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Adhesion as a safety factor

Atmospheric pressure plasma for safety-relevant industrial adhesive and sealing processes

All adhesive and sealing processes should produce good adhesive results. However, manufacturers' requirements concerning the adhesive properties of a material surface vary depending on the intended use of the finished product. When adhesion is not just functionally relevant, but also a matter of product safety, pretreating the material with atmospheric pressure plasma is often the only option to satisfy the high standards required.

If the expensive leather trim in a car comes loose, the edge of a worktop lifts or the sole of an expensive shoe comes unstuck, this adhesive bond failure is annoying for the consumer and may also damage the manufacturer's image – but it does not affect consumer safety. However, if the steering wheel control assembly of a car were to develop a fault due to a leaky protective housing, an aircraft radio malfunctioned due to moisture ingress in the electronic assembly or if the structural bonds on the superstructure of a truck or even the insulation on a gas tanker failed, failure of the adhesive bonds could be fatal. As the materials themselves and their adhesive characteristics become increasingly sophisticated in line with more exacting requirements, the importance of choosing the right pretreatment for adhesive and sealing surfaces has inevitably increased.

Surface energy is key

Insufficient adhesion in the interfacial layer between the adhesive and the substrate is the reason why adhesive bonds between two adherends made from additive-free materials may fail to adhere permanently or even at all, despite the use of a carefully selected, high-quality adhesive. This is usually because the material surface is not sufficiently clean and/or its surface energy is too low.

Whether the adhesive actually achieves the desired level of adhesion and tightness largely depends on the surface energy of the material to be bonded. The interactive

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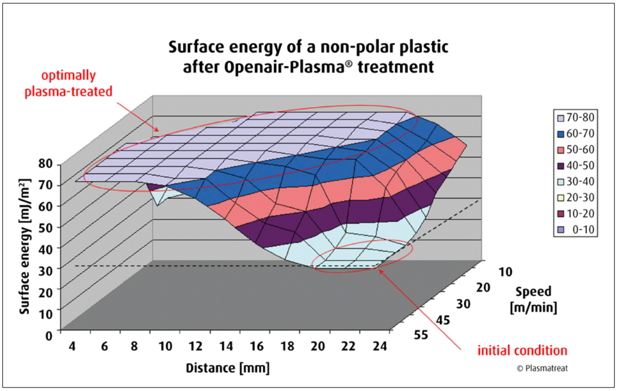

Fig. 1:Non-polar plastic surface which was pretreated with plasma as a function of distance and speed. Treatment renders the surface polar and the surface energy rises to >72mJ/m² with a large process window (Photo: Plasmatreat GmbH)

forces between the adhesive and the substrate that are responsible for adhesion can only take effect if complete and uniform wetting of the surface to be bonded with the adhesive is ensured. However, good wettability is conditional on the material surface being ultra-clean and the surface energy of the solid material being higher than the surface tension of the liquid adhesive. If a surface lacks the necessary cleanliness and energy, it is essential to pretreat it prior to applying the adhesive **(Fig. 1)**. Openair-Plasma, an atmospheric plasma jet technology that has been in use for over two decades, is a pretreatment method that is not only highly effective and environmentally friendly but also cost-efficient.

Threefold plasma action

The atmospheric plasma in-line process is dry and unlike conventional pretreatment methods performs three actions in one: microfine cleaning, static discharging and simultaneous activation of the surface. The result is homogeneous surface wettability and a long-time stable adhesive bond or coating even under challenging load conditions. Following plasma pretreatment, water-based and often UV-based adhesives adhere to adhesive-resistant surfaces such as non-polar plastics and in many cases a long-time stable bond can be obtained even with substrates previously thought to be incompatible.

Jet technology

The atmospheric pressure plasma (AP plasma) is generated inside the nozzle by a high-voltage discharge and transported to the surface of the part being treated in a flow of air. The entire pretreatment process takes place at high speed and when combined with fixed individual nozzles is capable of transporting components through

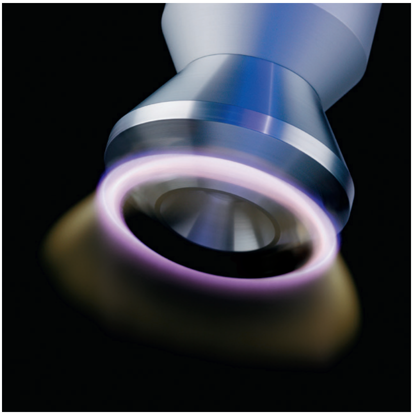

Fig. 2: Rotating at speeds of 2700 rpm-1 the patented rotary nozzles ensure a particularly gentle and uniform pretreatment of the material (Photo: Plasmatreat GmbH)

the plasma jet at speeds of several hundred meters per minute. Depending on the nozzle geometry, the plasma can be applied in a treatment width of 3 mm with static nozzles rising to 50 mm for individual rotary nozzles and approx. 100 mm for rotating double nozzle systems. Several nozzle systems can be combined to treat larger areas. Rotating at speeds of 2700 rpm^{-1} the patented rotary nozzles use a particularly gentle action to pretreat the material evenly **(Fig. 2)**. The process even makes it possible to pretreat highly sensitive assemblies and other delicate electronic components without damaging the electronics. This is due to the development of special nozzle heads which discharge the electrical potential to such an extent that the plasma impinging on the material surface is virtually potential-free. Plasma nozzles are area-selective. In other words, they pretreat only those parts of a component that actually require cleaning and activation. As a result, this process entirely eliminates the time-consuming masking process often required with conventional pretreatment methods.

Surface activation

The surface is activated – i.e. modified at molecular level – through the chemical and physical interaction of the plasma with the substrate. When the plasma hits a plastic surface, groups containing oxygen and nitrogen are incorporated into the mainly non-polar polymer matrix **(Fig. 3)**. Plasma activation renders the substrate polar and increases the surface energy. Energy-rich radicals, ions, atoms and molecular fragments present in the plasma release their energy at the surface of the material that is being treated and thus initiate chemical reactions which bring about this effect. Some of the functional hydroxyl, carbonyl and carboxyl groups that arise (as well as the oxygen compounds of nitrogen) form very strong chemical bonds with the coatings and so help to significantly enhance adhesion.

During treatment, the temperature of the plastic surfaces typically increases to $\Delta T < 30$ °C. Atmospheric pressure plasma is environmentally friendly; since it needs nothing

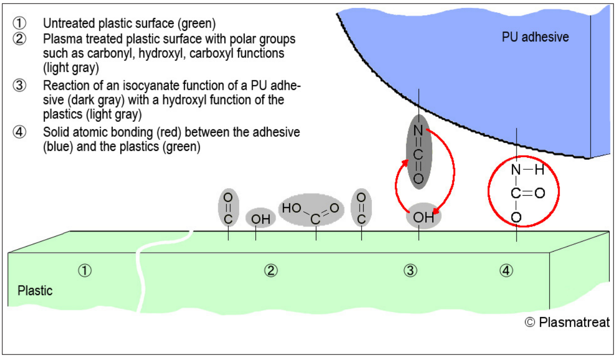

Fig 3: When the plasma hits a plastic surface, groups containing oxygen and nitrogen are incorporated into the mainly non-polar polymer matrix (Photo: Plasmatreat GmbH)

other than compressed air and electrical energy, VOC emissions (volatile organic compounds) during production are avoided from the outset. Layers of dust deposits or other contaminants can often compromise the naturally high level of surface energy in metals and glass, thereby impairing wettability. The microfine cleaning action of the plasma effectively restores the original surface energy to make complete wettability with the adhesive possible.

The plasma system producer's modern units are designed for fully automated, continuous production processes and are computer-controlled, screen-monitored and fully compatible with robotic applications, while the pretreatment processes themselves are robust and reproducible. Unlike wet-chemical pretreatment methods, this approach renders drying and interim storage unnecessary, so components can be processed downstream immediately after plasma cleaning, activation and coating.

Safety-relevant plasma pretreatments – application examples

Protection of electronics in vehicle construction

For over 10 years TRW Automotive in Gelsenkirchen, now part of ZF Friedrichshafen AG, has been using the Openair-Plasma technology along with the patented functional coating technology PlasmaPlus in the safety-relevant adhesive process for its die-cast aluminum motor pump assemblies **(Fig. 4)**. While the former serves for the fine cleaning and activation of the aluminium and prepares the surface for the subsequent plasma-polymer coating, the covalent PlasmaPlus layer applied directly afterwards provides an excellent adhesion base as well as a particularly high and environmentally friendly level of corrosion protection.

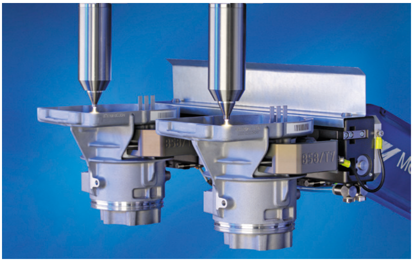

Fig. 4: Environmentally friendly corrosion protection – plasma cleaning and activation of the grooves in the die-cast aluminum housings before plasma-polymer coating and subsequent bonding (Photo: Plasmatreat GmbH)

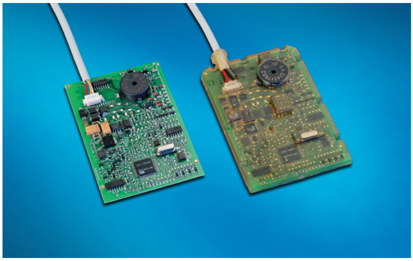

Fig. 5: Depending on the application, assembled printed circuit boards (left) are potted with hot melt (right) to protect them against moisture and mechanical damage. Its stable adhesion is achieved by pretreatment with AP plasma (Photo: Plasmatreat GmbH)

These assemblies are used in power steering systems and are subject to the highest requirements for environmental stability, such as corrosion resistance, thermal resistance and splash-water resistance. Mechanical, and above all, corrosive stresses that the component is exposed to during its service life must not lead to failure of the adhesive bond, as this would mean that the electric motor and electronic components would no longer be protected. The plasma-polymer coating plays a key role here. The SWAAT test (sea water acetic acid test) revealed that the adhesive joints of the plasma-protected housing resisted corrosion ten times longer than an untreated part. The time taken until penetration occurred (appearance of the first signs of corrosion inside the housing) – and thus the tightness of the housing – increased by around 50% with plasma pretreatment.

Alarm systems

The exterior of the electronic assemblies in alarm systems needs a high degree of protection since it is constantly exposed to the weather. Unlike control elements in cars, which must be accessible at any given time and are thus encased in a sealed housing, in this case after soldering the electronics are hot-melt potted to protect the assembled circuit boards from moisture and mechanical damage **(Fig. 5)**. If the hot melt does not adhere one hundred percent to the substrate, the alarm system is destined to fail. Here too, fine cleaning and activation of the circuit board material with AP plasma is a safety-relevant task. Once applied, the hot melt adheres so securely that the highest international protection ratings can be achieved, which among other things define the hazardous ingress of water into electrical equipment. After completion, this type of circuit board is inserted into an additional housing in order to serve as a burglar alarm keypad at the entrance to a house, for example. Failure of this keypad can lead to disruption of the security system, which is why one leading manufacturer - far beyond the requirements of the standard - subjects every single plasma-treated and potted circuit board to a twelve-hour underwater functional test.

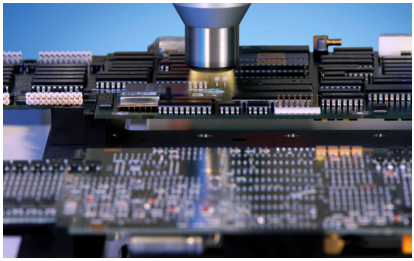

Fig. 6: At Rohde & Schwarz the potential-free pretreatment of the SMD assemblies for aircraft radio electronics with special rotary nozzles ensures the adhesion of the conformal coating (Photo: Plasmatreat GmbH)

Plasma in avionics

As a manufacturer of test and measurement equipment for wireless communications, EMC and digital terrestrial broadcasting applications and producer of aircraft radio systems for long-haul flights, Rohde & Schwarz is required to meet the highest safety standards in the manufacture of its electronic products. The heart of the aircraft radio antenna tuner developed specifically for civilian airborne radio communication and long-haul flights is a circuit board fitted with several hundred individual components. The function of this assembly unit with its tiny plastic-coated SMDs (surface-mounted devices) is to reliably tune the antennae, thereby ensuring overall radio communications. Openair-Plasma was integrated into the production line for these SMD assemblies when a problem with the adhesion of the conformal coating suddenly arose. The supplier had unexpectedly modified the composition of the plastic blend, rendering the surface energy of the plastic no longer sufficient to ensure the adhesion – and thus the tightness – of the protective coating. The use of AP plasma jet technology **(Fig. 6)** immediately remedied the problem. It was clear even from preliminary trials that the highly sensitive electronics had not been damaged in the slightest during the process due to the fact that the plasma was virtually potential-free. In inactivated state, the surface energy of the non-polar plastic surfaces of the components in question was below 30 mJ/m^2, but this rose to over 70 mJ/m^2 following plasma treatment. After activation, the protective coating had the necessary adhesive strength and the burn-in test, which is regarded as the toughest stress test available for electronic SMD assemblies, was passed with flying colors.

Sealing on a massive scale in ship building

From 2004 to 2006 the two biggest LNG tankers (liquified natural gas) in the world at the time, along with a smaller sister ship, were built in the docks of the traditional "Les Chantiers de l'Atlantique" shipyard in St. Nazaire, France. The huge tankers were

Fig. 7: Pretreating 12,000 m² per surface, the Openair-Plasma technology achieved the safety-relevant sealing against the liquified natural gas in LNG tankers
(Photo: Yves Guillotin)

almost 300 m long, 43.5 m wide and 50 m tall. An extremely complex insulation process took place inside the tankers up until the time of their completion, to which this plasma technology made an essential contribution in terms of safety. A new insulation technique was to be used to insulate the tankers which would increase the tanker capacity by 8000 m^3. In membrane tankers, an inner, impermeable metal membrane made of Invar steel forms the actual cargo container i.e. is in direct contact with the liquid natural gas. This membrane forms the first barrier. In the event of a leak in the metal membrane, the new insulation layer consisting of four levels was to act as a second barrier to prevent the liquefied natural gas cooled to minus 163 °C from coming into contact with the load-bearing double-walled steel structure of the tanker and embrittlement of the steel due to the extremely low temperature.

The purpose of the pretreatment was to prepare the bonding process for thousands of strips of flexible Triplex tape. These strips are 30 cm wide and have an overall length of around 40 km per tanker. They are applied to the edge joints between the insulating panels using a 2-component epoxy resin to ensure complete tightness. Although the bond functioned perfectly in the laboratory, when transferred to the huge construction site, the process failed due to inadequate adhesion of the tapes. Neither chemical processes nor surface flaming produced the desired results. Only when 20 robot-controlled plasma units were used could all the safety, efficiency and environmental requirements be met. In total, the plasma systems cleaned and activated an area of 12,000 m^2 per tanker, thus ensuring that the ships are still sailing the world's oceans today **(Fig. 7)**.

Structural bonding in truck manufacturing

Nowadays, modern vehicle superstructures are entirely bonded in order to achieve greater inherent strength and durability of the joints, whilst at the same time reducing

Fig. 8: Structural bonding in vehicle construction places extremely rigorous demands on the integrity of the adhesive bonds. Here, the adhesive joints of the refrigerated semitrailers are pretreated with AP plasma (Photo: Schmitz Cargobull AG)

production costs. This makes the vehicle manufacturing industry one of the largest consumers of structural adhesives. The requirements for structural bonding are correspondingly high and can be achieved only with a reliable, reproducible pretreatment process.

Since 2003, Schmitz Cargobull AG has pretreated over 16,000 refrigerated semitrailers **(Fig. 8)** each year with Openair-Plasma before bonding. The manual surface cleaning and keying that had been carried out until then was to be replaced by an industrial process. The primary goal was to dispense entirely with the organic solvents previously used for pretreatment, and thus eliminate the potential risk of environmental pollution right from the start. The refrigerated semitrailers are self-supporting systems – the entire modular structure is assembled without rivets. The adhesive bonding technology creates friction and positive locking joints without costly thermal bridging. The sandwich construction of the walls and ceilings of the 13.50 m long, 2.60 m wide and 2.8 m high box bodies is composed of vapor-permeable panels consisting of a high-density polyurethane foam core sandwiched between two plastic-coated sheet steel skins. By bonding the large-format panels in aluminum profile rails, the system becomes self-supporting. The areas of the panel surface to which the adhesive is applied are pretreated with plasma beforehand to achieve the required high adhesive strength and special tightness. Four plasma treatment stations with a total of 32 plasma nozzles, some rotating and some static, perform the environmentally friendly and process-reliable pretreatment.

Sealing of car headlights

Hella Australia, a subsidiary of the internationally active German automotive component supplier, has used rotary plasma nozzles for several years for the area-selective

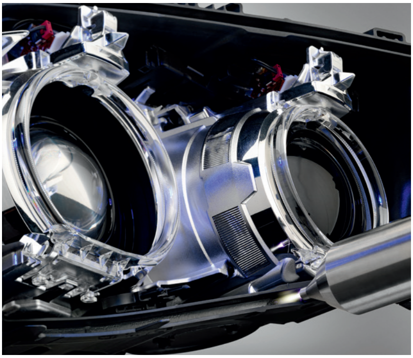

Fig. 9: The plastic housings of car headlights are activated with plasma inline immediately before bonding to ensure particularly strong adhesion and tightness (Photo: Plasmatreat GmbH)

pretreatment of its headlights. With these components, the adhesive bond between the polycarbonate lenses and their polypropylene housings must also satisfy strict safety requirements. Even the slightest leak would result in moisture penetration leading to impairment of the headlight lens. This would adversely affect the beam angle of the light, which could be dangerous for the driver when driving at night. Hella uses the plasma to clean and simultaneously activate the base and side walls of the grooves in the non-polar polypropylene housing inline immediately before applying a 2-component silicone adhesive **(Fig. 9)**. This has the effect of substantially improving the adhesive characteristics of the subsequent bond to ensure an especially tight headlight seal.

Hybrid fittings in medicine

As a systems supplier for the medical and pharmaceutical industry, Gira develops and manufactures components, assemblies and complex system products made from plastic. The processor uses plasma technology in multi-component injection molding to ensure process reliability when manufacturing complex hybrid fittings for use with oxygenators **(Fig. 10)**. The fitting is adapted to the oxygenator – a key component of a heart and lung machine. Inside this fitting is a stainless steel insert which is used to measure blood temperature during heart surgery. The metal and polycarbonate must be perfectly bonded to guarantee complete tightness. The plasma treatment performs a very important safety-relevant function in this case. Immediately before insertion in the injection mold, the metal sleeve is cleaned to microfine level and activated with plasma in a fully automated process under cleanroom conditions. This process removes all traces of organic contamination and increases the surface energy of the metal to >72mJ/m^2. As a result, uniform wetting of the metal surface with the plastic melt is ensured. The use of adhesion-modified compounds or an additional adhesion-promoting layer is not permitted. According to the manufacturer, the plasma process alone has made it possible to achieve complete impermeability to liquids in the compound by eliminating influencing factors such as shrinkage, minute air bubbles and gaps. Especially with sterilization rinsing, which can lead to negative test results even with the finest capillaries due to its extremely low viscosity, the tightness could be proven.

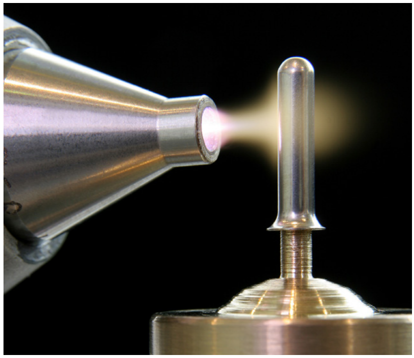

Fig. 10: In medical engineering plasma technology is used, for example, in multi-component injection molding to reliably manufacture complicated hybrid fittings for use on oxygenators (Photo: Gira, Giersiepen GmbH & Co. KG)

Summary

Innovative materials, new composite materials and surface characteristics play an increasingly important role in modern engineering. In parallel with this, the requirements for the sustainability and safety of manufacturing processes are becoming ever more stringent. Surfaces that require a highly effective and environmentally friendly pretreatment due to lack of adhesive properties will continue to exist in the future. As the examples of atmospheric pressure plasma applications given here show, there are practically no limits to the potential applications of this key technology.