Commercial Plasma Processes
For Enhanced Paintability of TPO Auto Fascia

By: Kaplan, Stephen L., Rose, Peter W., Sorlien, Per Harald, and Styrmo, Odd

ABSTRACT

Surface treatment of plastics via plasma processing has long been known as an effective method to enhance adhesive bonding. Because plasma equipment has been of modest size, plasma technology has been limited to either academic interest or treatment of parts of modest size. Thermoplastic resins, and especially thermoplastic polyolefins (TPO), have become the material of choice for exterior automotive applications, creating a need for large scale plasma equipment.

The gas plasma treatment is an advanced technology that is dry, clean, cost effective and environmentally safe. It increases the surface energy of the substrate and provides reactive groups, resulting in increased bonding strength between the substrate and coating. This technology is replacing more traditional methods, such as wet chemical, flame, abrasion, corona discharge, acid etching and adhesion promotion primers and coatings.

For the treatment of plastics, the plasma is a low pressure or vacuum process so the temperature is only slightly elevated above ambient, preventing thermal distortion of the molded article. Creating a uniform plasma within a large vacuum chamber has been a technical challenge. In recent years, the technical obstacles have been overcome and large plasma systems have been commercially available. With the introduction of equipment sufficiently large to permit treatment of large plastic moldings, such as automobile bumpers, plasma has emerged from the laboratory. Gas plasma equipment has been installed in production facilities and is in operation for the pre-treatment of plastic automotive parts prior to painting.

INTRODUCTION

Plasma is often described as the fourth state of matter. By supplying energy, a solid can be converted into a liquid and the liquid into a gas. As additional energy is applied to the gas, a plasma state is achieved. Exciting a gas to the plasma state liberates electrons and creates a variety of active species. If a polymeric material is placed within the plasma, the surface of the polymer will be modified. The type of modification will be dependent on the nature of the plasma gas. For example, in an oxygen plasma a variety of oxygen containing species, such as hydroxyl, carbonyl and carboxylic groups will be established on the polymer's surface. The modification is typically a few molecular layers deep, thus the bulk properties of the polymer is unaffected.

Plasma processes have been used commercially for several decades to enhance adhesive bond strengths for electronic connectors and medical assemblies, as well as for the modification of the wetting characteristics of medical devices such as catheters and culture trays. Over the past several years, large scale plasma equipment have become available. One driving force for the development of large scale equipment has been the increasing use of thermoplastic olefins (TPO) as a material of choice for automotive bumpers and claddings. While TPO possesses the mechanical properties desired for automotive applications they can not be painted without surface modification. The most common pre-treatment prior to painting has been either flaming (Europe) or the application of an adhesion promoter (North America). Flaming, while effective to a degree, is not practical with more sophisticated designs which have recesses, louvers, or deep accent grooves. Adhesion promoters in general provide a higher level of effectiveness than flame treatment. This is especially true if the part has contours or louvers. Since solvent based adhesion promoters contain a large proportion of volatile organic compounds (VOCs) they have been identified as a destructive environmental agent. Water borne adhesion promoters have not yet proven to be as effective and are more costly. In Europe, a combination of flaming and adhesion promoter has come into use enhancing the effect of either used separately. More recently, high VOC uv primers have also been placed into production.

In laboratory testing on molded plaques, plasma treatment in oxygen containing plasmas has proven to out perform all commercial pre-treatment processes or combinations of processes. Plasma treatment provides improved paint adhesion with resistance to all automotive performance tests such as humidity aging, thermal shock, chip resistance, and fuel soak. Paint adhesion has been shown to exceed the strength of the TPO base material, which has never been demonstrated with any other pre-treatment process. Translation of these laboratory results to full-size automotive bumpers in production worthy plasma equipment has been a desire of the automotive industry. This paper discusses results on one such system.

PLASMA PROCESSES

The parts to be treated are placed into a vacuum chamber and the chamber pressure is reduced, typically to 0.1 mbar. A process gas containing oxygen is introduced to the chamber and the chamber pressure stabilized at a pressure of

0.5- 1.0 mbar. In the work presented herein, high frequency (13.56 MHz) rf energy is used to create the plasma. The rf energy dissociates the gas, creating a plasma characterized by a distinctive glow. The color of the discharge is unique for each gas combination, thereby providing convenient spectroscopic quality control measures, if desired. Since the process is conducted at reduced pressures, the bulk temperature of the gas is near ambient temperature. This process is thus also known as cold gas plasma, glow discharge, or cold gas glow discharge. The electrons or ions created in the plasma bombard the polymer's surface, abstracting atoms or breaking bonds creating free radicals. These free radicals are unstable and seek to satisfy a more stable state by reacting with free radicals or groups within the plasma gas, establishing new moieties on the surface of the polymer. In this manner the polymer surface can be molecularly re-engineered to provide functional groups that enhance attraction of the paint and provide reactive sites that will result in covalent chemical bonding of the paint to the polymer. Covalent bonds greatly enhance the permanency and the adhesive tenacity of the paint to the polymer. In most applications the gas or gases used are innocuous, requiring no exhaust gas treatment in order to be in full compliance with "clean air legislation". It is a work place safe and environmentally friendly process.

A gas can be excited to a plasma with almost any type of electrical or thermal energy, but all plasma equipment is not the same and all plasmas are not equal. The work presented herein was performed to investigate the uniformity of the system developed and commercially offered to the automotive industry by HIMONT Plasma Science for the treatment of large automotive moldings.

EXPERIMENTAL DESIGN

Plasma processing was conducted in a large commercial batch system manufactured by HIMONT Plasma Science (Figure 1). The interior dimensions of the work area is approximately 1.73 x 0.76 x 1.02 meters (width x height x depth) for a total working volume of 1.34 cubic meters. The plasma is created by excitation with radio frequency energy at 13.56 MHz with a total power input capacity of 2500 watts.

Two different bumper grade thermoplastic olefin (TPO) formulations (A&B) supplied by Statoil were evaluated. A commercial bumper was used as a test fixture to which test specimens of the same formulation were affixed using double sided adhesive tape. In this manner, the influence of loading effects are eliminated. Two separate series of trials were conducted; molded plaques and cut plaques from molded bumpers. In the first set of trials, molded plaques were affixed to the bumper in a predetermined pattern to evaluate the uniformity of plasma along the length and height of the bumper. Replicate cycles were conducted with each material to determine reproducibility. Thus, this test elucidated both the uniformity of the plasma treatment within the chamber as well as the reproducibility from cycle to cycle. In a second series of trials, bumpers were cut into test plaques and then fixed on their matching locations on the bumper test fixture. In this manner, variation of plasma effectiveness because of molding variations could be evaluated. A 90^{o} T-peel strength test was used for evaluation. After plasma treatment, the treated plaques, approximately 100 x130 x 3 millimeters, were coated with a peelable water-borne coating (Gramos Chemical International SL15/C) to protect the parts from contamination during transport from California, where the plasma treatment was performed, to Europe, where the peel test specimens were prepared and tested. All peel test specimens were prepared into test specimens within a week of plasma treatment, but no sooner than 72 hours.

The plaques were painted with a two component solvent based urethane paint (Beckryflex TC-135/TV-130) onto which a plasma treated polyester scrim cloth was placed. A second coat of paint was brushed over the scrim. The samples were then cured for 50 minutes at $920^{o}C$ to form a composite structure. After further room temperature curing of 24 hours the scrim was scored to provide three strips of l5mm width on each plaque for peel testing. Testing was done in a commercial universal tester employing electronic load cells equipped with a traversing fixtures to assure a 90^{o} **pull along a 75 mm length of peel**.

RESULTS

Table I
Formulation A Molded Plaques Plasma Treated 90^{0} Peel Strength vs. Position

Position	**Trial 1**	**Trial 2**
	Peel Strength N/15 mm	Peel Strength N/15 mm
left wing (A)	32 ± 2	28± 2
left front (E)	29 ± 3	32 ± 2
left center (1)	28± 2	31.5 ± 4
right center (K)	33 ± 2	38 ± 5
right front (O)	28± 2	*
right wing (R)	38± 2	35 ± 3
* value deleted since it was obviously contaminated after treatment, but before specimen preparation.		

Table II
Formulation B
Molded Plaques
Plasma Treated
90^0 Peel Strength vs. Position

Position	Trial 1	Trial 2
	Peel Strength N/15 mm	Peel Strength N/15 mm
left wing (B)	32 ± 1	36 ± 2
top left (D)	32 ± 2	29 ± 5
top center (H)	31 ± 4	36 ± 2
top center (L)	35.5 ± 5	31 ± 2
top right (N)	32 ± 8	34 ± 8
right wing (T)	34 ± 3	32 ± 3

Table III
Formulation A
Plaques Cut From Plasma treated Molded A Bumper
90^o Peel Strength vs. Position

Position	**N/15mm**		**Position**	**N/15mm**
A	23		K	22.5
B	20		L	22.5
C	17.5		M	22
D	24		N	22
E	23		O	20
F	24		P	25
G	22		Q	22
H	26		R	20
I	25			
J	24			

Table IV
Formulation B Plaques Cut From Plasma Treated Molded Bumper
90^0 Peel Strength vs. Position

Position	N/15mm		Position	N/15mm
A	27		K	32
B	29.5		L	25.5
C	29.5		M	22
D	24		N	30
E	23		O	20
F	32		P	29
G	24		Q	32
H	32.5		R	32
I	19.5		S	30
J	30.5		T	29
			U	22.5

Table V
Molded Plaques vs. Molded Bumper Plasma Treated
90^0 Peel Strength N/15mm Formulation

	A	**B**	**A**	**B**
	Plaque	**Plaque**	**Bumper**	**Bumper**
Average	32.1	33.8	22.6	29.5
StDev	3.9	2.2	2.2	3.2
%	12.1	6.7	9.9	11.0

DISCUSSION

To determine or characterize plasma equipment variations, plaques were injection molded in a one cavity single gated mold. Control plaques, i.e. no pretreatment prior to painting, provides a 90^0 peel value generally less than 5 N/15 mm. Peel with adhesion failure values above 28 N/15 mm generally represents cohesive failure within the substrate and is witnessed by the drawing of polypropylene fibers from the substrate and retained TPO on the scrim.

Plasma treatment provided from 500 to 850% improvement in peel strength versus the control (Tables I & II and Figure II). More importantly, in most instances the failure mechanism shifted from adhesive between the paint layer and the substrate to cohesive within the substrate. A 5% to 12% variation was observed within a trial set, dependent on the material. The lower modulus material exhibited the higher variation within a test set. No pattern could be discerned with respect to position of the plaques in the plasma treatment. In the replicate sets of molded plaque trials, the reproducibility was 5% and 1% for the two TPO formulations respectively. Since all failures were cohesive, any measured variation could as easily be attributed to variations in surface morphology of the molded plaque or to the test procedure itself. Further, since the equipment was not changed in any way from one test to another, one must conclude that the trial sets with the least variation must represent the worst case for the equipment. Thus, uniformity within the plasma chamber was shown to be 95% or higher.

The second set of trials were conducted with test plaques cut from actual production bumpers. The plaques were adhered via double sided pressure sensitive tape to a molded fascia of the same material in the same relative position for treating. Eighteen to twenty-one positions were examined across the face of each bumper. The number of test pieces differed due to design limitations of the molding. Lower peel strengths were obtained for specimens cut from molded bumpers than from molded plaques. This was most significant for Formulation A (Table III), where the peel test was found to be 22 N/15mm, a 30% decrease, albeit the failure mode was cohesive, the same as it was for molded plaques. Formulation B (Table IV) exhibited only a 13% decrease. Variation dependence on position was similar for both materials, 9.9 and 11.0% respectively (Figures II & III). While excellent results were generally obtained, it was apparent that areas were affected by molding conditions, mold design, and/or part handling during specimen preparation.

Figure II.

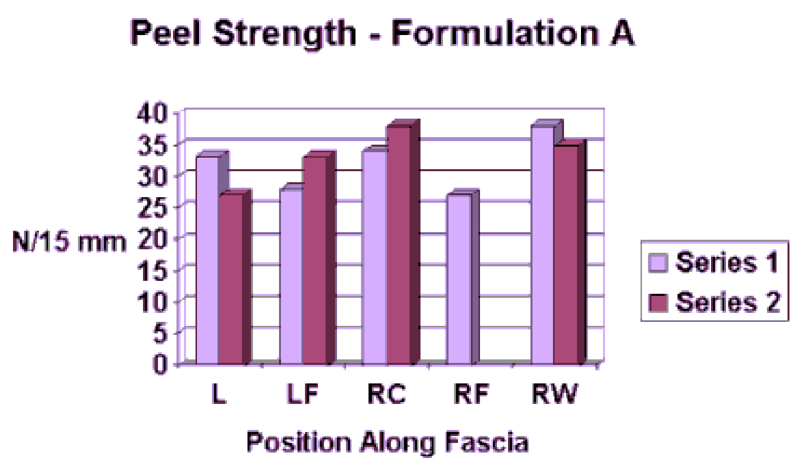
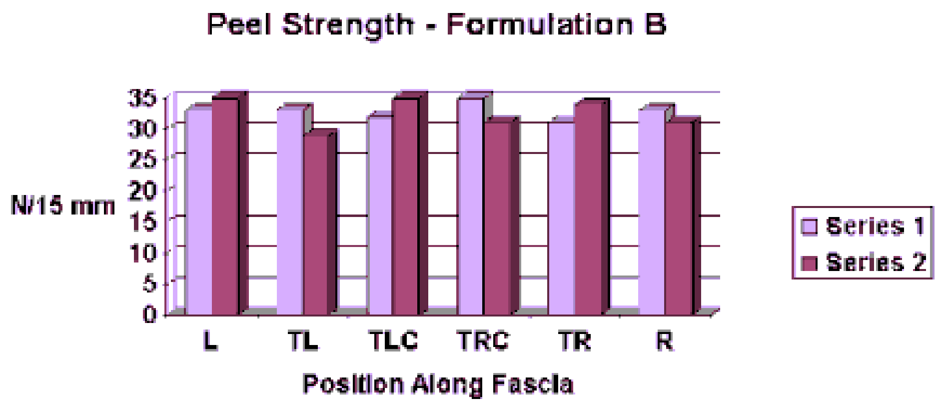


Figure III.



CONCLUSIONS

HIMONT Plasma Science equipment provides a high level of paint adhesion on full sized bumpers treated in production sized equipment. Adhesion was determined by imbedding a reinforcing scrim into the paint layer creating a composite, and then testing in a special fixture, the force necessary to separate the paint/scrim from the substrate in a 90^0 T-peel mode. With plasma treatment an adhesion improvement of 500 to over 800 % results with, in most cases, a change in failure mode to cohesive in the substrate. Uniformity within the large plasma chamber and the reproducibility from run-to-run was found to be 95% or better.

Molding conditions may have affected the level, and potentially the uniformity of the T-peel strength. Handling and contamination could also be involved. Further studies are required to determine the root cause. Differences, sometimes very significant, were observed between the level of adhesion obtained in panels cut from bumpers versus the level of adhesion exhibited in molded plaques treated, painted and tested in identical manners. Such effects must be due to changes to the surface morphology resulting in a reduction of the bulk strength of the material at the surface, not a reduction in the efficacy of the plasma treatment. Further studies need to be conducted to examine this area in more detail.

The data suggest that molding parameters and material variations will have the most predominant effect on variation from point to point on a given molding. The plasma equipment and the process parameters employed in this study are consistent with equipment necessary for commercial production and provides strong economic justification versus the use of adhesion promoters. Because plasma is a three dimensional process, at least in this equipment, plasma also offers the advantages of complete design freedom, a major limitation with flaming.

Plasma offers a cost effective means of treating large TPO moldings to provide paint endurance to the strictest of specifications. The process is not only extremely effective, but environmentally friendly and workplace safe. The process is self contained, eliminating weather or environmental influences and it is microprocessor controlled, allowing operation with unskilled labor. This combination of outstanding results, cost effectiveness, worker safety, reproducibility and environmental friendliness makes plasma surface treatment an attractive technology to the automotive industry.