TI 15/18: Handling of silicones

Silicones (poly organo siloxanes, SR) are distinguished by their excellent resistance against chemicals and weathering, besides a high temperature/thermal shock resistance and high flame retardancy. They are highly elastic and can easily be removed for repair. Their dielectric properties remain almost unchanged over wide ranges of temperature and frequency. When cured they generate extremely low heat and a very low shrink pressure.

When it comes to reliably protecting electronics against humidity and aggressive media at temperatures between -50 $^{\circ}$ C and >180 $^{\circ}$ C silicones are the best choice.

Due to many misunderstandings, the subject of silicones is particularly frowned upon in the automotive industry. But particularly there, silicones are in widespread use. They have made a decisive contribution towards electronics also establishing themselves in the hotter areas of the engine compartment. The engine compartment of all places, in which the heat and moisture, oil and fuel gases, dirt and salt create the most adverse conditions, is where silicones can offer the necessary protection for sensitive electronics both in low and high temperature ranges, due to their high temperature resistance.

The aversion towards silicone is mainly founded in the fear of contamination. Particularly in the case of automotive serial coating, low molecular silicones can lead to massive wetting problems resulting from their low surface tension. When using silicones as a protective coating for electronic components, there is no such risk as the electronics are only mounted after the coating.

When processing silicones next to silicone-free products certain precautions have to be taken in order to avoid the risk of silicone contamination.

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Cross-linking systems

The silicones available on the market differ from each other as to their way of cross-linking (also referred to as vulcanisation):

- RTV-1 room temperature vulcanising, 1-pack system
- RTV-2 room temperature vulcanising, 2-pack system
- HTV high temperature vulcanising, 1-pack system

As regards the chemical mechanism one can further differentiate between

- addition cross-linking
- condensation cross-linking
- radical polymerisation cross-linking (UV cross-linking)

Among the RTV-1-type silicones which cure by means of a reaction with air humidity, there are solvent-containing and solvent-free coating systems. With this reaction type specific separation products are generated – thus they are also known as "condensation cross-linking" silicones. Depending on the condensation product, these again can be split into acid, base and neutral systems. While the cheaper acid (acetic acid separating) systems are often used for sanitary products, naturally they are not suitable for electronic assemblies. In the electronics field neutral and base products such as oxime or alcohol separating systems are frequently used, whereby the alcohol separating types dominate. They exhibit quite a wide application range, however they should not be used in encapsulated environments, because under higher temperatures they are prone to reversion.

The range of addition cross-linking silicones includes either 2-pack-systems or as 1-pack systems the so-called HTV silicones. As a rule, all of these silicones are solvent-free and have established themselves in electronics applications. Since these products need a special platinum catalyst for cross-linking they show a sensibility towards catalyser inhibiting organic compounds, so-called catalyst contaminations.

The processing time of the 2-pack systems is limited since vulcanisation sets in immediately after mixing has been completed. Curing is very much dependent on temperature. While curing would take approximately one day at room temperature, it can be reduced to just a few minutes by increasing the temperature to 150 °C. A rough estimation is possible by the Montsinger rule or the Arrhenius definition which state that a temperature increase of 10 K cuts the curing time by about half.

The pot life of 1-pack silicones is not restricted provided that they are stored in a cool place away from moisture or protected from light.

In the case of addition cross-linking 1-pack systems the vulcanisation only starts at higher temperatures and is completed after a relatively short period of time.

Vulcanisation times of condensation cross-linking silicones are relatively long (approximately 1 mm/day). They can be slightly shortened by increasing the temperature.

As regards the cross-linking mechanisms described above, the silicones commonly used in electronics exhibit the following basic properties:

Addition cross-linking silicones

- no volatile reaction products
- no mass loss
- chemical volume shrinkage of < 0.1 % at room temperature
- no reversion application in encapsulated units possible
- possible disturbance of cross-linking through so-called catalyst contaminations (inhibition)

Inhibition of the curing of addition cross-linking silicones

Grease, moisture and contamination of the surface e.g. by organic tin compounds, sulphur and sulphur compounds, amides, amines, azides, urethanes may cause curing defects such as bubbles or voids. Among the typical effects of such contaminations there is the appearance of liquid, non-cured material remaining on the interface between the substrate and the silicone after curing. Impurities have an impact on the adhesion in such a way that water may collect between the substrate and the silicone and cause corrosion/failure.

An encapsulated curing of the material in the oven is of advantage since it protects against volatile impurities from the oven which may inhibit the curing reaction.

Condensation cross-linking silicones

- the condensation product is a volatile alcohol or oxime
- a slight mass loss takes place during cross-linking due to the volatile compound
- chemical volume shrinkage of approx. 0.2-2 % at room temperature
- reversion (of cross-linking) is possible at high temperatures
- cross-linking only inhibited by lack of moisture (air humidity)

Impact of products separated from condensation cross-linking silicones

Since the condensation product is a volatile alcohol or an oxime, materials (e.g. glues) in the direct vicinity or in an encapsulated casing can be attacked. The effects may vary considerably and range from cloudiness to decomposition. With that said, these condensation products only occur in low concentrations so that for the most part other materials are not at risk.

Radical polymerisation cross-linking (UV cross-linking)

Like most UV systems, UV cross-linking silicones cure in just a few seconds.

Processing of silicones next to silicone-free systems

When silicone-containing and silicone-free products are used simultaneously, defects e.g. dewettings may occur in the processing of the silicone-free products.

The most frequent cause of "silicone contamination" is manual transmission due to carelessness or ignorance. In rare cases contamination is caused by aerosols, air-transmitted pollution or condensation products.

The most important rule for the processing of silicones is:

KEEP EVERYTHING SEPARATE

Silicone contamination

As far as contamination by silicones is concerned, one can distinguish between three possible sources: A direct contact by bleeding and spreading, a direct contact via contaminated work tools and a contamination through volatile silicone.

Contaminations through direct contact can be securely avoided by good "industrial hygiene" such as separate work tools etc. (see also "Check list for the handling of silicones"). Open spray application presents a risk.

Volatile silicone may escape from the coating in the form of low molecular substances both during processing and after the curing process. However, it will escape less frequently from the cross-linked material than from any liquid material.

These outgassing products may deposit on contact areas such as relays, flex connectors and contact points and prevent a clear contact. When exposed to a potential electric spark the silicone molecule will decompose and form silicone dioxide residue; it may even create an insulating layer in such a way that the contact will be permanently interrupted.

By using hermetically sealed relays such problems can be avoided. The solderability of gold-plated printed circuit boards is only affected to a minor extent. Should this type of problem arise, precleaning is helpful.

Another solution is to use silicones with so-called "controlled volatility"; here the outgassing of volatile components is as low as just a few ppm, provided that the product is processed correctly. However, the material costs are distinctly higher.

Another point that should be considered is the mounting type of the coated assembly, whether in an encapsulated casing or allowing free air exchange. In the latter case, silicones have been employed over several decades already.

Why does silicone contamination occur?

Due to their chemical structure silicones have a lower surface tension than pure carbon-organic compounds. Even minor quantities on the surface can be the reason for a lower surface tension of the contaminated area, too. However, a liquid can only wet the substrate if it has a lower surface tension than the latter. For this reason, silicone-contaminated substrates cannot be wetted by silicone-free materials such as conformal coatings since the latter have a higher surface tension.

Check list for the handling of silicones

Keep your workplace and work tools separate in order to avoid contact between the various systems, e.g. via contaminated work tools. The check list below will serve as a guideline.

Basic principle: KEEP EVERYTHING SEPARATE

Work tools

For processing, work tools made of stainless steel and, if necessary, teflon coated hoses are especially recommended.

Clearly mark the equipment that is used for silicones. In practice a coloured marking with an eyecatching adhesive tape has proven its worth. Work tools include:

- spatula
- measuring devices like thermometers, flow cups, scales, pipettes, etc.
- protective equipment / work clothes like gloves etc.
- cups, funnels etc.
- cleaning cloths (special box)
- tools that are used for maintenance (where applicable)
- basin to clean equipment
- waste bins

Production equipment

- separate dip tanks
- separate ovens / UV curing units (a separate exhaust should be available in order to block the access of silicones into other production areas and vice versa)
- separate dip equipment
- separate hangings for assemblies
- labelling of product boxes (coating + cleaning agent)
- separate cleaning of the equipment

Premises

- separate storage for silicones and used cleaning agents
- separate storage for coated boards (so that in case of possible damage of the coating film no silicone components are diverted to other production areas)
- if possible separate workplace e.g. scales
- separate washing facilities

Employees

- · information/sensibilisation about the risk of diverting silicones
- general hygiene at work (wash hands, wear gloves if necessary)
- if necessary limited right of access

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