

PLASMA
The Chemistry Tool for the 21st Century
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INTRODUCTION

One hundred years ago, Sir William Crooke stated "... the investigation of the fourth state of matter - plasma - will be one of the most challenging and exciting fields of human endeavor". Even though it has found a major niche market (in excess of \$ 1 billion) for the fabrication of semiconductor devices, plasma remains an emerging technology still in its embryonic stage in the industrial market place.

The product designer by using plasma technology is unlimited in the choice of materials at his/her disposal for the design of any specific component. The surfaces of materials can be easily and effectively modified via plasma treatment for a variety of end uses without altering the properties of the bulk material. Thus the designer may chose a plastic best suited for the application by its mechanical properties and subsequently modify only the surface for optimum performance in a secondary operation such as painting or bonding. Plasma processing offers a means for cost effective surface engineering to provide performance and permanence to painting of even the most difficult to paint plastics. And, plasma processes are workplace safe and environmentally friendly. However, as will be discussed in this paper the most optimum results are most readily achieved when the materials and paint suppliers as well as the manufacturer work in collaboration.

PLASMA

Gas plasmas have existed since the beginning of time, long before the advent of solids or liquids. In fact, 99 percent of the universe is a plasma. Stars are plasmas. The solar corona is a plasma. Earth's natural plasma include lightning, the Aurora Borealis, and St. Elmo's fire. Table I lists certain plasma and characterizes them by particle density and temperature.

Table I
Ranges of Particle Density and Temperature for Various Types of Plasmas

Plasmas	Particle Density (No./cm³)	Temperature (*K)
Natural Plasmas		
Stellar interiors		
Stellar atmospheres	10 ²² -10 ²⁵	~10 ⁸
Nebulae	10 ¹⁰ -10 ¹⁶	10 ⁴ -10 ⁶
Interstellar Space	10 ³	10 ⁴
Earth's ionosphere	1-100	10 ²
	10 ¹⁰ - 10 ¹²	10 ² -10 ³
Manmade Plasma		
Thermonuclear plasma	10 ¹² -10 ¹⁴	10 ⁸ -10 ⁹
Constricted arc plasma jets	10 ¹⁶ -10 ¹⁸	1-5x 10 ⁴
Free-burning electric arcs	10 ¹⁶ -10 ¹⁷	7-10x10 ³
Combustion flames	0 ¹⁶ -10 ¹⁸	3-5x10 ³
Low-pressure arcs	10 ¹⁰ -10 ¹²	1-3x10 ³
Glow discharges	10¹⁰-10¹²	00-600

There are many definitions of the term "plasma" depending on one's particular discipline. It has often been referred to as the fourth state of matter; the generation of plasma being analogous to the transitions that occur when energy is supplied to a material causing solids to melt and liquids to become gases. Sufficient additional energy supplied to a gas creates a plasma. In the case of cold gas plasma, typical of that to be discussed in this paper, the process is excitation of a gas at reduced pressure by radio frequency energy. A plasma contains excited atomic, molecular, ionic and radical species. While on an atomic scale, plasma generation cannot be construed as a room-temperature equilibrium process, the bulk of the material remains near room temperature. The plasma contains free electrons as well as other metastable particles which upon collision with the surfaces of polymers placed in the plasma environment break covalent chemical bonds creating free radicals on the polymer surface.² These free radicals will then undergo additional reactions depending on the gases present in the plasma or subsequent exposure to gases in the atmosphere. The result is that these gas-radical reactions form a surface potentially very different from the starting bulk polymer. Since the process is conducted in a reactor under very controlled conditions, the end result is very reproducible.

Plasma processing is not one process but a "tool box" that can be classified into three categories: 1) plasma activation, 2) plasma induced grafting and 3) plasma polymerization. Plasma activation is the simplest and most cost efficient of these processes and more than adequate to prepare plastics for painting. This paper will focus on plasma activation processes exclusively.

Plasma activation is the alteration of surface characteristics by the substitution of chemical groups or moieties for groups normally present on the polymer chain being modified. The mechanism is the reactions resulting from the bombardment of the surface by photons, ions and neutral particles, all of the active species in the plasma react with the polymer surface. The by-products, typically CO_2 , H_2O and low molecular weight hydrocarbons, are readily removed by the vacuum system. The use of co-reactants can serve to modify the surface chemistry obtained with a single gas chemistry or to accelerate the reaction kinetics. For example, in an oxygen plasma, the breaking of the carbon-carbon and carbon-hydrogen bonds is the rate limiting step. When tetrafluoromethane is introduced as co-reactant, the O_2/CF_4 plasma yields excited forms of O, OF, CO, CF_3 , CO_2 , and F. Since fluorine or fluorine containing species are more effective in breaking the carbon-carbon and carbon-hydrogen bonds, the reaction rate is accelerated. The use of other gases permits the incorporation of other functional groups on the polymer surface. Examples include the use of ammonia, nitrogen and nitrous oxide plasmas to incorporate nitrogen on the surface and create nitrogen based functional groups such as primary and secondary amines.

The result of plasma modification of the polymer is an increase in the surface energy of the polymer and an attendant improvement in surface wetting. Adequate wetting of the surface by the adhesive contributes to an improvement in bond strength by increasing the apparent area of contact over which the load is distributed. Published studies³⁻⁵ suggest that this improvement in wetting directly contributes to the observed improvement in the strength of the adhesive bond. However, evidence has been presented in several studies⁶⁻¹⁰ that indicate that the major improvement of adhesive strength is dependent on the particular functional group that has been created on the surface of the polymer. In some cases, a direct correlation is drawn relating the nature of the chemical groups on the surface, the nature of the adhesive used and the observed improvement in adhesion. In other cases, the observed improvements are related to effects of hydrogen bonding and specific surface chemical interactions that do not necessarily result in covalent bonding between the polymer surface and the adhesive.

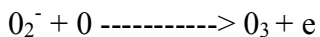
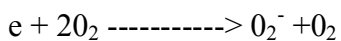
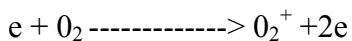
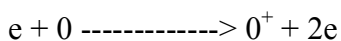
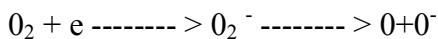
PLASMA PROCESSION EQUIPMENT

While most, if not all, plasma equipment consists of similar components, the design of the reactor chamber, the distribution of power, the excitation frequency, and the gas dynamics can all be critical parameters influencing the efficiency and properties of plasma reactions. There has been an extensive amount of work published that shows a direct correlation between excitation frequency and plasma reactivity. Manufacturers of plasma equipment employing radio frequency excitation use either low frequencies, i.e. less than 400 KHz, or the higher frequencies at 13.56 or 27.12 MHz as specified by the FCC. For applications involving the treatment of plastics 13.56 MHz is the preferred frequency. Also important is whether the material being treated is in a primary or secondary plasma. In a secondary plasma the plasma is created either between closely spaced paired electrodes which may function as shelves or in the annulus between the vessels outer wall and a ring or cage electrode. In a secondary plasma the treatment of materials placed within the working volume depends on the diffusion of active species created in the primary plasma, i.e., within the RF field. Diffusion of these active species is the very creation of free radicals and subsequent coupling of these free radicals with active species from the plasma environment. Depending on the process gas selected, a large variety of chemical groups can be incorporated into the surface. These groups may be hydroxyl, carbonyl, carboxylic, amino or peroxy groups. Most importantly, the insertion or substitution of these groups in the polymer chain is under the control of the operator. In this manner, the surface energies and the surface chemical reactivity of plastics can be completely altered without affecting their bulk properties.

PLASMA ACTIVATION AND REACTIONS ON THE SURFACE

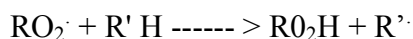
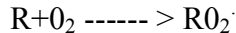
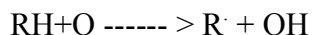
Although any gas can be ionized using RF excitation, gases such as O₂, N₂, He, Ar, NH₃, N₂O, CO₂, CF₄, and air or some combination of these gases are generally used for surface treatment.

One of the more common plasma processes used to enhance the adhesion of polymers is surface treatment in an oxygen plasma. An oxygen plasma is aggressive in its reactivity and forms numerous components. Within an oxygen plasma O⁺, O⁻, O₂⁺, O₂⁻, O₃, ionized ozone, metastable excited O₂, and free electrons are generally observed. The ionization of oxygen into the various species found in an oxygen plasma can be represented by the following reaction scheme.



These reactions represent a small sampling of those that occur in an oxygen glow discharge. As the components formed during the ionization recombine, they release energy and photons, emitting a faint blue glow and much UV radiation. The photons in the UV region have enough energy to break the carbon-carbon and carbon-hydrogen bonds in the materials on the surface that are exposed to the plasma. In the case of contaminants, the net effect appears to be degradative such that lower molecular weight materials are created. These lower molecular weight materials are subsequently removed by the vacuum. In this manner the surface that has been exposed to a plasma is cleaned. Lower molecular weight polymer fractions that comprise the weak boundary layers on the surface are also removed in this

manner. In a low pressure oxygen plasma, the following oxidation reaction scheme has been suggested.



Here the RO_2H and RO_2R' indicate the formation of acids and esters. Not indicated in the above reaction scheme are the possible formation of alcohols, ethers, peroxides and hydroperoxides. Thus, besides the dependent on pressure; the higher the pressure, the shorter the mean free path. The mean free path is the distance active species can most likely travel before undergoing collisions that deactivate radicals or neutralize ions. Therefore, when using a secondary plasma, the concentration of active species varies either across the diameter of a barrel system or between electrode pairs as the case may be. Thus, the physical laws of nature deem that the treatment within the working volume of a secondary plasma system cannot be uniform. By contrast when working within the RF field, or primary plasma, the gas is constantly being excited. Thus, polymeric articles being treated are immersed in a constant concentration of active species. Further, since diffusion is not a mechanistic limitation, significantly higher operating pressures may be used. This allows higher process gas flow rates assuring that off gassing molecules from the polymer are sufficiently diluted providing the full benefits of the desired process gas. In addition, the primary plasma is rich in ultraviolet radiation that is often an important initiation step in polymer reactions. Since UV radiation is line of sight, uniform treatment of multiple parts can only be assured when working within the primary plasma. Otherwise any part in the shadow of another will receive different radiation and therefore the effectiveness of the treatment is expected to vary. The plasma system used in the study reported herein utilized a system designed and built by Plasma Science. All Plasma Science equipment employ primary plasma in the treatment zone.

PERMANENCY OF PLASMA TREATMENT

One of the first commercial uses of plasma outside of the semiconductor industry was an activation process to enhance adhesive bonding of molded silicone rubber gaskets in the assembly of military cylindrical connectors. Plasma activation of the silicone allowed the use of conventional epoxy adhesives to achieve adhesive bonds of silicone to metal where failure is characterized as cohesive tearing of the silicone. These cylindrical connectors have been successfully using plasma in their manufacture for more than twenty years and actual real time studies show no deterioration of the bond quality with time, even though these connectors are exposed to harsh storage and use conditions.

In other studies¹¹⁻¹³ polyethylene fiber, Spectra 1000, was treated and the surface modification characterized using Electron Spectroscopy for Chemical Analysis (ESCA). The ESCA data showed that the types and concentration of functional groups initially established were unchanged after a year storage. Tests were not extended for longer periods, because there is no reason to believe that any change with time will occur, as long as the material is protected from contamination.

With some materials, such as TPO, a deterioration of plasma effectiveness with time may be observed. However, ESCA analysis shows that the functionality created by the plasma treatment has not changed, but rather, either an external or internal impurity has contaminated the surface. Many commercial

plastics contain additives which with time may migrate through the bulk material to the surface. Once at

the surface, because of the high activity of the plasma surface, it will spread rapidly and essentially bury the functionalized surface under this "new surface" (contaminant). However, this usually does not occur very rapidly and a properly designed facility with good house keeping practices should find little sensitivity to aging within the typical production line time spans. Of course only time and experience with specific materials and applications can guarantee the efficacy of a plasma treated surface over extended time.

EXPERIMENTAL SECTION

Twelve full size fascias molded from a commercial reactor grade thermoplastic polyolefin (TPO) were painted in a commercial automotive production line. The fascias were painted with a commercial one component (IK) base and clear paints; six fascias each of white and blue metallic. Six by four inch (6" x 4") plaques were cut from six (6) different positions as follows: drivers side ear, drivers side face, drivers top deck, passenger's side ear, passenger side face and passenger side top deck. The plaques were subjected to Chrysler specification MS-PA40-1 which requires subjecting the plaques to the following tests:

- Initial Adhesion (LP463PB1-5-01)
- 240 Hours Humidity (LP463PB-9-01)
- Cold Cycle Crack - Met. (LP463PB-22-01)
- Gravelometer (LP463PB-39-01)
- Gasoline Soak Resistance (MS-PA40-1)

The testing and data analysis was conducted by The Crown Group of Warren, Ohio.

RESULTS AND DISCUSSION

Two hundred eighty eight plaques (288) cut from molded bumpers were tested and the following results obtained.

Test	Specification		
	Value	White	Met. Blue
As received Adhesion			
"X" Scored	5A	pass*	pass*
240 Hour Humidity Aging - 100% RH@100.F			
Blisters	none	pass	micro & fine blisters
"X" Scored	5A	pass	pass
Cross Hatch	5B	pass	pass
Cold Crack Cycle (Cycle IV)			
Blisters	none	pass	pass
"X"Scored	5A	pass	pass
Cross Hatched	5B	pass	pass
Gravelometer			
1 pin	#8	pass	pass
Gas Resistance			
soak	no effect	pass	pass

*passes or exceeds specification requirements for acceptance

All of the white painted specimens were satisfactory as tested. All metallic blue panels failed 240 hours humidity exposure due to blistering. All other tests on the metallic blue met or exceeded the specification requirements. The blisters were of the very small micro type variety. However, specification MS-PA1-1 allows no blistering, thus failure. Interestingly, the blistered samples also passed adhesion tests, an indication that the blisters were not adhesive in nature. This was further proven by Electron Spectroscopy for Chemical Analysis (ESCA) which showed TPO bound to the bottom side of microtomed blisters. This type of blister is referred to as "solvent pop" where paint solvent migrates and dissolves into the TPO bulk and is subsequently released during the elevated temperature humidity soak rupturing the substrate causing lifting and the appearance of blisters. True blisters, i.e. paint film separation from the substrate, would have no adhesive strength to the substrate. The satisfactory performance of the white paint as opposed to the humidity soak failure of the metallic blue is best be defined as a paint formulation or substrate deficiency not a failure of the plasma surface treatment.

CONCLUSIONS

Whether it is the bonding of polymers to other polymers or to other materials or the painting of polymer surfaces, adhesion is a recurring and difficult problem for all industries that use polymer materials as key components in their products. Designers often must select specially formulated and expensive polymeric materials to ensure satisfactory adhesion (albeit, even these materials often require surface preparation). In some cases, whole design concepts must be abandoned due to the prohibitive cost of the required polymer or the failure of crucial adhesive bonds. Gas plasma processes are the great equalizer making all polymers and elastomers equally paintable eliminating paint adhesion or adhesion permanency as an issue in the selection of a given polymer. Gas plasma glow discharge treatment typically allows all polymers to achieve paint adhesion strength exceeding the bulk strength of the substrate or paint. Failures do not occur at the paint film / substrate interface but within the bulk of either the paint film or the substrate. And plasma is workplace and environmentally friendly providing significant cost savings over any other means of volume surface preparation.

However, plasma processing alone is not a panacea for all problems. As seen in the data presented herein there must be a collaboration or at minimum a cooperation between material and paint manufacturers to marry systems that will provide the highest performance. It is unlikely that the same plasma process that improves paint adhesion will alter the permeability of the substrate to reduce an its inherent sensitivity to specific solvents that results in blistering. Thus, the cognizant engineers at the manufacturing line must insist that the paint supplier provide paint properly formulated to the sensitivities of the substrate, or select a substrate with appropriate resistance to solvation by the paint system solvents.

The data presented shows that outstanding paint adhesion to TPO fascia is readily achieved with plasma pretreatment. However, one system failed to meet specifications because of microblistering after humidity soak. Despite the presence of blisters these same specimens met all adhesion tests. Microscopic and chemical analysis prove these blisters not to occur at the paint to substrate interface but, to occur within the bulk of the substrate. Thus, the failure was not one caused by lack of plasma treatment effectiveness, but a limitation of the substrate or solvent package of the paint or a mismatch of the two.

Gas plasma is an effective method to obtain optimum adhesion performance of painted plastic. Equipment is available that can cost effectively treat large moldings such as fascia, instrument panel, or body cladding. Equipment that is compatible with the manufacturing lines commonly employed in the automotive manufacturing environment. The effluents from the plasma process are minimal and usually

non-hazardous. The effluent typically does not require any treatment prior to release to the environment. Because of the energy efficiency of plasma processes in combination with their effectiveness, workplace cleanliness, safety, and environmental friendliness, the cost effectiveness of the total solution is unbeatable. It is 21st Century chemistry available today.

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