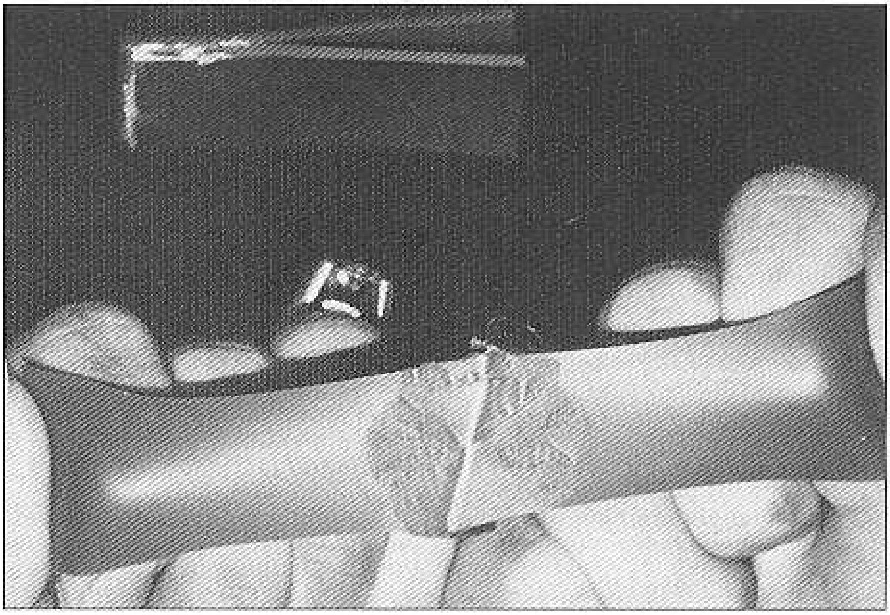
Plasma Processes Boost Bondability of Rubber and Metal

By **Maria Hozbor**, Applications Lab Manager, Himont Plasma Science, Foster City, California

Various methods of plasma treatment can enhance bonding of substrates. Cold gas plasma surface modification enhances silicone rubber adhesion. Also, the CFC-free plasma cleaning of metals and other substrates improves performance bonding.



Cohesive bond failure through the silicone substrate; note that the gray adhesive is not visible at the failure interface.

Plasma processes can be used to treat substrates in various ways to enhance bonding. Cold gas plasma surface modification improves adhesion of silicone rubber, while plasma cleaning of metals and other substrates facilitates performance bonding without using CFCs. This article addresses these two plasma treatment applications.

Bonding of Silicone Rubbers

Silicone elastomers are widely used in many industries, since they provide flexible, temperature-resistant components with desirable dielectric properties. However, their inherently low surface energy makes secondary applications such as bonding, marking or decorating difficult. Poor wettability hinders adequate spread and penetration of the adhesive.

The adhesion process is further complicated by the migration of low-molecular-weight oligomers to the surface, providing a weak boundary layer and further limiting bond strength. Cold gas plasma surface modification of silicone rubber provides a reliable, reproducible method to dramatically improve adhesion.

Experimental. Silicone rubber samples (silicone rubber, commercial grade pigmented red) were cut into 1 x 2 in strips. The samples were plasma treated in a PS0500 plasma unit using various oxygen blend gas chemistries for 2 min. The samples were bonded using a 3M two part epoxy (2216) using the 24 hr at 78°C cure in accordance to the manufacturer's recommendation. Untreated samples also were prepared and bonded as controls. Additionally, plasma treated samples were stored in KaPak heat sealed bags for various lengths of time prior to bonding, in order to investigate the effect of elapsed time after plasma treatment on bondability. Elapsed times of 1 min to 192 hr (8 days) between treatment and bonding were investigated. After curing, the samples were pulled to failure by hand and the mode recorded.

Additionally, four other silicone materials (clear GE LIM 3045, clear GE RMX-3 unfiltered, GE fluorosilicone blend pigmented red and a GE gray silicone) were treated using the same air plasma process. These samples were separated into two groups: one was bonded immediately after plasma treatment, the other was stored for 96 hr in KaPak heat sealed bags prior to bonding. The samples were adhesive bonded, cured and tested as described above. Untreated samples also were prepared and bonded as controls.

Results. The control samples were difficult to wet with the adhesive, and all exhibited adhesive failure. All of the plasma treated red silicone rubber samples showed cohesive bond failure, irrespective of the type of gas chemistry employed. Furthermore, no difference in bond integrity was observed between the samples bonded immediately after treatment and those stored for 192 hours prior to bonding.

Similarly, the four other silicone materials showed cohesive bond failure whether bonded immediately after plasma treatment or 96 hr later.

Conclusion. Process conditions have been identified which facilitate the bonding of silicone rubber. Cohesive bond failure of the silicone rubber can be achieved using a variety of gas chemistries under these process condi-

Reprinted from ADHESIVES AGE, December 1993

tions. Further it has been demonstrated that the modified surface resulting from plasma treatment is stable for at least 192 hours.

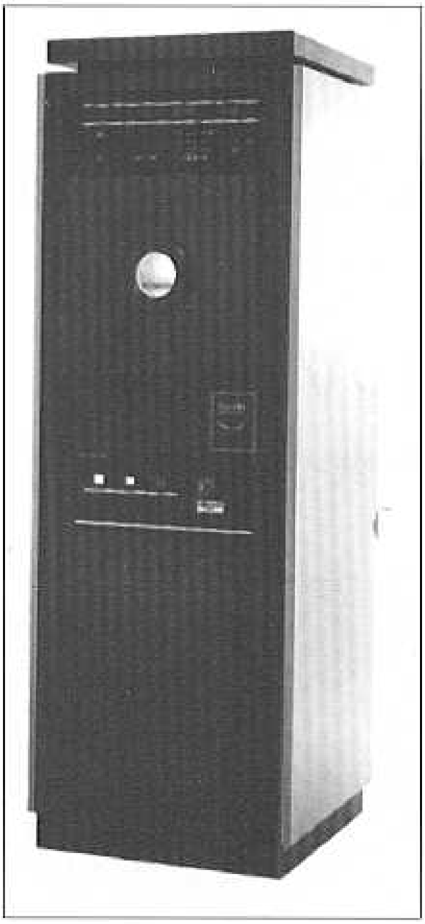
Plasma modification of silicone increases surface wettability dramatically, thereby promoting better adhesive spread and penetration, and thus improved overall adhesion. This high surface energy appears to be stable for an extended period of time. In addition, plasma treatment establishes functional moieties capable of reacting with most "curing type" adhesives providing covalent bonds. These bonds provide excellent stability to environmental attack by oxygen or moisture, enhancing the reliability and performance of the bonded material. The plasma process also has been shown to be effective with various silicone elastomer classes. Most importantly, plasma is not only a reliable and reproducible method for obtaining optimum adhesive bonding but is environmentally clean and workplace safe.

Cleaning of Metal Surfaces

The Montreal Protocol on Ozone Depleting Chemicals has mandated the replacement of chlorofluorocarbon (CFC) based cleaning solutions. Currently, CFC based cleaning methods are commonly utilized by many industries to remove hydrocarbon oils, greases and other contaminants from metal substrates without leaving potentially damaging residues. Although several alternatives are available to replace CFC cleaning solutions, their effectiveness at removing organic contaminants is less than optimal.

Additionally, many alternatives pose environmental, health or safety risks as well as increased costs. An effective alternative to chemical cleaning processes is plasma cleaning, which allows the removal of surface contamination from metal substrates while producing no undesirable health or safety problems. Unlike conventional chemical cleaning, plasma processes do not leave cleaning residues that complicate later processing steps.

Evaluating Cleanliness. To study the effectiveness of a cleaning process, several analytical techniques may be employed. One method is Electron Spectroscopy for Chemical Analysis (ESCA), a surface sensitive technique which provides elemental and chemical information from the outermost 40 to 80Å of a surface. ESCA uses incident x-rays, typically Al K alpha, to cause the photoemission of electrons from the material. The kinetic energy of the electrons emitted from the surface identifies the elements present. By measuring the exact binding energy and peak shape of a spectrum, the elemental and chemical composition of a surface can be determined. ESCA detects both organic and inorganic surface contamination.



Plasma Science PS0150 surface treatment system.

A second method to evaluate the removal of organic contaminants from the metal substrates is measurement of surface tension using deionized (DI) water and precisely formulated wetting tension test solutions. The solutions and test methodology are in accordance with ASTM D2578-79, using a Select Systems surface tension kit. To ensure accuracy, the samples were measured in several locations.

Experimental

Stainless Steel. Electropolished stainless steel coupons (316 L) were contaminated using WD-40 lubricant. The WD-40 was applied to the coupons from a distance of 4 in and sprayed continuously onto the surface for 10 sec. A control coupon and several contaminated coupons were analyzed by ESCA to determine the surface carbon concentration after machining (the as-received coupons) as well as after intentional organic contamination.

After analysis, the coupons were exposed to one of the following cleaning methods: 5 min oxygen plasma; 5 min argon/oxygen plasma; sonication (5 min) in a non-ionic surfactant with no plasma cleaning; sonication followed by a 5 min oxygen plasma; and sonication followed by a 10 min argon/oxygen plasma.

All coupons were labeled for direct comparison of carbon content between "contaminated" and "cleaned" surface.

Brass. Several brass coupons (C3600 free cutting brass) were examined by ESCA after machining, solvent cleaning or plasma cleaning. The change of carbon concentration on the surface of the brass coupons was determined after solvent and plasma cleaning and compared to the uncleaned (post machining) surface. The following cleaning methods were employed: 5 min oxygen plasma, 5 min argon/oxygen plasma and IPA solvent rinse.

Header Connectors (tin, gold and plastic combination). The surface energy of 200 new 0.100 in centerline dual row headers was measured as received, after exposure to a 5 min. oxygen plasma process, and after intentional contamination by sonicating in an IPA solvent bath to which several drops of water based cutting oil (Cimcool 5 Star 40 F, Cincinnati Milacron Marketing Co.) had been added. The intentionally contaminated parts were then exposed to an additional 5 min oxygen plasma cleaning process and the surface energy was recorded.

Results

Stainless Steel. The control coupon, typical of a stainless steel surface after machining, exhibited a surface carbon abundance of 54 atom percent. Theoretically, a typical stainless steel contains less than 1% carbon in bulk. As electropolished stainless has a chromium oxide passivation layer at the surface, carbon is not an expected constituent of the surface. In practice, however, metal surfaces are highly active, attracting 10 to 30 atomic layers of adventitious material, including oxygen, water and hydrocarbons adsorbed from the ambient environment. The contaminated coupons displayed carbon levels ranging between 85 and 94 atom percent of the surface analyzed. The top 40 to 80A of these coupons consists almost entirely of carbon. Subsequent bonding, painting, decorating or plating of such a contaminated steel surface would be hampered by the weak boundary layer of contamination indicated by excess carbon.

Both plasma cleaning (two processes) and sonication significantly reduce the intentional contamination levels. The sonication process (5 min in a nonionic surfactant) reduced the carbon level from 85 to 47 atom percent, significantly below the carbon abundance observed on the as-received material. An oxygen plasma treatment (5 min) reduces the surface carbon abundance to 38 atom percent, significantly below that achieved by sonication.

The treatment employing a 5 min argon/oxygen plasma (tailored for non-electropolished surfaces where oxide formation is a concern) reduced the initial 93 atom percent carbon level to 52 atom percent. The process employing sonication (to remove inorganic contaminants) followed by an oxygen plasma (5 min) reduced the hydrocarbon level from 87 to 35 atom percent. Sonication cleaning followed by a 10 min argon/ oxygen process reduced the surface carbon abundance from 88 to 27 atom percent.

Brass. The control coupons, representative of a standard process, varied from 79 to 85 atom percent surface carbon abundance. After solvent cleaning, the overall carbon concentration was reduced by approximately 7 to 13 atom percent. Plasma cleaning, however, reduced the amount of carbon on the surface by 28 atom percent, without tarnishing the finish of the brass.

Header Pins. Two hundred new 0.100 in centerline dual row headers were found to have an average surface energy of 54 dynes/cm. After a five minute oxygen plasma process, all areas of the pin were water wettable (73 dynes/cm). The pins were then intentionally contaminated by sonicating in an IPA solvent bath to which several drops of cutting oil (Cimcool 5 Star 40 F, Cincinnati Milacron Marketing Co.) had been added.

After "cleaning" with the contaminated IPA solvent, the surface energy to the headers had been reduced to approximately 40 dynes/cm. The samples were again submitted to a 5 min oxygen plasma cleaning. After the plasma cleaning process, all areas of the headers showed a surface energy of 73 dynes/cm.

The plasma method cleans a variety of metals, ceramics and plastics for subsequent adhesive bonding or metal brazing.

Conclusion

As the industrial community seeks safe, more environmentally friendly cleaning methods, plasma treatment for cleaning metal surfaces is gaining greater acceptance. Plasma processes are effective at cleaning metals which are not susceptible to oxidation (electropolished stainless steel) as well as those which may experience tarnishing (brass), albeit using different gas chemistries. An advantage of plasma is the ability to clean assemblies containing dissimilar materials such as the header pin, which contains both metal and plastic components.

No cleaning method can provide a "0%" carbon metallic surface if that metal is removed from a high vacuum, so one must ask how clean is clean or how clean is necessary. The plasma method currently cleans a variety of metals, ceramics and plastics for subsequent adhesive bonding or metal brazing. Plasma cleaning facilitates performance bonding with high reliability and reproducibility. Furthermore, the possibility of contamination introduced via a compromised solvent degreasing or cleaning bath is eliminated when using plasma cleaning.

Cold gas plasma effectively removes hydrocarbon contamination from the surface of 316 EP stainless steel C3600 free cutting brass, and gold and tin plated plastic header pins. Plasma cleaning produces volatile compounds which are removed during processing, so no residuals remain that may complicate further processing such as bonding or painting.

Plasma cleaning of metal surfaces poses no environmental, health or safety risks and reduces costs normally associated with chemical cleaning processes (disposal costs, safety equipment and training, etc.). Plasma cleaning is an effective, reproducible alternative to chemical cleaning processes, removing organic surface contamination from metal substrates while producing no undesirable environmental or safety problems.