium low release to a high release at four times the release value. It is a demonstration that the low temperature
system can be used with a variety of adhesives as well as double sided applications where differential release values separated by at least a factor of three are desired.

Anchorage, the ability of the coating to adhere to the substrate, is another key performance characteristic for silicone release coating. By comparison, when conventional paper release formulations are chemically modified for faster cure, they tend to anchor poorly to the substrate. For example, poor anchorage is often observed with faster curing crosslinkers. The measurement for anchorage is a simple rub-off test. The coated substrate is vigorously rubbed with a finger. If the silicone material “rubs off,” then there is poor anchorage. The silicone release developed for the low temperature cure systems anchor very well at the temperatures needed for temperature sensitive films.

**Conclusion**

The discovery and successful development of completely new, low temperature formulations is opening the area of temperature sensitive films for thermal silicone release coatings. Low temperature coating can be performed on a variety of films such as polypropylene, polyethylene and multilayered film laminates as well as substrates such as poly coated paper and paper. This was achieved by new discoveries in the three major components of the silicone formulation, the vinylsiloxane polymer, the silylhydride crosslinker and the platinum catalyst. The new systems allow the coater to produce liners with more temperature sensitive films while coating at faster line speeds or lower film thicknesses.
In addition to low activation energies, the novel structures present new opportunities for unique network formation that can be used for controlling release energy as well as defining the release profile properties of the silicone coatings. Thus release can be controlled from low, premium release to high release values. Similarly release profiles from dynamic to flat can be achieved.

Acknowledgments

A variety of people through their thoughts and hard work have made this research possible including John Cummings, Ed Landry, Brenda Wutzer, Melania Lapinski, Robert Frye, Susan Nye, Jos Delis, Tom Ray and Keith Weller. My thanks to all of them.
TECH 31 Technical Seminar Speaker

Low Temperature Silicone Release Coatings for Temperature Sensitive Films

John Kilgour, Ph.D., Momentive Performance Materials

John Kilgour, Ph.D., is a silicone chemist in the Paper Release Group at Momentive Performance Materials in Waterford, NY. He is currently involved in new product research and development in the area of thermally cured silicone paper release coatings. Kilgour received a B.A. in chemistry from Carleton College. Interrupted by two years of service at the U.S. Army Chemical Corp Research Center, he returned to Iowa State University to complete a Ph.D. in chemistry. Kilgour has spent more than 30 years in research in silicone chemistry, first at Union Carbide and then later at GE Silicones, which was sold to form Momentive Performance Materials. His other areas of interest include silicone surfactants, silicone coupling agents, fiberglass coatings and silicones for personal care.