Evaluation of Removal Rate of Cured Silicone Adhesive from Various Electronic Packaging Substrates by Solvent and Silicone Digesters for Rework Applications

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Abstract

Reworking electronic packages is an integral process related to diagnostics and salvaging valuable materials. It is a meticulous and time-consuming procedure that requires some knowledge of the package material composition to determine compatible cleaning solutions and processes. Silicone adhesives are being used more frequently due to their ability to minimize shear stress during temperature cycling. A common method for removing silicone adhesive is by swelling in solvent and removing by mechanical methods taking care not to damage fragile materials and leave minimal residue. Silicone digesters (emulsifiers) are another means of removing cured silicone. They are comprised of weak acids or bases and remove silicone by breaking the siloxane bonds that make up the polymer matrix. They are able to penetrate into areas that are difficult, or impossible to reach, greatly reducing the risk of causing damage due to mechanical removal. The purpose of this study is to evaluate the rate of silicone removal by solvents and silicone digesters on silicones bonded to copper and aluminum. The removal rate was determined by developing a rating system based on time intervals where silicone was observed to delaminate or dissolve. Silicone adhesives and Thermal Interface Materials (TIMs) were used in the evaluation of two commonly used solvents and two commercially available silicone digesters. Copper and aluminum panels were evaluated by using a ~ 0.5 mm thick layer of silicone to bond 2 panels together. The samples were placed in cleaning solution for 24 hours at 40 degree Celsius and evaluated at specific intervals for any changes in appearance of silicone. Based on the performance of combinations of silicone, substrate and cleaner, the engineer can chose which method is best for reworking based on their own assembly configuration and materials.

Key words: Silicone, rework, adhesive, TIM, silicone emulsifier, low modulus

Introduction

Rework is an integral process to the electronics industry in order to diagnose failures and salvage valuable materials within the package. This involves removing the adhesives through mechanical or chemical methods without damaging sensitive components. There are several types of adhesives used in microelectronic packaging. This can make it challenging in choosing compatible cleaning solutions and processes for reworking assemblies.

Silicone adhesives are gaining popularity for use in microelectronic hybrid assemblies due to their inherently low elastic modulus. This low modulus provides stress relief during thermal cycling between substrates with different Coefficients of Thermal Expansion (CTE) such as copper and aluminum.

Silicone adhesives can be formulated to have a variety of mechanical and chemical properties that can influence the chemicals and processes one would use for rework. The chemical compatibility of the substrates that the package is composed of must also be considered (as well as any other associated hazards) when choosing the applicable method for rework. To better understand how various chemicals can affect silicones, it is important to understand their general composition.

What mainly defines silicone adhesives is the silicone polymer. This is characterized by the siloxane bond (-Si-O-Si), where the silicon atom will have at least one bond to an organic molecule. This is commonly referred to as polyorganosiloxanes, $(-R_2SiO-)_n$. The most common organic group found on the silicon atom for adhesives is methyl (CH_3). There are other organic groups that can be reacted onto the silicon atom giving the silicone different chemical and physical properties such as solvent resistance and increased thermal stability. Other functional groups will be present based on the specific cure chemistry for a particular formulation.

The most commonly used cure mechanism for microelectronic applications is hydrosilation (also known as Platinum cure or Addition Cure). The other is alkoxy and requires moisture to cure and the cure rate is dependent on available and exposed surface area. The platinum cure system allows the cure reaction to be accelerated by heat and is also desirable since there are no chemicals released during the curing reaction as there are with alkoxy cure systems. Other advantages to platinum cure systems for electronics is they are have relatively good shelf stability compared to one part alkoxy and need only ppm levels of platinum metal to function.

Silicone polymers alone have weak mechanical properties when crosslinked into a cured matrix, so they are reinforced with fillers (commonly fumed silica) and/or silicone resins to increase the elastic strength of the cured silicone rubber. These methods of reinforcing the silicone affect how the silicone adhesive flows and mechanical properties. How the silicone flows is directly related to how it is dispensed and processed, where the cured properties will dictate performance in the application. Silicone adhesives that contain silicone resins have a rheology similar to honey–they can coat a substrate by flowing around intricate design patterns. Adding silica will give the adhesive shear thinning properties (a.k.a. thixotropic) and will not flow without shear. These are used as glob tops and in other applications where the adhesive does not need to flow. Silicones also have intrinsically high dielectric strength that can be optimized to have electrical or thermally conductive properties by adding ceramic or metallic fillers. This allows them to be used in many applications ranging from a dam and fill application to

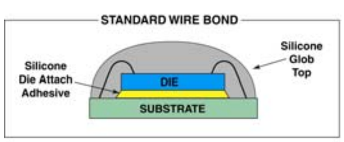
Thermal Interface Materials (TIMs) where the silicone adhesive matrix can be > 80 % filler (w/w).

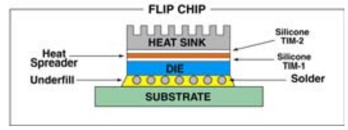
There are generally two methods to remove the silicone for rework and each has its own set of challenges. Historically, soaking microelectronic assemblies in solvents, such as xylene, has been used to swell and soften the silicone to allow removal by mechanical tools. This method may cause damage to the substrates and assembled package due to the intricate and compact nature of microelectronic assemblies. It may also fail to remove any remaining silicone residues on substrate surfaces. The use of silicone digesters (also known as silicone emulsifiers) is becoming a popular method to remove silicone. The digesters are comprised of weak acids or bases that cleave the siloxane bonds and revert the cured silicone matrix back into discrete polyorganosiloxane molecules. Using silicone digesters can greatly reduce the need for additional mechanical methods to remove silicone, and thus decreases the potential for damaging the part as well as leaving minimal silicone residues on the substrate [1].

Experimental Evaluation

Testing was conducted to evaluate individual combinations of silicones, substrates and cleaning solutions. The substrates and silicones chosen for the experiment are commonly used in microelectronic assemblies (Figure 1).

Figure 1: Applications for Silicone Adhesives in Microelectronic Packaging





The removal rate was determined by developing a rating system based on time intervals where silicone was observed to delaminate or dissolve (Table 1).

Table 1. Removal Rate Ranking System

Ranking	Complete digestion /delamination time
1	< or = 3 hr
2	3 hr < Time < 8 hr
3	8 hr < Time < 24 hr
4	> 24 hr

The silicones, solvents and silicone emulsifiers chosen for evaluation are listed in Table 2.

Table 2. Silicones, solvents and silicone emulsifiers evaluated

Silicone Sample ID	Silicone Type
SFA	Silica Filled Adhesive
TIM	alumina Thermal Interface Material
DA	silver filled Die Attach
RFA	Resin Filled Adhesive
Cleaning Sample ID	**Solvent Type**
IPA	Isopropanol Solvent
Xylene	Xylene solvent
Silicone Emulsifier Sample ID	**Silicone Emulsifier Type**
D1	Commercially available
D2	Commercially available
D3	1 % TBAF (tetra-n-butylammonium fluoride trihydrate) in Dowanol PMA

D1 and D2 each contains a proprietary active ingredient [2,3]. Per the manufacturers instructions, D2 is recommended for use below 49° C is not compatible with certain plastics and may react slightly with aluminum. Both these solutions are not soluble in water, but are compatible with many composites and do not contain halogenated solvents. The final silicone digesting solution, referred to as D3, is a

1 % TBAF (tetra-n-butylammonium fluoride trihydrate) in Dowanol PMA (propylene glycol methyl ether acetate) solution that was prepared by our laboratory [4].

The silicone was cured between 2 panels of the substrate in question per the manufacturer's instructions under constant pressure and to achieve a cured silicone diameter of 6-7 mm with a thickness of 0.5 mm. Substrates were not exposed to any surface treatments to improve adhesion, but were wiped with IPA prior to applying silicone to remove any oily residues. Cured silicone/substrate sample panels were placed in each cleaning solution at 40° C and monitored over time for changes in appearance and/or delamination.

Experiments were initially performed in ambient conditions, but it was found that the elevated temperature did accelerate the delamination and/or digestion process and 40° C was below the boiling points of solvents and solutions being evaluated. Observations were made every hour for 8 hours and then once at 24 hours.

The combinations of silicone, substrate, and cleaner were rated based on time to demonstrate delamination or silicone emulsification (where the silicone is broken down and dissolved). 'Delamination' was determined to be the point at which the silicone had 100 % adhesive failure (from one or both substrates) where as 'digestion time' was determined to be the point at which the silicone was completely dissolved into the silicone digesting solution from both substrates. Each sample substrate panel was weighed before and after silicone was either separated from the substrate or completely dissolved to evaluate if there was a weight gain or weight loss that could be indication of remaining silicone residues or dissolution of substrate itself. Any change in the physical appearance of the substrates before and after immersion was also noted.

Results

The results of the study had three significant findings: removal effectiveness of solvent or silicone emulsifier based on visual delamination of silicone and digestion of silicone (Tables 3 and 4), effects of silicone type on rate of removal (Table 5) and change in substrates evaluated.

Table 3. Time intervals where silicone was observed to delaminate from substrates.

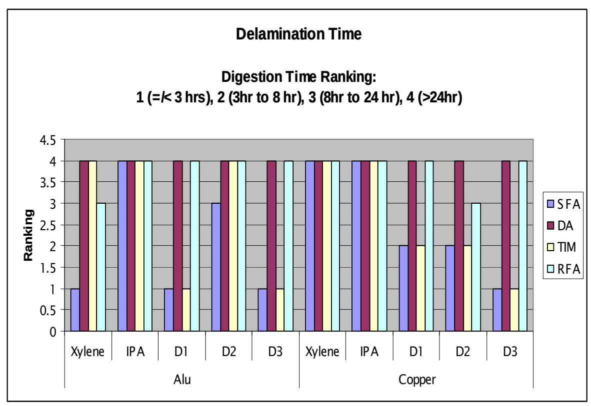


Table 4. Time intervals where silicone was observed to be completely digested.

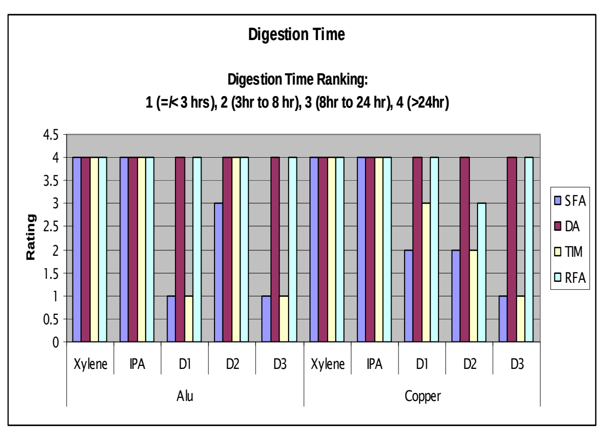
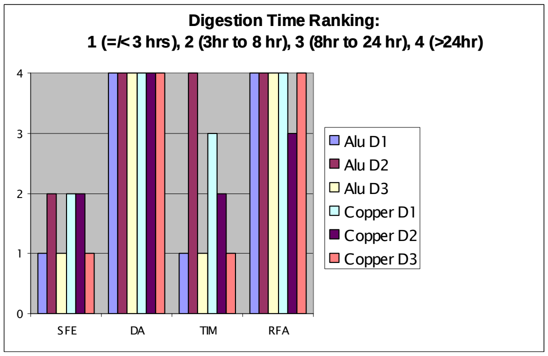


Table 5. Comparison of silicones digestion rate versus substrate in combination with silicone emulsifier



As hypothesized, the solvents did not dissolve or breakdown the siloxane bonds. IPA did not produce delamination between the silicone and substrate within 24 hours. Xylene showed slightly better performance on aluminum. Note that electronic grade IPA is typically recommended for use as a final wipe to remove residues left from cleaning solutions and residual water.

The silicone emulsifiers evaluated ranked in the following order from most to least effective in dissolving silicone within the shortest time: D3 > D2 > D1. The commercially available silicone emulsifier, D2, completely dissolved most silicones within 24 hours (4). The prepared silicone emulsifier solution, D3, dissolved most silicones within 8 hours (3) and in some cases, within 3 hours (1).

It was noted that the silicone formulation may have a significant affect on how easily the silicone can be removed, with less influence from the substrates on removal. For example, in all cases the Die Attach (DA) and Resin Filled Adhesive (RFA) silicones were not dissolved within 24 hours in all but one test condition. The commercially available silicone emulsifier, D2, was the only silicone emulsifier able to dissolve RFA when adhered to copper. On the other hand, the Silica Filled Adhesive (SFA) and the Thermal Interface Material (TIM) where dissolved within 8 hours in all but two test conditions. The TIM and DA formulations each contain ~80% (w/w) of dense fillers (therefore having low overall concentrations of silicone). Each reacted with the silicone digesters differently--the DA was difficult to dissolve on all substrates and the TIM was digested relatively quickly (the rate varied slightly based on the substrate).

The effects on substrates from the solvents and silicone emulsifiers were inconclusive based on weight loss. Only the final weights of the samples where the silicone was completely removed through delamination and/or digestion within 24 hours were measured. Any weight loss or weight gain was less than 0.05% and was considered insignificant. All the silicone digesters changed the color/appearance of the aluminum to some degree. There were also visual changes seen in the color of copper substrates exposed to D1 after 1 hour at 40° C. What may have caused the appearance change (and what affect it may have on substrate) is unclear. Further substrate exposure experiments will be conducted to determine if there are any significant surface effects from the silicone emulsifiers. In practice, depending on the substrate, observed surface effects may or may not alter the device performance.

Summary

In general, solvents were not as efficient in removing cured silicone as the silicone digesters. With the exception of the Die Attach, each of the silicone digesting solutions evaluated dissolved the silicone within 24 hours. Commercially available silicone emulsifiers evaluated in this study may not have dissolved the cured silicone as quickly as the 1 % TBAF solution but they demonstrated a reasonable effectiveness in removing various types of silicone and were easy to use. A general-purpose silicone emulsifier solution appears to be an effective means to remove silicone when taking into account the substrate material compatibility and the cleaning solution's ideal performance conditions. Research is recommended to determine material compatibility and ensure elevated temperatures will not degrade temperature sensitive chemicals in silicone emulsifier solution.

We have seen that there are many variables that may affect the rate of removal of the cured silicone with known silicone and substrates. The difficulty of removing silicone from within a microelectronic device itself is much more complex since the device is composed of various substrates, the type of silicone(s) is sometimes unknown and there is a minimal amount of exposed surface area.

Many aspects can influence the rate of removal/emulsification of the cured silicone, such as removal conditions (time/temperature), solubility of silicone in cleaning solution and adhesion. Further studies will be performed to determine the significance that each of these factors may have on the removal of silicone.

Special Acknowledgment
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