SILICONE BENEFITS FOR TAPE APPLICATIONS

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Despite silicone having a major role in almost all label products, usage in pressure sensitive tape applications is somewhat sporadic. Silicone is nearly essential to some applications, while for others it is a particularly poor choice. This paper will examine some of the positive and negative attributes of silicone as a release coating. The first parts will detail stable release, low release, and adjustable release applications. Pigmenting will follow these, as will overviews of low friction and low contamination properties.

Silicones in Stable Release Applications

Traditional tape release coatings consist of film forming organic polymers with low surface energy additives. A typical system could consist of acrylic or vinyl acetate polymers with a release material such as surfactants or waxes. The problem with such systems is that release has a tendency to change over time. The most common problem is that release increases with time, and does so more quickly and to a higher degree in the presence of elevated humidity.

Multiple Phase Release Systems

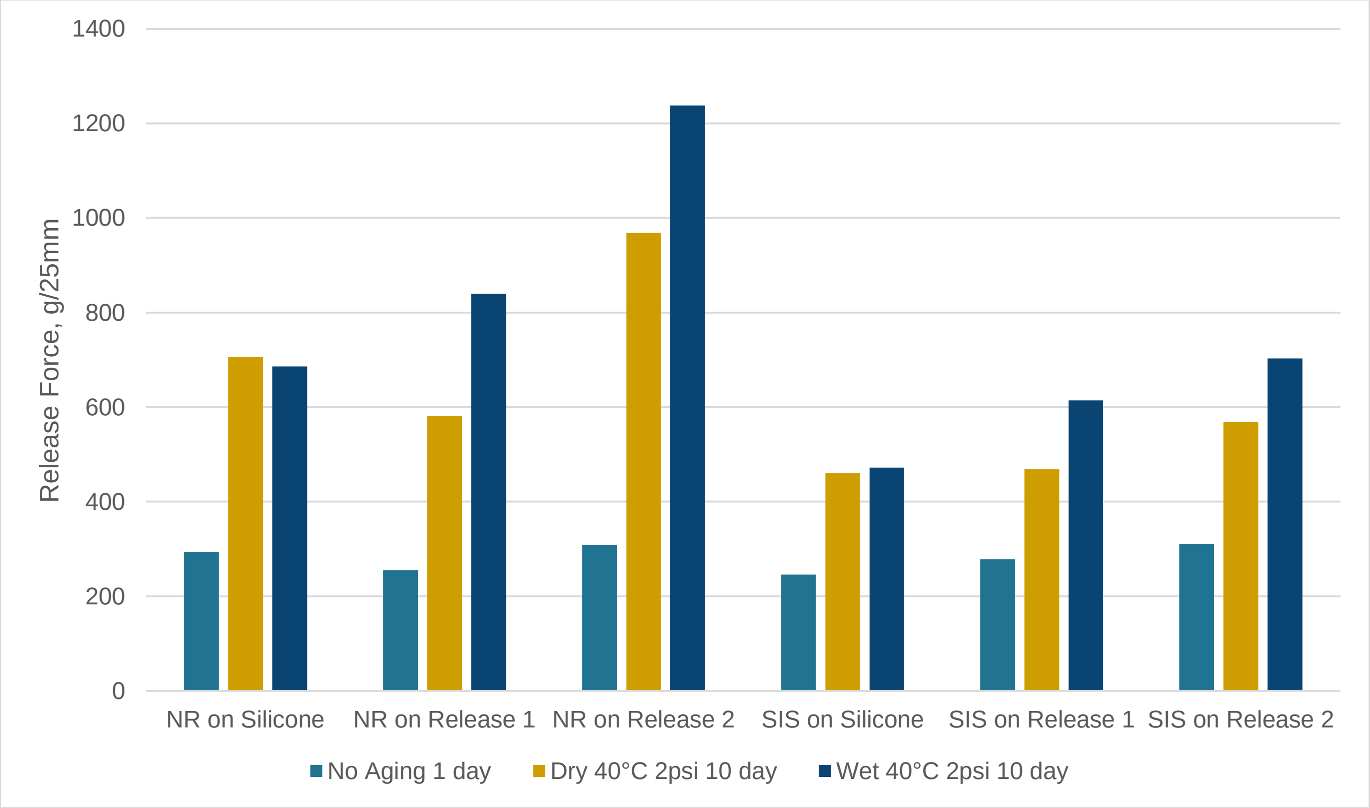
These changes in release can most often be attributed to the mismatch in surface energy that is inherent between organic emulsion polymers and low release materials. There are higher repulsive forces between a PSA and a low surface energy material than there are for a high surface energy material. Therefore, the lower surface energy material will preferentially be displaced away from the surface of the release coating, rendering it inactive. Consequently, the surface concentration of the release agent decreases over time. Generally, there is some moisture sensitivity on the part of the release agent or polymer or both, so high humidity increases the mobility of the system components due to water vapor ingression. Temperature, as it does with virtually all systems, increases the reactivity and mobility as well and serves to increase the aging rate. Sensitivity of temperature versus humidity depends on the chemical nature of the components in use, and some will not experience any release-based aging until a threshold of one or the other is reached. As is always the case, a lot depends on the adhesive. Mechanical wet-out of the adhesive with time is always a factor as well. The rate of this wet-out varies greatly with both the hardness of the adhesive and the pressure on the layers. Softer adhesives and higher pressure from firmer winding of rolls both will age faster than the alternatives.

Single Phase Release Systems

Some of the early release systems in tape consisted of low surface energy polymers cast in solvent. Some of these aged extraordinarily well, simply because there was only one component present and no displacement would take place. The same is true with silicones, which can be cast in solvent, as an emulsion, or as a pure silicone oil. 100% silicone systems generally age very well. Many times, silicone resins can be used to affect release, and these often contain some α-olefin such as 1-hexadecene or 1-dodecene to improve release and coatability. Both the resins and the α-olefins can have an effect on aging. Release modifiers will be discussed in more detail in the next section.

The following chart shows the aging behavior of three different types of release coatings. Two of the release coatings are from common types of tape. Both the release layer and adhesive layer of these tapes are tested independently. One is a general-purpose natural rubber masking tape, the release coating layer of which will be referred to as Release 1. The other is a painter's masking tape with a styrene-isoprene-styrene (SIS) adhesive and a release layer referred to as Release 2. Both are well recognized market-leading products from two of the industry's leading manufacturers. The adhesive layer of the two tapes were then tested against their own release coating layer, as well as each other's release coatings. Both tapes' adhesives were also tested against silicone, which serves as a third release coating here. The silicone was coated on SCK liner paper. Initial release data was collected, as well as wet and dry aging data. Aging was done for 10 days at 40°C under weights producing 2.0 lb/in^2 of pressure to simulate in-roll conditions. The wet aging was done at 50% relative humidity. The silicone had 65% of release modifying resin added, which was enough to roughly equal that of the starting release of the two tapes (Release 1 and Release 2).

Chart 1: Release Performance of Silicone and Non-Silicone Releases Using NR and SIS Adhesive



Both of the tape release coatings (Release 1 and Release 2) performed fairly well, as would be expected from premium market products. As would be expected, the natural rubber adhesive aged at a faster rate than the SIS adhesive. Silicone release showed almost no impact due to humidity level, while the other two systems aged quite a bit worse with high humidity present. Silicone outperformed both systems in wet conditions. In dry conditions, silicone was comparable to Release 1 while it outperformed Release 2. Both releases are believed to be polymer and surfactant, but the exact compositions are not known.

Adjustable Release Using Silicone Resins or Sodium Silicate

Silicone polymer alone will generally only make a narrow band of possible release levels available to users. Unless an adhesive is an extremely aggressive variety such as bitumen, the release will generally be very low. In many cases, an adjustment is required to achieve a high enough level of release to suit a particular product or application.

There are varieties of technologies available to achieve this increased release effect. The most common three are reactive MQ resin, non-reactive MQ resin, and sodium silicate.

Reactive MQ Resin

MQ resin is a material made from mono-functional and quaternary-functional silane building blocks. The Q units form a rigid 3-dimensional core for the molecule that is essentially quartz, as it is simply a network of silicone and oxygen atoms. The M units give the molecule an organic covering with siloxane type properties, and they also serve as the boundaries of the particles. MQ resins can vary greatly in size. They serve to break up the smooth, uniform surface of a silicone coating and thereby increase its release force.

In release systems, the MQ resins will often include functional groups that are the same as one of the reactive components in the silicone coating being used. In the case of platinum or rhodium cured systems, this is an unsaturated terminal hydrocarbon group, or vinyl group. If a tin catalyzed system is in use, then hydroxyl groups will be present The advantage of functional groups is that they lock the MQ resin in place, resulting in more stable aging and more predictable release force. The disadvantage is that they are less efficient than their non-reactive counterparts.

Non-Reactive Release Modifiers – MQ and Sodium Silicate

MQ resin can be made without functional groups. Sodium silicate, also called water glass, functions much the same way as a non-functional MQ resin. Both have partial immiscibility with siloxane polymer, so both concentrate at the surface of a coating between the time that it is coated and cured, even though this can be less than a second. Because of this, they are generally more efficient than functional offsets, sometimes needing only 2% to see a noticeable release effect. The disadvantage for these is that they are significantly harder to control. They can be sensitive to coat weight and line speed. In addition, they often have large swings in release force as the product ages. Process upsets are more likely to alter release with these chemistries. Additionally, they can show up in silicone extractable tests, which is misleading because they are less detrimental to adhesive performance than uncured silicone polymers.

Release altering resins in general cost a little more than silicone polymers. They also slow down cure a bit, which requires more catalyst, further increasing costs. But, the proper release level is critical to most applications. The following chart shows how much more efficient a non-functional MQ resin can be than a functional one. It also gives some idea of release response to resin content. The chart after this one shows the difference in aging behavior.

Chart 2: Effect of Functionality on MQ Resin Release Response

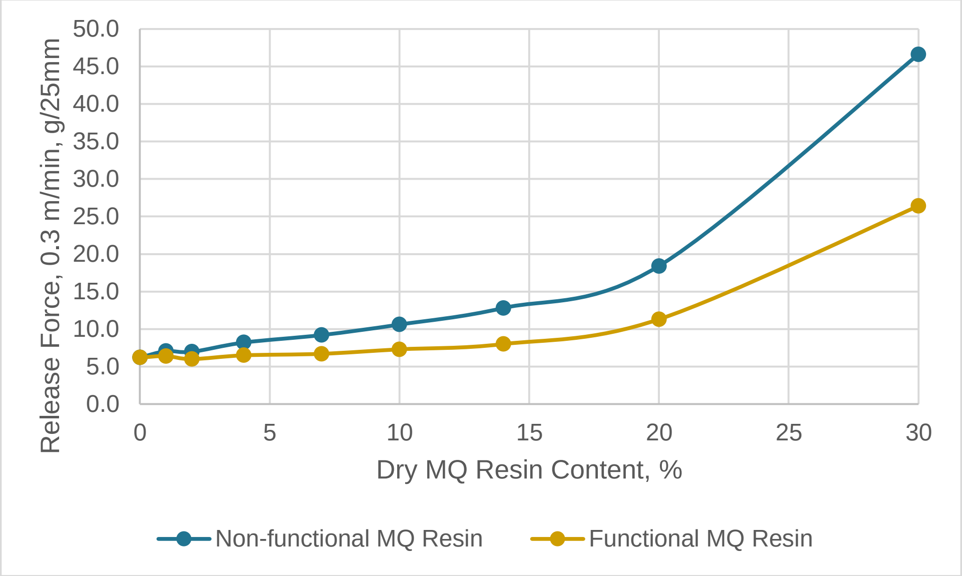
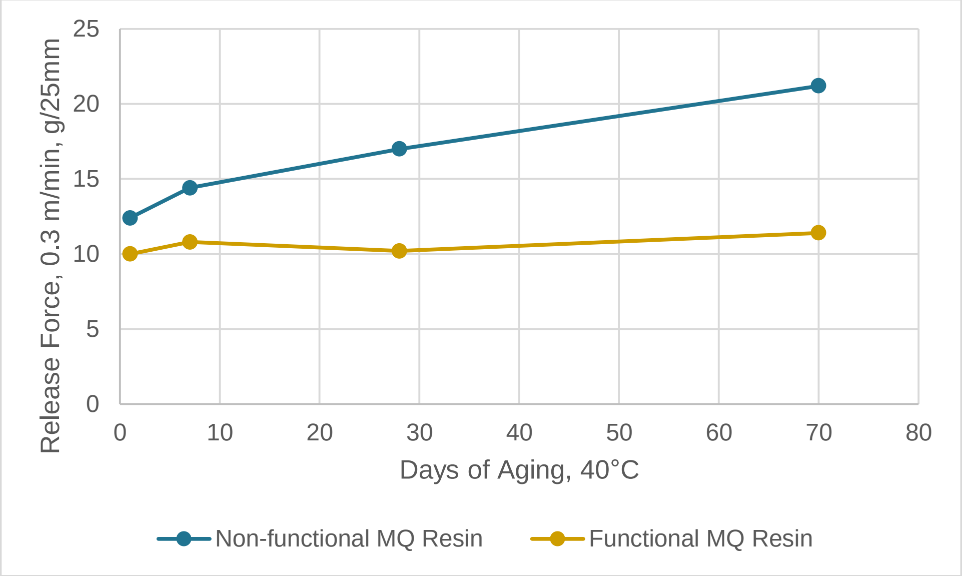


Chart 3: Aging Behavior of Functional and Non-Functional MQ Resins



As can be seen in Chart 2, the non-functional resin is about twice as efficient as the functional resin in raising release force values. However, Chart 3 shows the non-functional release nearly doubling with time while the functional one barely changes at all. Both coatings represented in Chart 3 had 40% dry MQ resin in their formulas. All of these were done with a high crosslink density polymer, which does not react very efficiently to resins. Softer polymers will have a more exaggerated response to such resins.

Process-Based Release Modification

Coating weight, silicone cure, and coverage quality can all affect release force if they are too low. While any high level of release can be achieved when these are not ideal, this is not used in practice to control release. The problem is that process controls are never precise enough to consistently give the needed release. Even with coat weight, which would be the easiest to control, this is not possible in a practical sense. 0.50 g/m^2 of coat weight may shred the backing because it is too firm, while 0.60 g/m^2 already gives very low release. Additionally, if 0.55 g/m^2 gives ideal release today, very small changes in the next roll of substrate or other variables can cause a huge shift one way or the other. In addition, these techniques are neither widely used nor recommended.

The coating technique used to apply adhesive can have a major impact on release values. Adhesive is often applied to a carrier, but it can be applied directly to the silicone-coated liner. This can produce a large differential in release force, even if the same silicone has been applied to both sides of the liner. Adhesive is always applied in some fluid form, whether this be hot melt at elevated temperatures or an adhesive in solvent or emulsion form. The lower viscosity and energy input cause a much tighter bond between the adhesive and silicone than if a finished and cooled adhesive were simply laminated to the liner. In many cases, this is sufficient to create the needed release differential.

Pigmenting of Silicone

There are numerous colors of silicone pigments available on the market. These are most often used in rubber articles, such as silicone bakeware, gloves, gaskets, caulks, and wire casings. The same pigments can be used in silicone release coatings. Because release coatings are very thin, deep colors are not possible in most cases, but strong pastel colors can be achieved.

Requirements of Silicone Pigments

The pigments have to be ground very fine. Since a typical silicone coating on tape is only about a micron thick, pigments have to be ground into the nanometer range. After this, the pigments have to be completely dispersed into a silicone oil. Pigments are often not compatible with silicone and require a silane to make them compatible. Not all types of pigments are compatible either, as there are some that interfere with the hydrosilylation curing mechanism. These pigments are most often sold as a high viscosity paste that must then be mixed with the silicone oil that makes up the bulk of the coating. Settling is possible once mixed, but this takes place very slowly over several days, if it happens at all. Dyes are often polar organic compounds and therefore not remotely compatible with silicone.

Emulsion Pigments

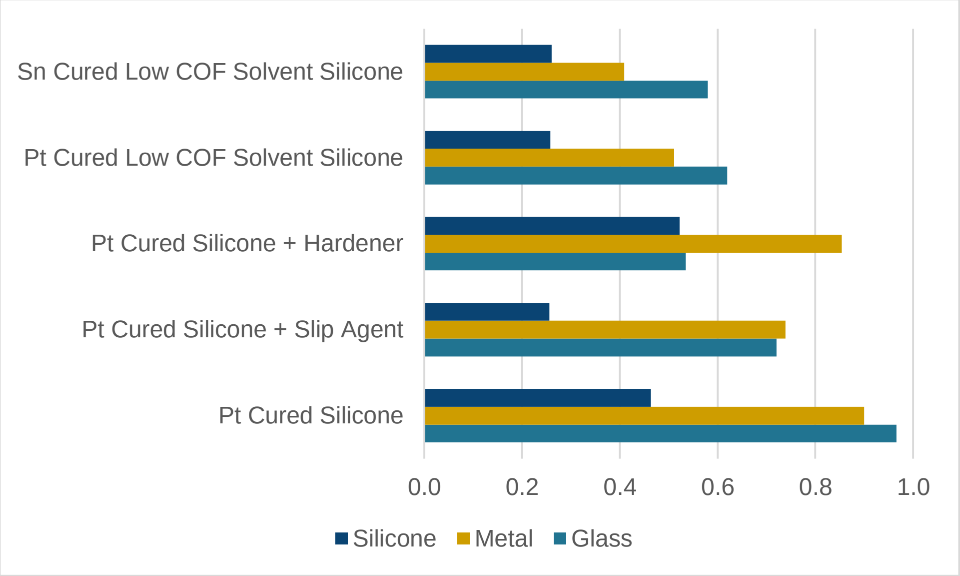
When silicone emulsions are in use, pigmenting is easier. Since many pigments and dyes are available as aqueous dispersions and solutions, blending is quite easy. Coarser ground pigments may increase release force, and interference with curing remains a concern. There is also a risk of poor appearance or bleeding if the colorant is not compatible with silicone.

Low Coefficient of Friction Silicone Coatings

Low COF silicone coatings have traditionally been made from the tin (Sn) curable systems in solvent, as these naturally have a low COF. Users have slowly gotten away from tin systems in favor of platinum (Pt) curing silicones. Platinum systems' biggest advantages are that it can be solvent free and can run at much higher speeds, both of which more than offset the cost of the Pt. Another reason is that tin is poisonous and many customers want tin free products. In any case, the gradual reduction of tin-based coatings has made it harder to find low COF silicone coated structures.

There are tin-free options available, though none seem to work quite as well as the original. Slip agents and hardeners can be added to rubbery-feeling Pt based coatings to give some improvement. There are also solvent-based options available with Pt catalysts that come close to tin's COF performance. Friction depends on the material that the silicone is rubbing up against as well. A study was done looking at glass, steel, and more silicone. The details can be found in the following chart.

Chart 4: COF of Various Silicone Coatings against Glass, Steel, and Silicone



As the chart shows, the typical Pt cured silicone coating at the bottom has roughly double the COF of the tin coating at the top. The solvent-based Pt coating comes pretty close to the tin system. The hardener was only effective on glass and the slip agent had a modest effect on all three materials but worked best on a different silicone coated sheet.

Low Contamination Silicone Systems

All fully cured silicone systems will have some residual uncured silicone oil. While it may be as little as 1% of the total silicone mass, this uncured silicone is free to migrate and contaminate anything that comes into contact with the coated silicone layer. For some applications, significant quantities of uncured silicone is not problematic. For most tape applications, small, normal amounts of silicone do not present a problem for adhesive performance. However, some applications are very sensitive to silicone contamination.

Non-functional Content

Many silicone coatings are made with simple linear silicone polymers. These polymers have two crosslinking points on either end of the chain. As long as either reactive site crosslinks in, the silicone will become covalently bonded to the coating matrix. However, if no part of the chain crosslinks in, that silicone is free to move wherever repulsive or attractive forces push or pull it. Most of this un-crosslinked material is in the form of a cyclic structure which has no functional groups. A small percentage of these structures form whenever any silicone polymer is made. The vast majority of them are small and therefore volatile, so they are stripped from the polymer during production. Inevitably, a small amount remains with the polymer. These ring structures can be of any size, so the larger ones are unable to be stripped off. They remain in the polymer after coating and can contaminate adhesives and substrates.

Extraction Testing

The amount of extractable silicone can be measured by any number of methods. These generally use solvents such as toluene, heptane, MIBK, or xylene, to extract free silicone. A coated sample is measured for coat weight using XRF and then placed in the solvent with enough time to allow for extraction. Then, the sample is either re-measured for coat weight to determine how much silicone was taken off, or the solvent is measured to determine its silicon concentration via AAS or ICP. This test will determine the amount of extracted silicone. The extracted silicone will include both silicone that had no reactive groups like cyclics, and silicone that was reactive but was not exposed to enough energy for it to react with an available crosslinking site.

The result is generally expressed as a percentage of the total silicone coating mass. Most systems are considered adequately cured when less than 5% is extracted, but lower numbers can be used for sensitive applications. Some applications with heavy adhesives tolerate 10-15% without issue.

Polymer Options for Low Extractable Content

Different types of silicone polymers are better than others for achieving very low extracts. Shorter linear chains yield fewer large cyclics and have inherently better extractable performance than large ones. Branched multifunctional polymers also have lower possible extracts than linear systems, because the branch sites will be randomly dispersed throughout the cyclic structures and will add an available crosslink site if they are present. This is true regardless of the branch length and type. So, highly branched polymers with a relatively low degree of polymerization offer the lowest available extractable levels. With extended heating for curing, some of these coatings can routinely provide values less than 2% extractable content.