ULTRAVIOLET LIGHT AS AN EFFECTIVE CLEANING, AND SURFACE PREPARATION PROCESS FOR ADHESIVE BONDING AND PAINTING OF POLYMERS, COMPOSITES AND METALS

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ABSTRACT

Contemporary vehicles utilize a mix of materials in their construction consisting of metals, plastics, and composites. These materials must possess suitable surface properties to achieve desired performance when these parts are adhesively bonding or painted for field service. Surface preparation methods now in place oftentimes use solvents or caustics, an increasingly unacceptable approach in an era of mounting environmental regulations. New methods of surface preparation are called for that are environmentally benign and economically feasible while meeting the stringent quality standards of the automotive industry. The use of energetic ultraviolet light is emerging as a promising technology to compete with the old methods of surface preparation. This paper reports the utility of using energetic UV light to generate appropriate surface chemical composition on plastics, composites, and metals for subsequent painting or adhesive bonding operations. UV treatments have the potential to replace the old methods of treating assorted materials used in the automotive industry in an environmentally responsible and cost-effective manner.

BACKGROUND

The worldwide production of passenger and commercial vehicles in 2000 approached 60 million units [1]. The need for increased fuel efficiency has resulted in greater use of plastics and composites alongside traditional metallic materials such as steel and aluminum. Increasingly, the cars of today are composed of a wide variety of raw materials that are required to have suitable surface properties in order to be effectively painted or bonded.

The surface preparation of the adherend whether for adhesive bonding or painting requires careful removal of labile organic compounds as well as the addition of chemical functionalities to the adherend surface that can interact strongly with the adhesive. Manufactured polymer, polymer composite and metallic surfaces always contain undesirable compounds or additives that reduce or limit adhesion to the adhesive or paint film. Mechanical surface treatments (e.g. abrasion) are currently used as surface preparation techniques but are time consuming, labor intensive and can damage the polymer composite adherend surface. Furthermore, organic solvents used for surface preparation also are being eliminated in order to reduce volatile organic compound (VOC) emissions[2]. It is desirable to have a surface treatment method that can both clean a surface as well as create a beneficial chemistry for optimum adhesive bonding of polymer composites[3]. One environmentally acceptable alternative under study is the use of energetic ultraviolet light to clean and prepare metallic and non-metallic surfaces for painting or bonding.

Ultraviolet light in the 180-280 nm wavelength is known to interact with atmospheric oxygen and ozone to produce nascent oxygen, which is a strong oxidizing agent. UV photons can induce the formation and destruction of ozone by the reaction pathway illustrated in Figure 1.

$$O_2 + UV_{185nm} \rightarrow 2O$$
$$O_2 + O \rightarrow O_3$$
$$O_3 + UV_{257nm} \rightarrow O_2 + O$$

Figure 1. The reactions of oxygen in the presence of UV irradiation.

Table 1. UV and Molecular Bond Energies.

UV Wavelength (nm)	Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
365	328	C-C	347.7
253.7	472	C=C	607.0
184.9	647	C-H	412.4
		O-O	138.9
		O=O	490.4
		O-H	462.8

The quantum yield for ozone formation is approximately 2, meaning that for every photon absorbed, two ozone molecules are formed. Ozone absorption of the 253.7 nm light is responsible for its photodecomposition back to atomic oxygen and molecular oxygen. As shown in Table 1, UV-A radiation, 320-380 nm, has sufficient energy to cleave carbon-carbon single bonds. As the wavelength decreases, the highly energetic UV-C region, 180 nm to 280 nm, can cause the dissociation of carbon-hydrogen bonds, single and double oxygen bonds, and oxygen-hydrogen bonds. The twin mechanism of molecular bond cleavage with the simultaneous production of an oxygenating atmosphere provides an effective means to decompose and oxidize contaminants on metallic and nonmetallic surfaces.

UV oxidation and surface activation has the potential for creating a low-cost, fast, robust method for surface preparation of polymer, polymer composite and metallic surfaces for adhesive bonding. The UV oxidation and surface activation process can be: *i)* capable of treating any polymer or metallic surface; *ii)* adaptable to treat flat or convoluted external surfaces; *iii)* inexpensive, with short cycle times; *iv)* is environmentally benign since it does not emit VOC's; and *v)* tailorable for optimum mechanical performance of adhesive joints (and coatings). We report the use of UV irradiation to clean and prepare assorted materials of relevance to the automotive industry for subsequent bonding or painting operations. Steel, aluminum, polymer, and composite surfaces were UV treated and evaluated for changes in wettability or adhesive bond strength. These results support the use of UV irradiation as an environmentally acceptable alternative for surface preparation of a variety of materials used in the automotive industry.

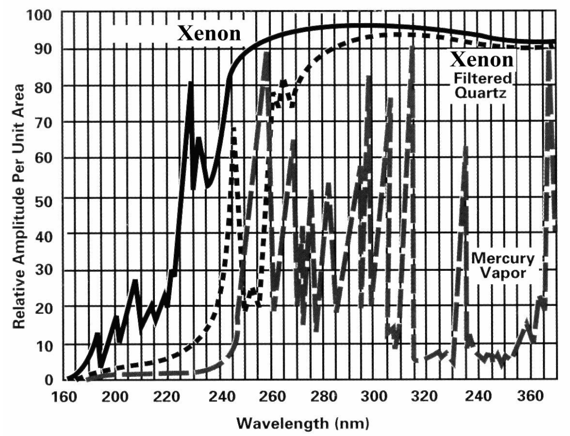

Figure 2 Typical UV spectral output from pulsed lamp.

EXPERIMENTAL

Both pulsed and continuous UV lamps were used to conduct the surface cleaning. The typical output of a xenon filled, pulsed UV lamp is shown in Figure 2. One of the advantages of using pulsed UV lamps is the flexibility in controlling the exposure time and intensity of the radiation, especially in the treatment of polymers that are sensitive to temperature. Typical pulsed UV lamps have pulse widths of 100-200 μs and pulse frequencies ranging from 3-120 Hz. Thus the emission of UV radiation is accomplished in short bursts with relatively long dark periods during which heat transfer and chemical reactions can occur. As the operating frequency is decreased, the energy/pulse can be increased along with a larger cooling period between pulses to allow dissipation of heat from the irradiated surface. Table 2 summarizes the emission parameters of the UV lamps used in this study.

Table 2 UV Lamp Emission Parameters

Lamp	Type	Spectral Output	Power	Ozone
RC-500B	Pulse-120Hz	185 mm to Far IR	12.5 W/pulse	Yes
RC-740B	Pulse-10 Hz	185 mm to Far IR	150 W/pulse	Yes
F600	Continuous	200 mm to Far IR	6 kW	No

The effectiveness of the UV treatment was evaluated by measuring the water contact angle with the substrate immediately following UV treatment. Ten droplets were measured using a Rame-Hart goniometer apparatus for each treated substrate. The efficacy of UV treatments to promote adhesion was assessed with a button pull-off test. The PATTI [4] instrument and method conforms to ASTM D4541, "*Pull-off strength of coatings using portable adhesion testers*".

RESULTS AND DISCUSSION

Metallic Substrates. Alternative eco-friendly strategies are being sought in the manufacturing of cast aluminum wheels which now undergo a series of caustic washes in preparation for final finishing and

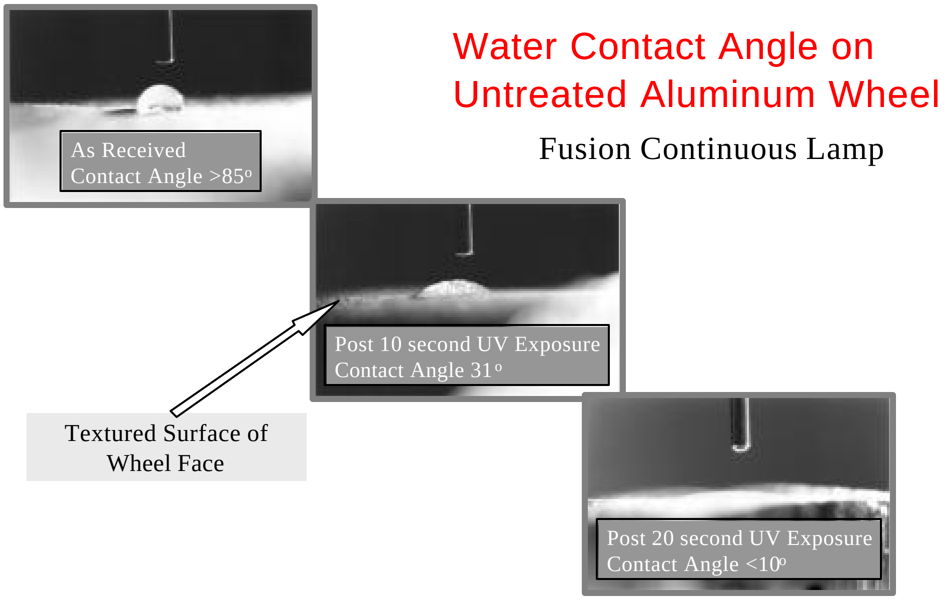

Figure 3. The effect of UV treatment on water wettability on aluminum

painting. UV irradiation for short periods produced significant changes in wettability on aluminum wheels. Following two-10 second treatments to UV light the water contact angle decreased from 85° to less than 10° as presented in the photographs of Figure 3.

In another study, metallic substrates were intentionally dosed with mold release compounds to produce a set of samples representative of a highly contaminated surface. Two aluminum and one steel substrate were evaluated. Small, laboratory size test panels were acquired without any corrosion or protective coatings and were used without further preparation. Aluminum 3105 H24 is a general-purpose alloy and is used in a wide range of products in the automotive sector. Aluminum 2024 T3 is a high strength alloy that is more typically employed in aerospace applications. The third metal evaluated consisted of low carbon, cold rolled steel, found in general sheet metal applications. The results of this study are summarized in Figure 4. The application of the mold release agents increased the water contact angle relative to the as-received condition with the exception of the Safety Lube compound. A two minute dose of UV was effective in all cases of greatly reducing the water contact angle.

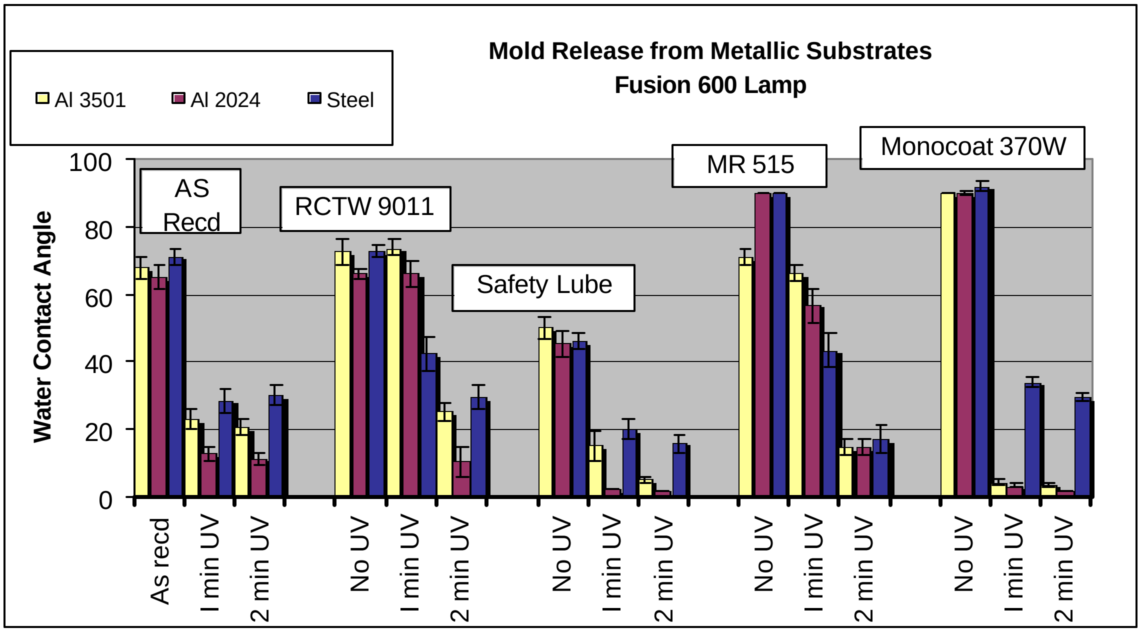

Figure 4. Water contact angle of metal surfaces following removal of mold release compounds by UV surface cleaning.

UV irradiation may also be used to surface clean metals prior to painting. In one study, 2020-T3 aluminum was surface cleaned using UV irradiation. In one set of experiments, an aluminum test panel was treated with a continous emission lamp, and anther test panel was treated with a pulsed lamp with supplemental ozone introduced above the part surface. The UV treated panels were powder coated with a an acrylic clear coat and then conditioned at 50°C-95%RH for 140 days. For comparison, an aluminum test specimen that was prepared by phosphoric acid anodization was included. As shown in Figure 5, the panels surface treated by UV irradiation were indistguishable from the phosphoric acid anadized specimen. No surface blemishes, defect, or blemishes were visible following the humidity conditioning of the aluminum panels.

Surface Treatment of Polymers. A large variety of polymeric substrates have been investigated, but a few select examples will be presented here. UV treated polymer substrates exhibited markedly improved PATTI pull-off strengths following UV treatment. A two minute UV treatment resulted in a 300% improvement in tensile adhesion bond strength for TPO (Figure 6). Similar improvements in pull-off strengths were found for UV treated polyimide (Figure 7). The enhanced bond strengths result from improved wetting and an increase in surface oxygen concentration [5].

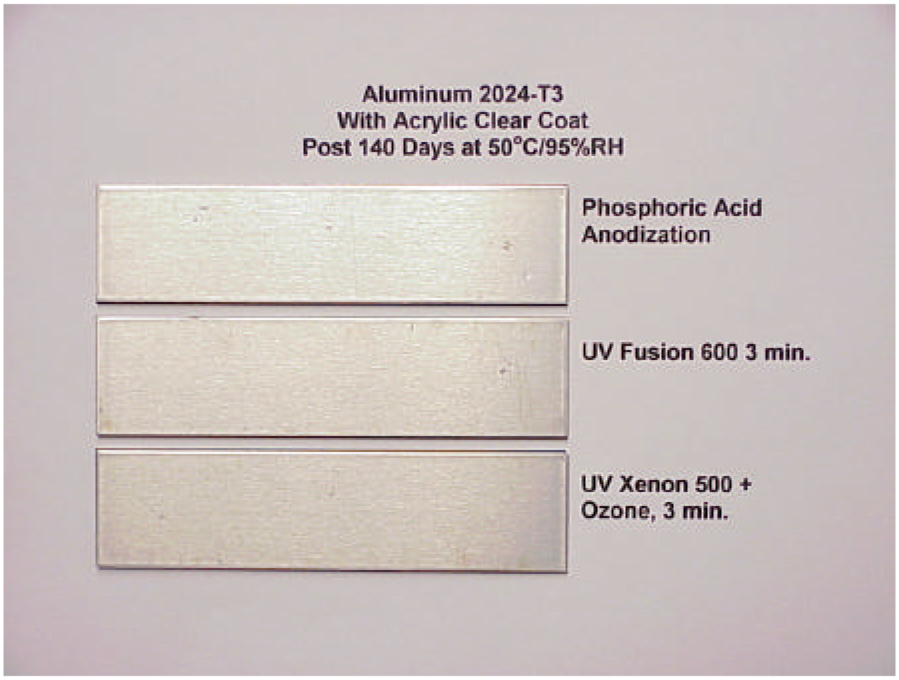

Figure 5. Painted 2024-T3 surface treated with UV or phosphoric acid anodization following humidity conditioning.

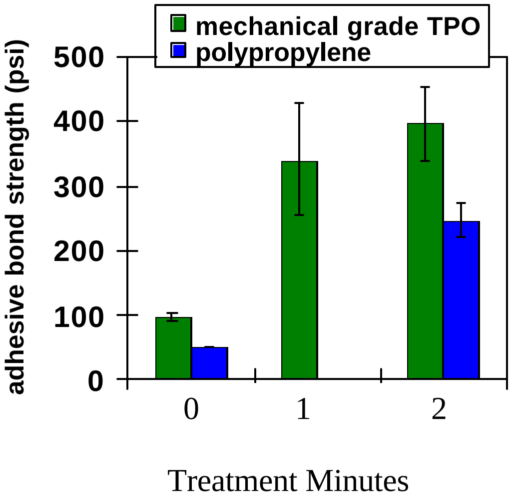

Figure 6. PATTI test adhesive bond strength following UV treatment of polymer surface.

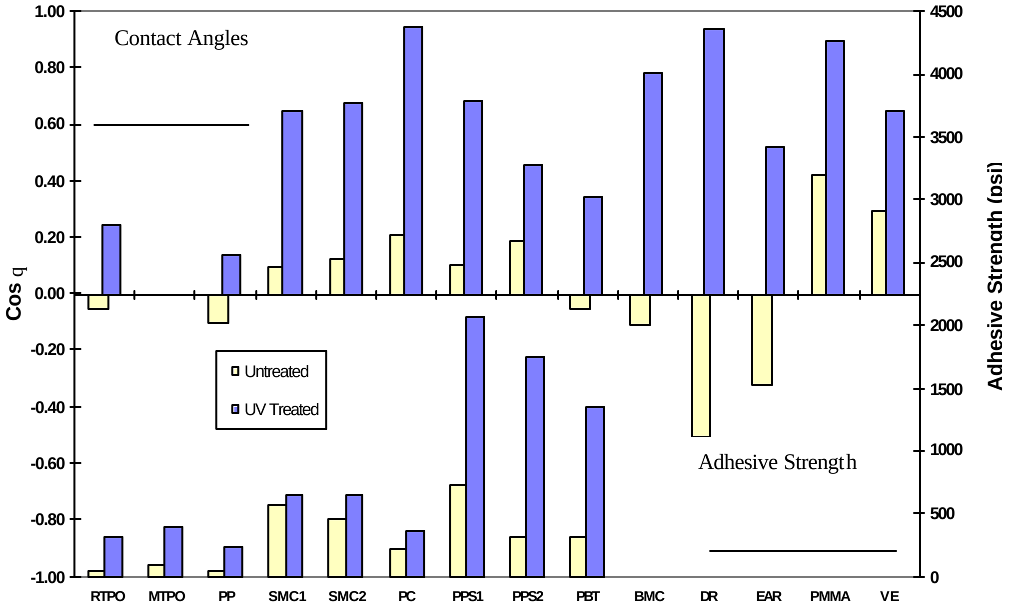

Figure 7. Summary of changes in wettability and adhesive strength for: Reaction grade thermoplastic polyolefin (RTPO), Mechanical grade TPO (MTPO), Polypropylene (PP), Sheet molding compound (SMC1, SMC2), Polycarbonate (PC), Polyphenylene sulphide (PPS1, PPS2), Polybutylene terephthalate (PBT), Bulk Molding Compound (BMC), Diene Rubber (DR), Ethylene Acrylate Rubber (EAR), Polymethyl methacrylate (PMMA) and Vinyl ester (VE)

CONCLUSIONS

The use of UV irradiation was demonstrated to effectively remove unwanted surface contaminants and to create favorable surface chemistry to promote wet-out for improved adhesion. UV irradiation was used to remove mold release compounds and to prepare metallic substrates for painting. For polymers, UV irradiation was shown to be an effective process to increase adhesive bond strengths. Solvents and VOC's generated using existing methods of surface cleaning could be diminished by irradiating metals, plastics and composites with high energy UV light. UV radiation in the 185-300nm region was found to be necessary to treat polymers and an increase in the supplemental ozone concentration enhances the rate and extent of surface oxidation. Temperature is also a critical control parameter and excessive substrate temperature is believed to cause surface restructuring or rotation of the polar surface groups into the bulk. Treatment of polymers by adjusting the UV lamp pulse rates and intermittent exposure schemes can limit the surface temperature of the polymer. Experiments performed on a wide variety of materials have shown that UV treatment can functionalize the surface, improve wettability and adhesive strength. The parameters that need to be understood in order to control the surface treatment process are: i) UV lamp output (wavelength and irradiance), ii) ozone concentration and iii) temperature. Future work is planned to quantify the effect of these process conditions on the extent of surface treatment and evolution of surface properties.

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