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WHICH ONE IS FAKE?

Silicone Conformal Coatings

CAD-to-CAM Data Transfer Case Study

Flex Circuit Outer Layer Planes

Protecting Silicon with Silicone

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With each passing day, the use of silicone rubber is becoming more and more pervasive; products made from silicone are showing up in our hospitals, your cars, the kitchen and bath, even in my golf bag. Flexible bakeware and cooking utensils, fuel-resistant hoses and gaskets, airbags and touch pads, shampoos, skin care products and much more are all made possible with new silicone technologies. Dr. Fredrick S. Kipping, the father of silicone chemistry, could never have envisioned the plethora of uses into which his “sticky mess” has grown. From the earliest days of commercialization silicones have always been selected for any high-performance, specialty application that requires extreme durability and out-standing physical properties.

Silicone chemistry is a unique combination; neither purely organic (i.e., carbon based) nor purely inorganic (i.e., silicon based) but a molecular-level hybrid of both. The nature of the Si-O bond in the polymer backbone creates low rotation barriers and large bond energies. This inorganic polysiloxane backbone provides the foundation for building materials with superior thermal properties, environmental resistance and extreme flexibility even at temperatures below -70^{o}C. The methyl groups pendant to the Si-O-Si chain provide for very low surface energies and the low rotation barrier along the backbone allows the polymer to freely orient these groups to the exposed surfaces. The hydrophobic character and soft-touch feel of silicone based materials is a direct result of this exceptional combination.

Silicone elastomers are currently used as sealants, adhesives and coatings where they are fluid applied and cured in place, but they may be also molded into a multitude of shapes and used to produce functional products in a wide range of applications. There are two predominate cure types: condensation-cure and addition-cure. Condensation cure products may be either single-component or dual-component, generally use tin catalysts, require moisture to react and liberate alcohol or other monomers as by-products during cure. Addition cure materials may also be either single-component or dual-component, are either free radical cured or rely on precious metal catalysts, but perhaps the biggest distinction is that there are no by-products generated during cure.

Certainly nearly home owner is familiar with single-component, condensation cure silicones; perhaps even using some to caulk the bathtub or kitchen sink. The familiar smell of vinegar as acetic acid is liberated during the condensation reaction. Single component, moisture cure, RTV silicones (**R**oom **T**emperature **V**ulcanizing) are valued for their ease of use, excellent adhesion, superior physical properties and environmental resistance. The products are manufactured under dry conditions and stored in moisture proof packaging. Once applied the material draws humidity from the atmosphere and begins to cure. The cure proceeds from the outside inward with the rate of cure determined by the amount of catalyst in the formula but more importantly by how much moisture is available. The by-product liberated is dependent upon the leaving group of the cross-linker used in each specific formulation (see Figure 1).

Within the electronics industry, moisture-cure RTV's are often employed as staking compounds where vibration dampening and stress relaxation are important. These types of staking compounds are most often shear-thinning pastes that once applied resist flow and may be used to build up a protective barrier around sensitive components. When fully cured these materials become relatively soft (i.e., Shore A 25-45), durable, low modulus rubbers. Many silicone conformal coatings are also based on this type of chemistry. The advantages are ease of application, solvent-free formulations and environmental resistance of the cured films. Silicone conformal coatings are most widely used in high temperature environments making them the primary choice for under the hood automotive applications. However, because moisture from the atmosphere is needed to catalyze the cure single-component, RTV's must only be applied in thin cross sections, typically less than ½ inch and the assembly must be racked over night to allow for slower cure speeds.

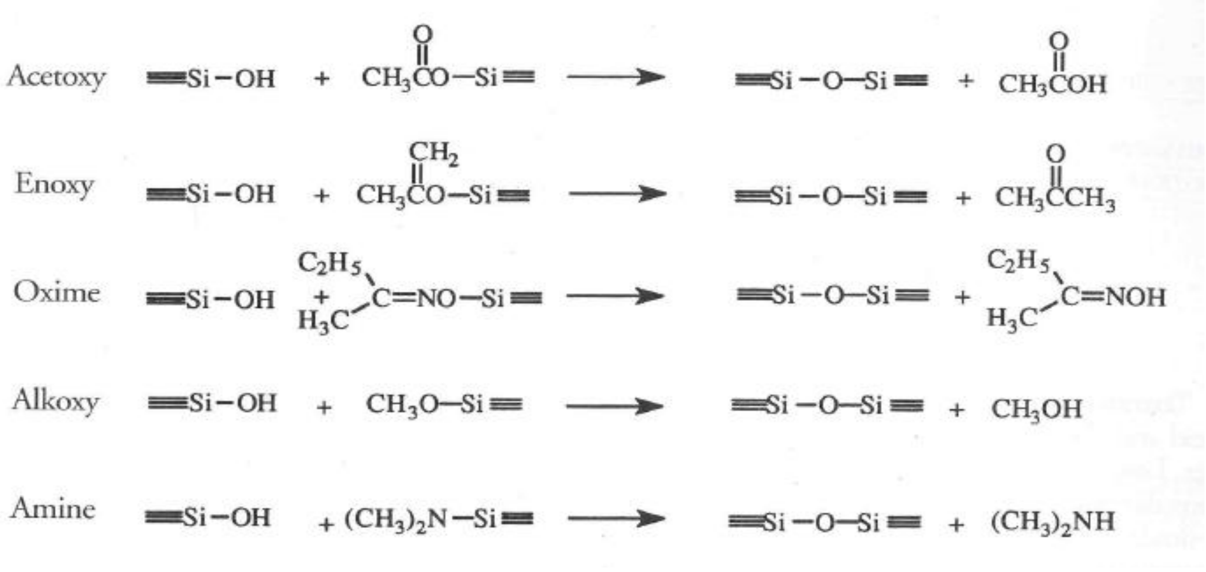


Figure 1: *Cross linker chemistries and by-products for single-component, moisture-cure silicones*

Less familiar, but no less functional, are the dual-component condensation cured silicones where the cross linker and catalyst are contained in separate packages that must be mixed prior to application. Here the moisture is an integral part of one component making these formulas much less sensitive to environmental conditions. Also, because the reaction is not dependent on the transport of moisture from the atmosphere these materials are able to cure in thicker cross sections. However, a by-product is still generated during cure so shrinkage is relatively high.

High consistency silicone rubber (HCR) compounds may be processed by injection molding, compression molding, and extrusion or calendaring. These are the original single-component, addition cure rubbers. Typically, ready-to-use blends of silicone rubber with fillers, modifiers and vulcanizing agents that are heat cured to form elastomeric components. The vulcanizing agents are generally peroxides that break down with heat generating free radicals that initiate the cross-linking reactions.

The liquid silicone rubbers (LSR) are also based on addition cure chemistry. Generally, two-part pumpable materials that must be mixed and often heat-cured to form elastomers that are ideally suited for intricate designs manufactured in large, automated quantities. LSR's rely on precious metal catalysts, usually platinum, to promote cross linking. As with the condensation cure two component formulations the catalyst and cross linker are contained in separate packages that must be mixed prior to application. LSR's and fully-fluorinated LSR's currently represent the fastest growing branches of the silicone family tree.

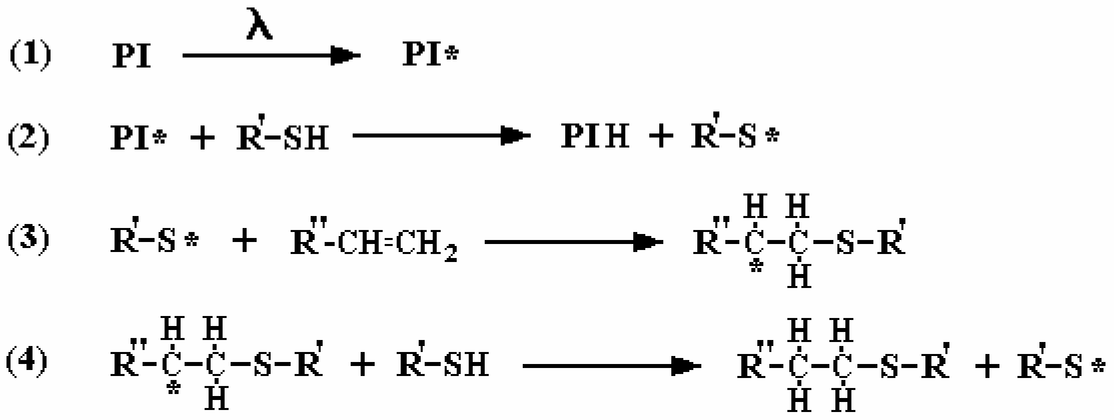
Platinum-catalyzed, addition-cure silicones may be formulated with an extremely wide range of physical properties and cure characteristics, which makes these materials very popular. One of the most exciting new developments is the introduction of low viscosity, truly optically clear potting and encapsulating compounds. LED's, photovoltaic sub-assemblies and other light sensitive devices require radiation-resistant, non-yellowing encapsulants for protection and improved light transmission. For radiation energy to initiate any chemical changes, causing a break down in properties and yellowing, the polymer molecules must first absorb it. Because of the absence of any double-bonds or other ultraviolet (UV) light-absorbing groups polydimethyl siloxane based, addition cured silicones absorb very little ultraviolet radiation in the 300-400 nm region. Additionally, as mentioned earlier, the bond strength of the silicon-oxygen linkages in the polymer chain is exceptionally high, which also prevents oxidation and loss of properties.

In the past, there were many concerns about silicone oil migration and/or bleed out that would contaminate sensitive electronic components. Early formulations used silicone polymers that were not stripped of low molecular weight contaminants, and electronic devices relied heavily on mechanical switches. These low molecular weight oligomers could volatize and condense on switches; because silicones are excellent dielectric materials this could cause poor contact and device failure. Today, silicone polymers go through a much more extensive stripping process to remove and control contaminates. Additionally, device design has improved so the technology is not as susceptible to any potential contamination.

Heat cure, moisture cure, mixing, ovens, those are fine and effective means for curing products to generate pieces and parts for a great many applications. The real interest and some of the most fascinating performance advances are in the field of UV curing silicone rubbers. The advantages of speed, ease of application and energy efficiencies associated with traditional UV curing to produce elastomeric materials with all of the performance enhancements of silicone.

The concept of UV curing silicones is not new. Acrylic end-capped, free-radical cure silicones were first commercialized in the early 80's. While they are technically UV cure, these dual-cure systems rely quite heavily on the traditional moisture reaction to affect full cure. The acrylated-silicones are sensitive to oxygen inhibition, require fairly significant energy input to initiate the reaction and need prolonged exposures to complete the cure. Perhaps because they are not so robust, these materials have not enjoyed the market success of hydrocarbon-based UV cure technologies.

The thiolene 'click' reaction is very powerful chemistry. Click chemistry is not one specific reaction, but more of a concept or a philosophy introduced in 2001 by K. Barry Sharpless, PhD of the Scripps Research Institute (1). By definition, click reactions are simple, and robust. They use only readily available starting materials, require no solvent, or chemically benign solvents (e.g., water), and proceed to high conversions. Applying these concepts to polymerization reactions yields materials that are extremely dynamic. Thiolene chemistry is the reaction between thiol groups and vinyl functionality. If the molecules involved contain higher functionality (i.e., $F_{(x)}$ >/= 2) than the reaction will produce polymeric materials. The process is normally photoinitiated and proceeds via a very rapid step-growth mechanism; an idealized outline of the initiation – propagation – chain transfer reactions is shown in the following diagram.



$$(1)\quad PI \xrightarrow{\lambda} PI^{*}$$

$$(2)\quad PI^{*} + R'\text{-}SH \longrightarrow PIH + R'\text{-}S^{*}$$

$$(3)\quad R'\text{-}S^{*} + R''\text{-}CH{=}CH_2 \longrightarrow R''\text{-}\underset{*}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}S\text{-}R'$$

$$(4)\quad R''\text{-}\underset{*}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}S\text{-}R' + R'\text{-}SH \longrightarrow R''\text{-}\underset{H}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}S\text{-}R' + R'\text{-}S^{*}$$

In addition to the polymerizations reactions discussed earlier, the thiolene reaction may also be used as a cross-linking mechanism. High molecular weight, vinyl functional polymers may be cured with short-chain, or monomeric, multi-functional thiolene curing agents via the same photoinitiated reaction. It is essentially an addition reaction so no by-products are produced and shrinkage is low. There are hundreds of vinyl and thiol combinations. Vinyl functional, polydimethylsiloxanes are abundant and readily available and there is a fairly wide selection of short-chain mercapto-functional polysiloxanes. This combination may be employed to produce UV cured silicones.(2,3) These systems were originally investigated as possible release agents for paper coatings.

The chemists at Novagard Solutions extended this chemistry to include a secondary moisture reaction for curing in shadow areas and to further increase cure strength, adhesion and system dynamics.(4) Clear materials based on this new system are much more robust, cure to greater depths with much lower energy requirements than conventional acrylated silicones. This translates to increased processing speeds and faster turn arounds. Essential for protecting electronic circuitry and significantly extending the service life of printed circuit boards, conformal coatings are an integral component of the entire sub-assembly. Eliminating moisture and contamination is a key element for protecting sensitive electronics. Silicone conformal coatings provide an effective barrier in even under the most severe services conditions. Now UV cured conformal coatings which offer all of the enhanced performance characteristics of conventional silicone based materials but with processing speeds unmatched by other technologies are available. The unique and patented UV-cure silicone chemistry found in the Novagard conformal coatings provides dual-cure capabilities where a secondary moisture cure effectively eliminates any problems associated with shadowing on complex parts and printed circuit boards.

Perhaps more importantly, these new UV-cure, silicone resins may be filled, which means pigmented and even electrically conductive UV-cure silicone products are now possible. Flexible and printed electronics (FPE) incorporate several new technologies and emerging processes and materials across a variety of applications. FPE may be twisted, bent or shaped without damage enabling endless innovation and unlimited possibilities. Thin, flexible and printed electronics are transforming the way circuits are produced and in the process transforming the way we live and interact with each other. This is a growing market with emerging technologies that will revolutionize the way electronics are integrated into products and applications. UV cured electrically conductive silicone products from Novagard are helping to shape that revolution.

When an application requires high performance, exceptional durability and out-standing physical properties a silicone based product is the obvious choice. No other chemistry provides the environmental resistance and superior performance at thermal extremes. While it is true that silicones are critical for applications under the most sever and harsh conditions it is also true that the enhanced adhesion, increased flexibility and excellent UV and moisture resistance are important for many less demanding applications. New UV cure products with increased processing speeds put the superior performance of a silicone within the reach of all.

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