

# DEVELOPMENT OF IMPROVED CONTROLLED-RELEASE POLYMERS FOR SILICONE RELEASE COATINGS

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## Introduction

Pressure-sensitive adhesives are ubiquitous in commerce. These materials appear in the form of tapes, labels, and free-standing films that frequently require a release liner to be bonded to the adhesive surface of the article. Solid, crosslinked polydimethylsiloxane (PDMS) has been known as a good release liner surface for 60 years.[1] The chemistry and physical structure of PDMS results in hydrophobicity, low reactivity, low surface energy, and very low  $T_g$ .

A typical laminate construction consisting of a facestock, PSA, release coating, and liner substrate may have a thickness of approximately 6 mil. Of this dimension, less than 1% is silicone release coating. Thanks to advances in high speed coating technology and silicone chemistry, less than 1 micron thick defect-free silicone coatings are routinely applied and cured on papers and films at line speeds exceeding 1000 meter/minute (this corresponds to production of about 300 miles of release liner in an 8 hour shift).

The silicone surface of the release liner is produced by coating the liner substrate with a mixture of reactive siloxane fluids that subsequently undergo a crosslinking reaction and cure to form a network solid. In the past, siloxanes were commonly applied in the form of dilute solutions in aromatic and aliphatic solvents. However, these organic solvents are associated with environmental, health, and safety risks and market demand has led to the dominance of thermally-cured 100% silicone solids release coatings.[2] One consequence of solvent reduction has been the need to carefully control the viscosity of the siloxane fluids that make up the coating composition so that it remains workable on high speed coating equipment.

In order for a label construction to function properly, the cured release coating must securely adhere to the PSA surface and then easily release from it. Failure of the liner's thin silicone coating to detach from the PSA in a predictable manner renders the label unusable. The release performance of a release liner is determined by measuring the work or force required to peel the facestock and adhesive away from the liner (or to peel the liner from the facestock) at a specified speed and angle. Instruments are used to precisely measure release of laminate constructions that have been slit into tapes of fixed widths and the results are reported in terms of force per unit of width (commonly reported in N/cm or gf/inch). For example, 5 gf/in is considered "easy," or low release; 200 gf/in is considered "tight" or high release.

Tighter release liners are desirable for use with repositionable labels and other products where premature delamination is a concern as well as with transferable adhesive films that require a differential in release

force between two liners. The release force of a laminate can be tuned by the addition of a controlled release polymer (CRP) to the coating formulation. Depending on the application, the CRP can constitute 80% of the coating. This is why we believe it is more appropriate to refer to these components as controlled release *polymers* rather than additives.

Typically, a CRP composition consists of a reactive siloxane resin, PDMS, and a diluent. After coating, the resin participates in the curing reaction and becomes integrated into the coating's polymer network. These resins are glassy network solids at room temperature and are readily soluble in aliphatic or aromatic hydrocarbons, but disperse in PDMS fluids. The incorporation of resin into the release coating modifies the rheology of the coating and increases the release force of a laminated adhesive.

Because some applications require high CRP loadings in order to achieve sufficiently tight release, it is desirable for a CRP composition to have a high concentration of siloxane resin. This gives the formulator more freedom in designing coatings. However, the amount of resin that can be dispersed in a CRP is limited by the final viscosity of the coating formulation.

The viscosity of a CRP solution can be reduced by the addition of diluents that more readily dissolve siloxane resin, which allows the resin concentration to be increased.[3] Volatile organic solvents have been used successfully with solvent-borne release coatings, but the added solvent would negate many of the benefits of the solventless systems that are now favored. Volatile cyclic dimethylsiloxanes have also been used as diluents, but their vapors can produce silica dust in the coater oven and thermal oxidizer. The use of high flashpoint  $\alpha$ -olefins or other "reactive diluents" is more favorable with respect to safety and efficiency. Ideally, reactive olefin diluents will participate in the siloxane curing reaction and become incorporated into the silicone matrix so that no free diluent remains and nothing is lost to evaporation. Therefore, these systems can be said to contain 100% solids and over time this has become the conventional wisdom. However, our own field studies comparing silicone consumption and final coat weight have found discrepancies that we attribute to a loss of the majority of olefin by evaporation.

The evaporation of olefin diluent reduces the efficiency of the coating process for the following reasons. First, the lost olefin is a non-value-added component that increases materials and shipping costs without contributing to coat weight or release performance. Second, the lost olefin is a combustible liquid and its vapors can produce smoke in the coating oven or thermal oxidizer. In some cases, it is necessary to limit production speed in order to control this unwanted smoke generation. Furthermore, we have found that CRPs containing higher concentrations of olefin diluent are more prone to excessive foam formation at the coating head. This foam can cause defects in coating coverage and may force the operator to discard the foamed coating bath, creating delays and waste.

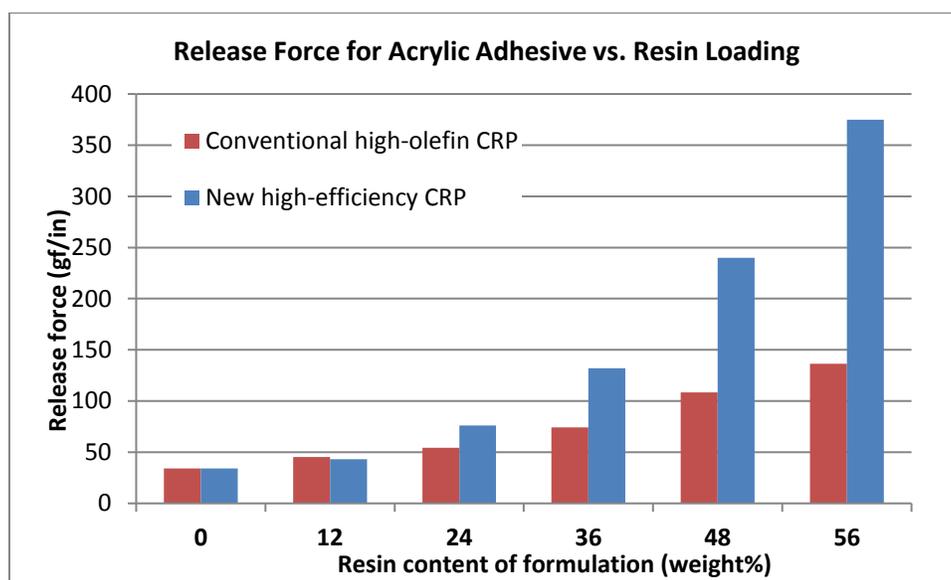
Therefore, we have developed a new high-efficiency CRP that can help reduce the final cost of tight-release coatings by using a unique, reactive siloxane carrier fluid to replace  $\alpha$ -olefin diluent without sacrificing the high resin loading that is needed for tight-release applications. The higher siloxane content of the new CRP can improve process yield and reduce the evaporation losses, smoking, and foaming associated with olefin diluents. Furthermore, we found that the new CRP can be more effective

at increasing the release-force of coatings than a conventional CRP. A comparison between the new high-efficiency CRP and a conventional CRP containing a high level of  $\alpha$ -olefin is described below.

## Results

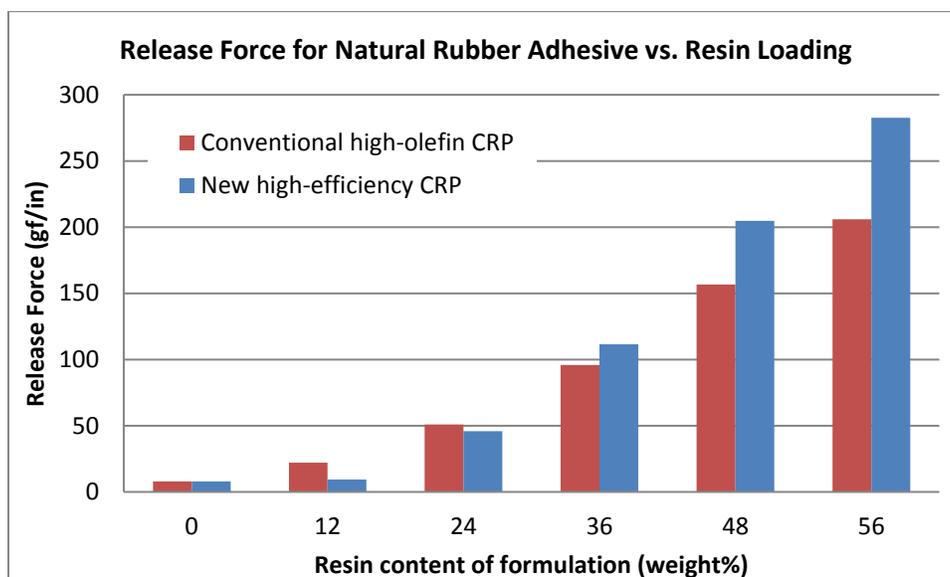
Pilot coater trials were conducted to compare the release performance of the new high-efficiency CRP with a conventional CRP with a high level of  $\alpha$ -olefin. Glassine paper was coated with 0.8 lb/ream of silicone using a five-roll coater and cured with an oven dwell time of 5 s and an exit web temperature of 160 °C. All formulations had a SiH/vinyl molar ratio of 2.25. Release performance was tested using a commercial natural rubber adhesive tape and a commercial acrylic adhesive tape, which is known to be sensitive to residual hydride.

We found that the new carrier fluid improved the resin efficiency of the high-efficiency CRP. For coating formulations with the same resin content, the high-efficiency CRP produced liners with higher release force than a conventional high-olefin CRP. The higher response can allow tight-release coatings to be produced with less CRP than before. This improvement in efficiency was observed with both the acrylic (Figure 1) and natural rubber adhesives (Figure 2), which indicates that the effect was not due to the presence of residual silicon hydride. Liners were retested after one month and both CRPs exhibited stable release. We also found no difference in the amount of extractable “loose” siloxane between the two CRPs.



**Figure 1.** Release performance of conventional and high-efficiency CRPs. Liner was peeled from the acrylic adhesive tape at a rate of 12 inch/min after aging 20 h at 70 °C.

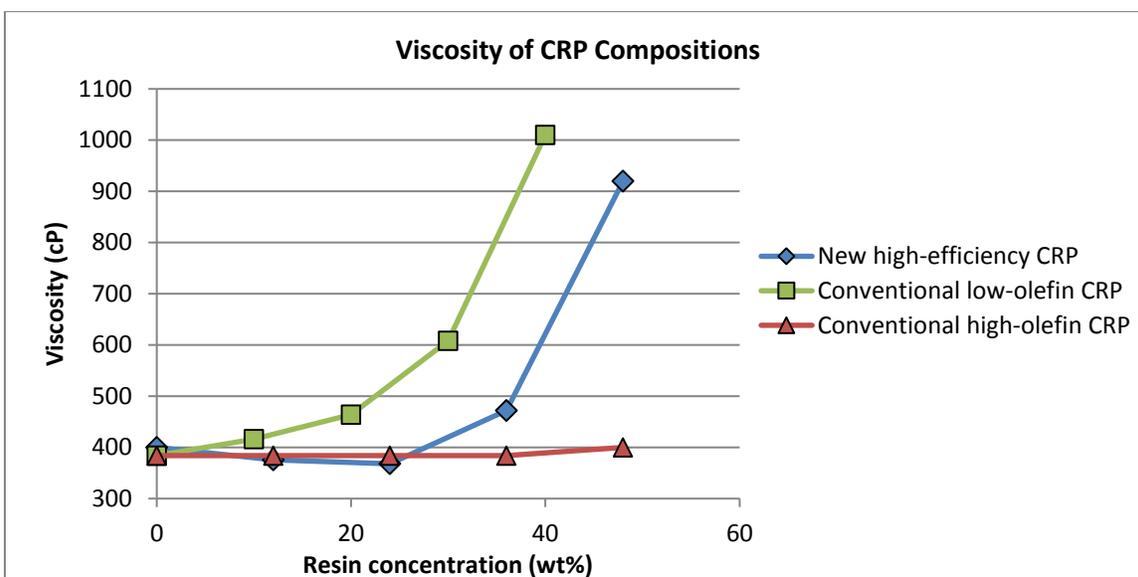
Note: Test data. Actual results may vary.



**Figure 2.** Release performance of conventional and high-efficiency CRPs. Liner was peeled from the rubber adhesive tape at a rate of 12 inch/min after aging 20 h at 70 °C.

Note: Test data. Actual results may vary.

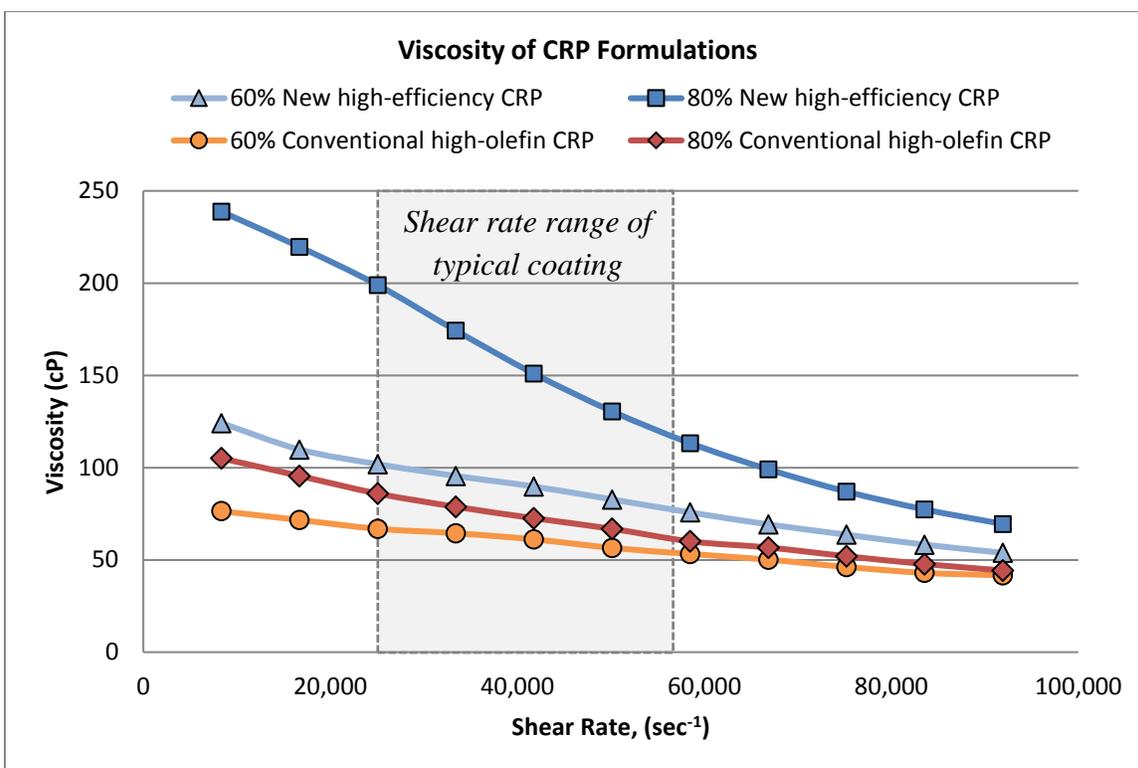
Viscosity measurements were performed on formulations containing the high-efficiency CRP and the conventional CRP dispersed in vinyl-terminated polydimethylsiloxane fluid with a DP of 150 using Brookfield rotary viscometer. At resin concentrations greater than 30%, the high-efficiency CRP formulation had a higher viscosity than the conventional high-olefin CRP (Figure 3). For comparison, another commercial CRP containing a low level of olefin diluent was also tested. The high viscosity of the low-olefin CRP, which does not benefit from the new siloxane carrier fluid, can restrict the amount of resin that can be added to the final coating formulation.



**Figure 3.** Viscosity of coating baths formulated with different CRP compositions in  $M^{Vi}D_{150}M^{Vi}$  siloxane fluid; normalized for final resin concentration.

Note: Test data. Actual results may vary.

We also examined the shear thinning behavior of the high-efficiency CRP and the conventional CRP dispersed in vinyl-terminated polydimethylsiloxane fluid with a DP of 80. A Kaltec Scientific high-shear rheometer was used to measure deflection versus torque at a shear rate of 10,000 to 90,000  $s^{-1}$  and apparent viscosity was calculated. The high-efficiency CRP experienced shear thinning that was not apparent in the conventional CRP. It is worth noting that commercial coaters frequently operate in a shear range of 40,000 to 60,000  $sec^{-1}$ . As can be seen in Figure 4, the viscosities of the formulations containing 60-80% of the new CRP were higher than those containing the conventional CRP.



**Figure 4.** Shear-thinning behavior of CRPs blended with  $M^{Vi}D_{80}M^{Vi}$  siloxane.

Note: Test data. Actual results may vary.

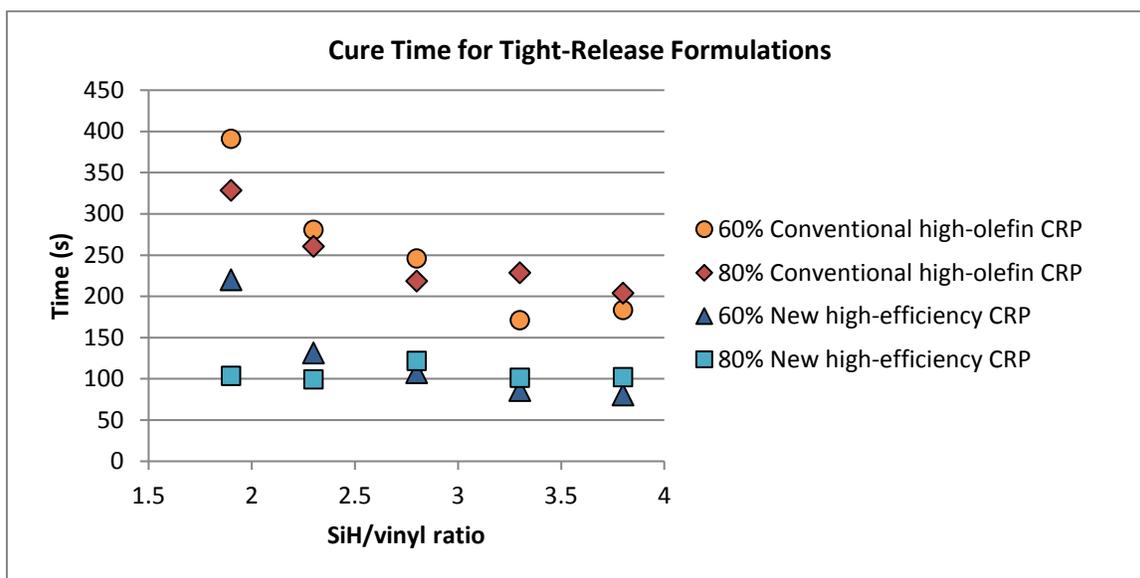
In order to prevent premature cure, convertors require that silicone release formulations exceed a minimum bulk- and thin film bath life. Both measures of bath life depend on several factors, especially the type and amount of inhibitor used in the formulation. Inhibitors are distinguished by their volatility and ability to coordinate to platinum. We tested the effect of the new high-efficiency CRP on bath life of a coating formulation containing vinyl-stopped PDMS fluid with a DP of 80; poly(methylhydrogensiloxane) crosslinker; and 1-ethynyl-1-cyclohexanol (ECH) inhibitor, which is known for promoting fast cure, at a concentration of 0.25 wt%. The thin film bath life exceeded the recommended 15 minute minimum and the bulk bath life was below the maximum 100% viscosity increase after 4 hours at 40 °C. The results are shown in Table 1 below.

**Table 1.** Bath life of formulations containing high-efficiency CRP.

Note: Test data. Actual results may vary.

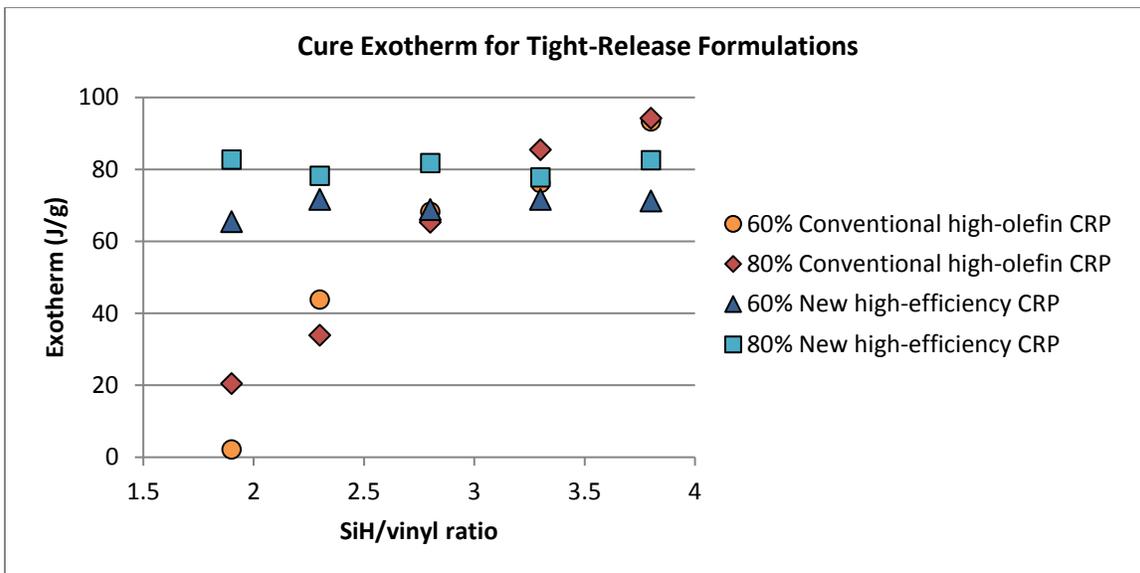
High-efficiency CRP (%)	20	40	60	80
SiH/vinyl ratio	2.2	2.2	2.2	2.2
Pt concentration (ppm)	100	100	100	100
Thin film bath life	83 min.	96 min.	100 min.	120 min.
Initial viscosity (cP)	216	232	272	560
4h, 40 °C Viscosity (cP)	248	256	304	616
Change	+15%	+10%	+12%	+10%

The rates of cure for coating formulations containing the high-efficiency CRP and the conventional CRP were measured using differential scanning calorimetry (DSC). Each CRP was dispersed in vinyl-stopped PDMS base polymer, poly(methylhydrogensiloxane) crosslinker, 0.25% ECH inhibitor, and 100 ppm platinum. The high-efficiency CRP finished curing in less time than the conventional CRP as shown in Figure 5. The DSC data also show that the high-efficiency CRP required a smaller excess of crosslinker to achieve complete cure as shown in Figure 6. Using a smaller excess of crosslinker can be desirable because the residual SiH in the coating can react with acrylic adhesives.



**Figure 5.** DSC data showing curing time vs. SiH/vinyl molar ratio for the high-efficiency CRP and the conventional CRP. The cure time is the difference between cure onset and 95% completion at a temperature ramp rate of 10 °C/minute.

Note: Test data. Actual results may vary.



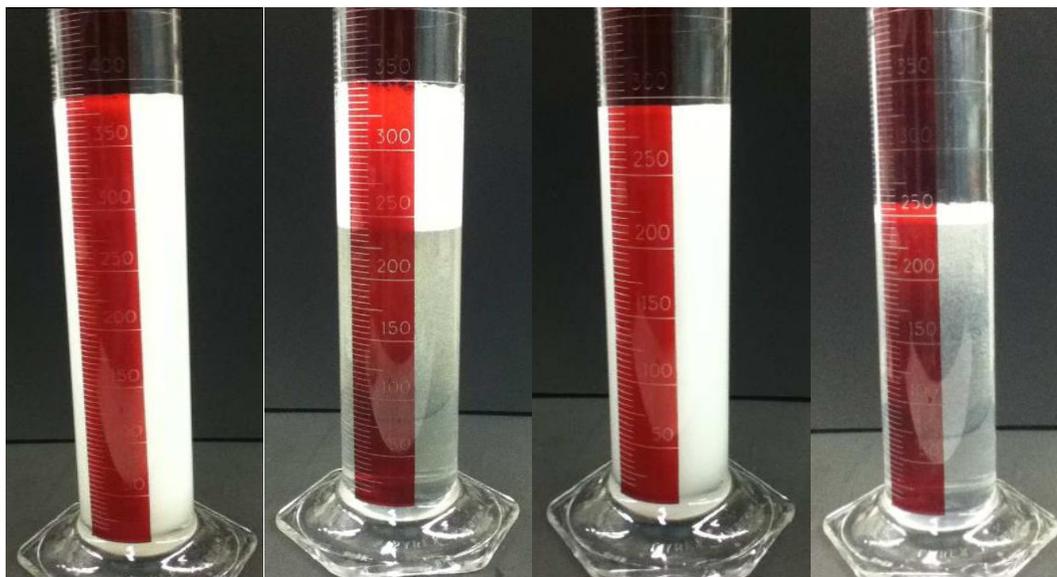
**Figure 6.** DSC data showing the cure exotherm vs. SiH/vinyl molar ratio for the high-efficiency CRP and the conventional CRP. A larger exotherm indicates a higher degree of crosslinking. Note: Test data. Actual results may vary.

The smoking of the high-efficiency CRP and the conventional CRP was evaluated by placing 0.5 g of a siloxane coating bath containing 50% resin solids into an aluminum weighing dish on a hot plate and covering the pan with a stoppered glass cylinder as shown in Figure 7. The hot plate temperature was increased to 230 °C and the atmosphere in the tube was observed for five minutes. The bath containing conventional CRP quickly generated a dense fog inside the tube while the bath containing high-efficiency CRP generated very little smoke. This result was confirmed during field trials on a commercial coating line wherein the customer was able to improve productivity.



**Figure 7.** Smoke generated by heating coating baths containing conventional CRP (left) and high efficiency CRP (right). Note: Test results. Actual results may vary.

The foaming of the high-efficiency CRP and the conventional CRP was evaluated by placing 250 mL of a silicone coating bath containing 50% resin solids into an Oster 6694 kitchen blender and agitating on high speed for two minutes. The frothy liquid was then poured into a 500 mL graduated cylinder and the volume was measured (Figure 8). The conventional CRP bath had increased in volume to 390 mL, while the high-efficiency CRP bath had increased to only 295 mL. After 30 minutes, the volume of the conventional CRP bath had decreased to 345 mL (110 mL foam layer), while the high-efficiency CRP bath had decreased to 255 mL (15 mL foam layer). The smaller volume of air entrained in the coating bath during agitation and the more rapid defoaming indicate that the high-efficiency CRP was more resistant to foam formation. This result was confirmed during field trials on a multi-roll commercial coating line, wherein the customer was able to improve productivity.



**Figure 8.** Defoaming of coating baths containing 50% resin solids. The bath containing conventional CRP is shown at 0 minutes (far-left) and after 30 minutes (center-left). The bath with the new low-olefin CRP is shown at 0 minutes (center-right) and after 30 minutes (far-right).  
Note: Test results. Actual results may vary.

## Conclusion

We have developed a new high-efficiency controlled release polymer composition that utilizes a unique siloxane carrier fluid to replace  $\alpha$ -olefin diluent. This carrier fluid allows the new CRP to maintain a low viscosity and high resin concentration beneficial for tight-release applications while losing less material to evaporation. Pilot trials showed that the new CRP produced tight-release coatings using less resin and crosslinker material than a conventional CRP. The new CRP also generated less smoke and foam than the conventional CRP, which may allow for better process productivity.

## **Acknowledgements**

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## **References**

1. R. S. Avery (1957) US Patent 2,419,809
2. R. P. Eckberg (1981) US Patent 4,256,870 and references therein
3. A. Dallavia (1985) US Patent 4,526,953 and references therein