

# Plasma Surface Modification for Adhesion

Ron Nickerson

Advanced Surface Technology, Inc.

## *Abstract*

*This seminar is intended to provide a general understanding of:*

- 1. What is a plasma?*
- 2. The interaction mechanisms between polymer surfaces and plasma.*
- 3. A brief overview of process and system configurations.*

*Plasma is the most environmentally safe method of both organic removal and surface modification to date. Plasma processes can be tailored to produce hydrophobic or hydrophilic surfaces on metals, plastics, glass or polymers. Recent advances in the uses of polymers and as a result the need for hydrophilic surfaces for adhesion has fueled the development of the plasma surface modification industry. This seminar will review the current industry and how it addresses the adhesion issue in terms of available equipment and future potential.*

## *What is Plasma?*

Plasma can loosely be defined as a partially or wholly ionized gas with a roughly equal number of positively and negatively charged particles. It has been dubbed as the "fourth state of matter" because of its general properties which are similar to both a gas and a liquid.

There are both high and low temperature plasmas. High temperature plasma is found at atmosphere in its manmade form as a plasma torch or naturally in the form of lightning. Low temperature plasmas, as used in surface modification and organic cleaning, are ionized gases generated at low pressures. These low pressures allow for a relatively long free path of accelerated electrons and ions which are essentially at ambient temperatures. With relatively few collisions there is a low energy transfer thus keeping the temperature of the reaction in the ambient range.

The ionization of the gas is accomplished by applying an energy field using one of three government regulated source frequencies:

1. Low frequency or < 100 KHZ.
2. RF frequency or 13.56 MHZ.
4. Microwave frequency or 2.45 GHZ.

The frequencies selected for these sources are controlled by international agreements to prevent use of sources which would interfere with communication bands worldwide. Unfortunately for manufacturers, the least desirable method of generation is

also the least expensive - low frequency. Low frequency plasmas are the least efficient for several reasons which go beyond the scope of this presentation. The efficiency is related to the energy necessary to sustain the ionization and both the intensity and frequency of vacuum ultraviolet (VUV) radiation.

Most plasma system manufacturers use either RF frequency or MW frequency sources. Anatech Ltd. uses almost exclusively RF sources because of the overall advantages associated with this method. RF plasmas have been shown to exhibit significantly higher levels of VUV which in part explains the higher concentrations of electronically charged particles than found in the other plasma sources. RF plasmas have also been noted to be more homogeneous which is critical in treating irregularly shaped and overly large objects.

MW source plasmas are generated "downstream" or in a secondary environment. This means that the plasma is generated in one chamber and the active species are drawn by vacuum differential into the work area. Though this can be advantageous for organic removal it does produce a less homogeneous process and as a result provides reduced uniformity across the work area. In areas of surface modification the effective depth of the modification is tens of nanometers so the uniformity of the process becomes increasingly important.

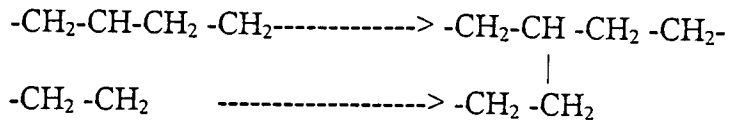
There are several resultant effects to the plasma interaction with the surface, each of which has a reaction to the adhesion process. These effects are, but are not restricted to:

1. Organic removal
2. CASING (Crosslinking via Activated Species of Inert Gases)
3. Ablation
4. Surface chemical restructuring

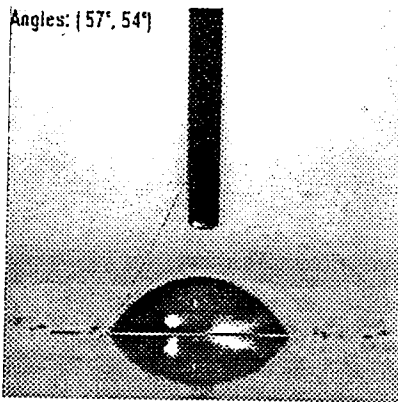
### *Organic Removal*

One of the prime problems with adhesion is the presence of organic contamination on the surface. This contamination may be in the form of residues, mold release agents, anti-oxidants, carbon residues or some other organic. Oxygen plasmas are excellent in removing organics but care must be taken to be sure the organics are completely removed. It is possible to "surface modify" the contamination and thus still have a barrier layer which will cause the adhesion to fail. An oxygen plasma is a chemical reaction and thus is viable in both the down-stream configurations and in the secondary plasma.  $O_2$  when exposed to the RF energy field is broken down into monatomic oxygen (O),  $O^+$  and  $O^-$ . The O at pressures above .1 torr is the most reactive element in the plasma and will readily combine with any organic hydrocarbon. The resultant combination is water vapor, CO and  $CO_2$  which is carried away in the vacuum steam. The reaction is by its nature complete with no residual surface products; however non-organics such as salts are not so readily removed. Sufficient RF energy must be applied to produce a high plasma density. Lower power densities do not just remove contamination at a slower rate but can actually

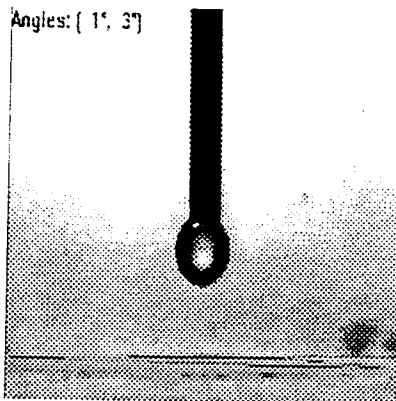
impede the removal process. While the top layers of organics are being removed with low power density, underlying layers may actually crosslink in three dimensions creating a stable but unremoved new structure.



Based on the above situation it can be seen that the power density must be carefully monitored. Complete removal can be illustrated by the use of contact angle measurement. The actual surface energy can be calculated using the same method and the application of three different liquids. The tests in all of the following cases were conducted using an Advanced Surface Technologies, Inc. model VCA 2500 contact angle measurement device.



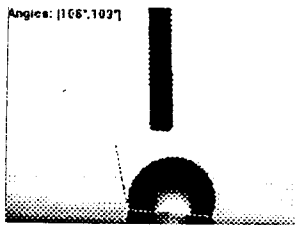
Aluminum coupon with cutting oil contamination. Contact angle before of 57/54° using certified water



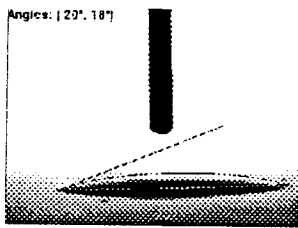
Contact angle after plasma treatment below readable limits.

## *CASING*

CASING is an acronym referring to the use of inert gas plasma treatment on polymer surfaces. It was noted that when generating a plasma using inert noble gases such as He or Ar the plasma would break C-C or C-H bonds by ion and VUV bombardment. These free radicals in turn recombine on the surface causing a stable crosslinking of the surface structure. The improved bond strength of the surface can be a very desirable effect. As in other plasma reactions CASING formation is at or just below the polymer surface with the radicals formed having a long life. This can give rise to post plasma reactions but again it may be used to advantage. In the case of PTFE treatment it has been found that the pretreatment in He followed by a plasma of  $\text{NH}_3$  will facilitate the bonding of a barrier layer to the PTFE which in turn will be receptive to adhesion. This is illustrated by the before and after contact angle measurements below:



Before plasma treatment  
Contact angle of  $106/107^\circ$  using certified water



After plasma treatment He/ $\text{NH}_3$   
Contact angle of  $20/18^\circ$

## *Ablation*

The etching of surfaces can also be accomplished in a plasma. Roughening of the surface can play a significant part in adhesion by increasing the total contact area between the adhesive and the subsurface. The etching is a result of gas selection or just the length of time the surface is exposed to the plasma. Ablation can be accomplished with either active or inert gases and can be run to excess. Extremely porous surfaces may be the result of too long an exposure to plasma.

The semiconductor industry has used plasma etching as a primary source for the production of semiconductors for over twenty years. In addition the circuit board industry has used plasma as a means of etching polymers smeared in the drilling process. These hole smears prevent contact with plated through holes on multi-layer circuit boards and are easily removed by plasma ablation.

## *Surface Chemical Restructuring*

Perhaps the area offering the greatest potential is the actual plasma modification of the surface structure. This was briefly touched on in the application of a barrier layer during the treatment of PTFE. By adding polar functional groups to the surface structure of the polymer we can greatly increase the surface energy and thus aide in the adhesion to other substrate materials.

Plasma treatment can be used to provide for the oxidation of the surface in much more uniform methods than by corona discharge or flame treatment. Large irregular surfaces can be treated with little the possibility of over treatment, a drawback of both corona and flame methods. Plasma has shown great gains as an effective method in the treatment of automotive polymers such as car bumpers and panel boards. Elimination of primer coatings for paint adhesion by plasma surface preparation is currently the method of choice be several automobile bumper manufacturers.

In addition to rendering surfaces hydrophilic plasma can render a surface hydrophobic by fluorinating. Barrier layers on chemical tanks and even textiles are possible by the application of fluorinated plasmas. Plasma polymerization is yet another available process in the structural change of the surface.

## *Plasma Reactions*

Reactions fall into two categories: chemical and mechanical. Chemical reactions are reactions as a result of an actual chemical interaction of the plasma with the surface of the product or contaminant. These reactions would include oxidation and ablating the surface with such gases as fluorine or chlorine. Mechanical reactions are generated with the use of noble gases such as argon or helium. Since these inert gases exists in their monatomic state the reaction is a kinetic energy transfer or, in simple terms, a sand blast. The dislodged contaminants can be swept away in the vacuum stream before they can redeposit on the product or allowed to recombine with the correct process parameters. These inert gas plasmas are used to remove organics and particulate from surfaces which might readily oxidize such as silver or copper or for CASING as mentioned earlier.

## *The Physical Equipment*

All current plasma systems fall into the same basic configuration:

1. A chamber for the reaction.
2. An energy source for the gas ionization.
3. Control circuitry to regulate the time, gas flow and amount of energy.
4. A vacuum system to provide the low pressure environment.

### *The Chamber*

Chambers are manufactured in either metal or glass depending on the application and the method of ionization. Quartz chambers are used in highly critical environments where submicron particulate generation is an issue. This would include the semiconductor, hybrid and medical analysis industries.

For industrial applications, metal chambers are more prevalent and allow for the rougher handling environment accompanying that industry. Systems are even produced with tumbling chambers for the surface modification of a large volume of small parts.

Aluminum chambers offer an advantage over stainless steel chambers; aluminum will develop a natural oxide layer which becomes a tough barrier to secondary reactions. Even the best stainless steel has been known to oxidize in a plasma environment and over time the oxidized surface can be a source of particulate which is undesirable.

### *Uses of Plasma Today*

Plasma systems range from a small two inch chamber to ten foot walk-in chambers capable of processing as many as seven automobile bumpers at a time. Though there are standard sizes available, your needs should dictate the system.

Surface modification has given rise to the continuous or in-line plasma system. These systems have attempted to address the web and sheet treatment of commercial products. Batch processing is still less expensive due to the vacuum limitations of continuous operations.

The following are actual case studies of plasma applications.

#### Case Study "A"

A controlled study to find the effectiveness of the removal of common oils such as 143AA, 5606, 24139 grease and 2190 TEP was conducted by a US Government agency in conjunction with Anatech LTD. Stainless steel coupons were cut 1" x 1" and weighed. A drop of oil between 10-12mg was applied to each coupon and then exposed to different plasmas. The following table illustrates the effectiveness of different gas combinations.

contaminate	plasma gas	time in plasma	percentage of removal
143AA OIL	Oxygen	15 min	100%
5606 OIL	Oxygen	8 min	100%
5606 OIL	Oxygen	5 min	100%
5606 OIL	Argon	15 min	70%
24139 GREASE	O <sub>2</sub> /CF <sub>4</sub>	15 min	100%
2190 TEP OIL	O <sub>2</sub> /CF <sub>4</sub>	15 min	100%
5606 OIL	room air	15 min	87%

#### Case study "B"

Connectors with residue of parylene inside the female assemblies were exposed to an O<sub>2</sub>/CF<sub>4</sub> plasma for 20 minutes. All traces of parylene were removed from inside the connector housings without adverse effect to the assembly. The removal of the parylene was critical to the application of adhesives in further production steps.

#### Case Study "C"

PTFE sheets were received with a contact angle of 106 degrees. After exposure to a plasma of He followed by NH<sub>3</sub>, the contact angle was reduced to 20 degrees. The lower contact angle is representative of a higher surface energy which would allow adhesion. The surface was effectively changed from hydrophobic to hydrophilic.

#### Case Study "D"

Automobile bumpers are being processed in an in-line plasma system immediately following mold injection. Mold release and organics are removed allowing adhesion of paint without a primer phase. Bumpers are processed seven at a time in an in-line assembly operation for a total cost reduction of 50% over previous cleaning methods.

#### Case Study "E"

Stainless steel plates were received with a contact angle measurement of 92 degrees and were processed in a CF<sub>4</sub> plasma to produce a hydrophobic state with a contact angle of 120 degrees.