Addressing Silicone Contamination Issues

Edward M. Petrie | Omnexus, March 2013

Introduction

Since adhesives and sealants must function by surface attachment, the nature and condition of the substrate surface are critical to the success of any bonding or sealing operation. One of the most important parameters is surface cleanliness or the absence of contaminants that can impair adhesion. There are many sources of possible contamination to worry about. Some of these are indicated in Table 1, but the list is by no means all-inclusive.

Source	Examples
Primary Materials	Plasticizers, curing agents, debris, rust and corrosion products
Secondary Materials	Tapes, gloves, cloths, mold release, greases and oils, rinse water, etching solutions, solvents
Humans	Body oils, cosmetics, food
Equipment	Machine oils
Adjacent Processes	Silicone mold release, ovens where silicone polymers are cured, fluorine vapor
Atmosphere	Moisture, sea salt, pollutants, dust

Table 1: Several Sources of Substrate Surface Contamination

It is the author's experience that in the majority of unexpected adhesive failures, improper surface condition is the culprit. Often the adhesive or coating material or curing process is blamed, but in actuality a weak boundary layer is the root of the failure. Unfortunately weak boundary layers are common and take many forms.

Perhaps the most insidious of contamination problems is due to silicone because of its propensity to wet nearly any surface and because of the adhesive's or coating's inability to bond to silicone. Silicone contamination sources are plentiful and they have a tendency to travel through a manufacturing facility either by physical contact or even by the air stream (low molecular weight silicones have high vapor pressures). Furthermore, silicone contamination is difficult to identify and remove.
Considerable time and expense is spent in processes to inspect, clean, and maintain bonding surfaces that can become exposed to silicone.

This article will address the various issues related to silicone contamination including how it disrupts adhesion, detection methods, and cleaning processes. The best policy is to avoid silicone contamination to keep problems from occurring in the first place. As a result, preventive contamination strategies will also be disclosed.

Mechanism of Contamination

Silicones are very unusual materials since they can either prevent or assist adhesion. Silicones have very low surface energy so they wet most surfaces extremely well. As a result, silicone based adhesives and sealants show a high degree of wetting and adhesion on all practical surfaces. Certain silicone materials are even used as adhesion promoters in many formulations. However, the problem occurs once the silicone (either liquid or solid) is on the substrate surface. Since it has a low surface energy, other adhesives, sealants, or coatings will not wet or bond to the silicone surface.

If unwanted silicone attaches to the substrate, the result is the formation of a "weak boundary layer". The silicone contaminant prevents the direct contact between the adhesive and the adherend. When an adhesion failure is examined, it visually appears to have occurred as a failure at the adhesive-to-adherend interface. But on closer examination, the failure is due to a cohesive separation within the silicone contamination layer.

There are a number of cases reported in the technical literature describing how silicone contamination leads to production problems. One source has indicated that silicone contamination is the cause of over 1/3 of the bonding problems that occurs in an aerospace manufacturing plant. As little as about 1/2 a monolayer coverage of silicone on a surface can cause severe reduction in bond strength.[1] Silicone contamination problems are not limited to only adhesives and sealants. Trace amounts of silicone can cause primers, paints, or other coatings to "fisheye", separate, and lose adhesion.

There are many sources of silicone contamination including mold releases, tapes, lubrication oils, and other silicone adhesives and sealants. Their presence, even in quantities so minute that they are difficult to detect, can cause havoc with other adhesive and coating systems. Silicone contamination can be spread by direct physical contact with materials or equipment. Humans are also a potential source of silicone contamination. Many creams, cosmetics, hair products, antiperspirants and some eye-glass cleaning tissues contain silicones.

The high volatility of silicone can also promote cross contamination of the bonding surface without direct contact with the surface. For example, serious coating problems have occurred in auto finishing operations where silicone mold release used in one part of the plant had been transmitted through air ducts to surfaces being painted in other parts of the plant.

Detection

Detection of silicone contamination is important for quality control purposes as well as to identify the potential cause of early bond failure. However, Identification can be quite difficult in the case of silicone contamination.

Analytical surface techniques such as x-ray photoelectron spectroscopy (XPS), scanning Auger microscopy (SAM), Fourier transform spectroscopy (FTIR), scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS) have all been used. The choice will depend on the particular problem and the availability of equipment and expertise to use it.

High resolution XPS has been found to be an effective analytical method. Conventional XPS will not distinguish between elemental silicon which may be in a silicone compound, and silicate which may be associated with the substrate or an additive in the adhesive system. However, by using XPS in the high resolution mode, it is possible to distinguish between the two alternatives by taking advantage of a chemical shift difference.[2]

However, it has been found that many of these analytical techniques result in poor sensitivity on very thin surface layers. Research has indicated that the only appropriate detection technique for very thin silicone surface layers is the conventional contact angle method. The sensitivity seems sufficient for safely detecting a layer of 5 x 10-3 μm.[3]

Removal

Cleaning silicone contaminated substrates using a solvent wipe method generally improves the subsequent bond performance, but rarely brings the performance back to the baseline.[4]

If one considers solubility parameters and conventional solvents, hexane, heptanes, toluene, or isopropyl alcohol would be the first choices for cleaning surfaces contaminated with silicone. Although these are good solvents for silicone fluids, none have been found to be good dissolvers of silicone greases or pastes.

A number of studies have focused on the cleaning of surfaces contaminated with silicone. In one analysis a number of silicone contaminants were applied to a glass surface, cleaning was attempted by wiping with different cleaning agents, and contact angle detection measurements were used to determine the efficiency of the cleaning process. The cleaning was done by simply moistening standard paper tissues with the cleaning agents and wiping the purposefully contaminated glass surface. The cleaning was repeated five times for each of the contaminated plates, using fresh moistened tissues each time.

The results of these tests and descriptions of the contaminants and cleaning agents are given in Table 2. No single cleaning agent proved to be the most effective for all contaminant types. It was found that certain types of contamination (e.g., vacuum grease) were very difficult to remove and certain cleaners worked well only on specific contaminants.

Cleaning Agent	**Contaminant (Described Below)**					
	330LV	DC200	DC705	DC93-500[a]	DC93-500[b]	DC 340
Methylene Chloride	+2	0	-1	-1	+1	-1
Toluene	+2	0	+1	+1	+1	-1
n-Hexane	+1	-2	-1	-1	-1	-2
Fluxclene (Electolube)	+2	-1	+2	+2	+2	-1
Silgest SD0001 (Polymer Systems Technology Ltd)	0	+1	+1	+1	+1	+1
Ortimex Alkaline Cleaner (H.C. Stehelin)	+1	-2	0	-1	0	-2
SWAS, Safewash Super (Electrolube)	0	0	+1	+1	+1	-1
Vericlean defluxer (Microcare)	+1	+1	+1	0	+1	-1
Vertrel CCA (DuPont)	+1	-1	-2	+1	-1	-1
Vertrel CMS (DuPont)	+1	-2	0	-1	-1	-2
Dowclene 1601 (Dow Chemical)	+1	-1	0	-1	0	-2
Dowclene PX-16S (Dow Chemical)	-1	-1	0	-1	-1	-2
CH2Cl2/ Toulene (1:1)	+1	-1	-1	-2	-1	0
CH2Cl1/ n-Hexane (1:1)	+2	0	+1	+1	+1	-1

Table 2: Summary of Silicone Contaminant Cleaning Tests[3]

[a] = Applied by rubbing on the substrate
[b] = Applied as an extract in tetrachloroethylene

Contaminants:

330LV mold release agent, silicone emulsion from Basildon Chemicals
DC200 polydimethylsiloxane oil from Dow Corning
DC705 pentaphenyl-trimethyl-trisiloxane oil from Dow Corning
DC93-500 cured silicone resin from Dow Corning
DC340 thermally conductive vacuum grease from Dow Corning

It should be noted that there are a number of commercial cleaners available other than those tested in Table 2. Some of these are claimed to have excellent results in removing silicone deposits from surfaces. Several of these are identified below.

- Dow Corning DS-2025 silicone cleaning solvent (to remove cured silicone)
- Dow Corning DS-1000 aqueous silicone cleaner (to remove uncured silicone)
- Betabrade F1 (Dow Automotive Systems) surface contamination remover specifically developed for auto-glass assembly

TECHSIL Recommends:

- Techsil® Pronatur Solvent (cleaner & degreaser)
- Techsil® Silstrip Liquid (silicone remover & digester)
- LPS® Precision Clean (multi-purpose cleaner)

This addition by Techsil does not necessarily represent the views of the Author; it is purely an addition to the range of products available.

Grit blasting might be considered as a potential method for cleaning silicone contaminated surface, but one should be particularly aware of potential problems with this method. The blast media could become contaminated with the silicone and transfer the contamination to other pieces that are waiting to be cleaned. If a strict procedure of solvent washing, then blasting, followed by another solvent welding is not followed, the contamination can be driven deeper into the substrate making it more difficult to remove and creating the potential that the bond strength may look adequate initially but could degrade with service.

CO2 jet spray has also been investigated for large surfaces such as solar cells. The jet spray was successful in achieving visibly clean surfaces, but silicones are only partially soluble in CO2 and some remaining residue is likely.

Although the methods of cleaning described above may not be encouraging, one researcher has found that sensitivity to silicone contamination can be reduced significantly or eliminated completely but the use of a silane adhesion promoting primer.[4] The beneficial effects of silane primer are magnified by exposing the silane treated substrate to elevated temperature of 110°C.

Prevention

An awareness of the great number of silicone sources as well as the pathways by which contamination can occur is an important first step in preventing contamination issues. Characterization of incoming materials can be useful in stopping potential contaminants from entering the bonding area. A generic approach to the problem involves four steps:

1. Identification of the contamination and its source,

2. Determination of contamination levels at which the bond is degraded,

3. Development of a corrective action plan, and

4. Verification that substrate cleanliness has been achieved prior to bonding.

Because of the problems associated with silicone contamination as described above, it is common practice to exclude the use of silicones whenever possible. This exclusion includes room temperature vulcanized resins, mold release agents, pressure sensitive tape, greases, oils and other products that may contain silicone.

Ovens are a good source for cross-contamination. One needs to maintain the cleanliness inside the oven to prevent particles, dust, and other solids from possibly contaminating the adhesive or substrate. Chemicals and vapors are also a potential contaminant. Vapors from silicone based materials (antifoaming agents, coatings, potting compounds, etc.) can be especially troublesome. The silicone from one batch can contaminate the oven and transfer unexpectedly to parts in another batch. Once contaminated with silicone, the oven is extremely difficult to clean. Generally, ovens that are used for high performance parts are used only for curing adhesives. Paints, casting compounds, and other products are cured in separate ovens.

References

1. Davis, G.D., "*Contamination of Surfaces: Origin, Detection and Effect on Adhesion*", **Surface and Interface Analysis**, Vol. 20, 1993, pp. 368-372.
2. Venables, J.D., "*The Science of Adhesive Bonding and Its Transfer to Technology*", **The Journal of Adhesion**, Vol. 39, No. 2-3, 1992, p. 86.
3. Liedtke, V., et. al., "*Cleaning of Silicone Contaminations: Development of Test Methods and Assessment of Cleaning Efficiency*", **ESA Report**.
4. Anderson, G.L., et. al., "*The Effects of Silicone Bond Contamination on Bond Performance of Various Bond Systems*", **The Journal of Adhesion,** Vol. 86, 2010, pp. 1159-1177.

Contact us for more information on addressing silicone contamination issues:

T: +44 1789 773232

E: sales@techsil.co.uk

W: www.techsil.co.uk

Contact Details

Techsil Ltd
Unit 34, Bidavon Industrial Estate, Waterloo Road, Bidford on Avon, Warwickshire, B50 4JN
Tel: +44(0)1789 773232 Fax: +44(0)1789 774239 Email: sales@techsil.co.uk Web: www.techsil.co.uk