

Advances in Adhesion with CO₂-based Atmospheric Plasma Surface Modification

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Abstract

The use of gas and/or liquid-phase carbon dioxide (CO₂) with atmospheric plasma discharge surface pretreatment technology can remove micron and submicron particulates and hydrocarbon-based contaminations on plastics and metals. The cleaning process is based upon the expansion of either liquid or gaseous carbon dioxide through an orifice. The paper provides an understanding of the basic removal mechanism and provides experimental evidence of remarkable adhesion improvements relative to a broad range of applications in electrical, medical, and automotive manufacturing communities.

Introduction

To compete in the global marketplace, an appropriate competitive response by a manufacturer is a three-pronged strategy. The first employs improved training, consolidated processes, improved processes and the elimination of waste. The second integrates automation, and hybridizes/implements cellularity. The third attempts to eliminate, or at least reduce, regulated activities by external forces. Clean manufacturing solutions make more efficient use of people, materials, energy and other resources to produce more reliable and competitive products with less waste. One such clean manufacturing solutions employs clean surface preparation technologies for bonding, such as CO₂ surface cleaning and modification technology. Conventional surface preparation techniques, such as batch solvent cleaning, can be ineffective in microscopic particle removal, typically requires rinsing and drying for aqueous cleaning, and generates VOCs which requires permitting. Manual solvent wiping typically has a smearing effect on surface contamination, is equally ineffective for removing microscopic particles, generates VOCs and exposes a workforce to nuisance odors. Vacuum plasmas are typically performed off-line for bonding, provide low level cleaning, and are ineffective in removing particle contamination.

CO₂ surface treatment technology has only recently been explored as a potential robust method for producing consistent bonding surfaces for higher technology applications such as aeronautic devices,

optical devices, sensors, integrated circuits, disk drives, medical devices and other applications. Competing with CO₂ surface pretreatment are a diversity of “combinational” dry surface treatment schemes which can be considered, including:

- § Selective Spray
- § Immersion Solvent
- § Extraction Solvent
- § Atmospheric Plasma
- § Low Pressure (Vacuum) Plasma
- § UV-Ozone Treatment
- § Microabrasive Snow

A major advantage of dry CO₂ surface pretreatment approach is that CO₂ itself is a byproduct of industrial and natural processes such as refineries, CaCO₃, wells and bakeries, and is recyclable and renewable.

Among potential pretreatment solvents, Table 1 details the ozone depleting potential (ODP), OSHA permissible exposure limit (PEL), and VOC emission of each:

Table 1. Solvent Health/Safety Chart

Solvent	ODP	PEL	VOC
Carbon Dioxide	None	5,000ppm	No
Perchloroethylene	~0	25ppm	Yes
Carbon Tetrachloride	1.10	2ppm	Yes
Methylene Chloride	~0	500ppm	Yes
Trichloroethylene	~0	50ppm	Yes
1,1,1-Trichloroethane	0.15	350ppm	Yes
n-Propyl Bromide (nPB)	~0	100ppm	Yes

The key physical property of carbon dioxide is its excellent solvent properties (see Table 2) for many nonpolar organic compounds. Like most solvents, the solvent properties of CO₂ improve as the pressure and temperature increase. In cleaning, we rely upon the liquid phase solvent properties. It is important to note that thermodynamically, liquid carbon dioxide is unstable at room temperature and atmospheric pressure but this thermodynamic condition only refers to equilibrium states, not non-equilibrium states.

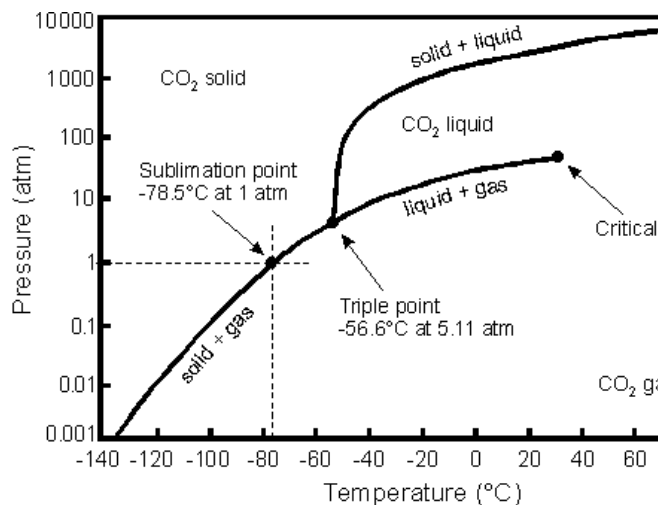
Table 2. CO2 Solvent Properties

	Carbon Dioxide			Acetone
	Solid	Liquid ¹	SCF ²	
Density (g/ml)	1.6	0.8	0.5	0.8
Viscosity (mN-s/m ²)	0	0.07	0.03	0.32
Surface Tension (dynes/cm)	0.5-10	5	0	24
Solubility (MPa ^{1/2})	22	22	14	20

1. 20C, 900psi (Liquid CO₂ (SCF)) **2. 35C, 1500 psi** (Superficial Fluid CO₂ (SCF))

The carbon dioxide phase diagram (Figure 1) has 3 phases -- gaseous, liquid, and solid. The triple point (pressure 5.1 atm., temperature - 56.7C) is defined as the temperature and pressure where three phases (gas, liquid and solid) can exist simultaneously in thermodynamic equilibrium. Above the critical point (pressure 72.8 atm., temperature 31.1C) the liquid and gas phase cannot exist as separate phases. This region, known as the superfluid or supercritical phase, has properties indistinguishable from the liquid and gas phases.

Figure 1. Carbon Dioxide Phase Diagram



Another feature is the solid-gas phase boundary. Physically, this boundary implies that the gas and solid can co-exist and transform back and forth without the presence of liquid as an intermediate

phase. A solid evaporating directly into the gas is called sublimation. At normal atmospheric pressure and temperature, the stable carbon dioxide phase is gas. This means that the final product is gaseous carbon dioxide and this final state is independent of the initial phase, cleaning process, or mechanism. Any solid CO₂ will just sublime. With the CO₂ present as a gas, the contamination can be separated from the exhaust stream and the CO₂ is available for venting outside or recovery.

From the above, we see that surface pretreatment via “snow” cleaning can be done with either a liquid or gas CO₂ source. Each feed would have its advantages and disadvantages. Gas fed systems would tend to be cleaner (easier to filter a gas than a liquid), have less heavy hydrocarbon contamination, and have less consumption per unit time. Liquid-fed systems can most likely produce more snow, allow for faster cleaning, but at a higher consumption rate. Both phases do not produce cleaning agent waste, such as spent solvent, rinse water, filters, wipers, etc.).

Compatibility with bonding surfaces is an advantage of using CO₂ in this study, with metals, composites, polymers, glass, ceramics, organic/metallized films, textiles and coatings all useful for contamination removal using solid, liquid or supercritical phase CO₂.

Particle vs. Organic Contamination

Creation of CO₂ cleaning “snow” is typically accomplished by delivering several expansions of CO₂ after pressure drops from 800 psi to 80- psi (using either gaseous or liquid CO₂) through treatment device orifices, leading to a conversion to solid dry ice. Collisions between the impinging dry ice particles and surface particulates give rise to momentum transfer and particle removal. The removed particles are then carried away by the gas flow. While effective in removing particle contamination, CO₂ cleaning processes are less effective in completely removing surface organics at the same processing speed.

The organic removal mechanism involves the presence of liquid CO₂ (which is an excellent solvent for hydrocarbons and other nonpolar substances). During the short impact time, high stresses exist at the snow - surface interface and the pressure can easily exceed the dry ice yield stress and triple point pressure. The dry ice particle liquefies and acts as a solvent while in contact with the surface. When the particle starts to rebound off the surface, the interfacial pressures decrease and the dry ice particle

re-solidifies, removing the contamination. Although effective, this process requires considerable dwell time for even light contamination levels. Also, it has been reported in literature that the snow cleaning process currently does add some contamination to parts being cleaned - seen on surfaces as very small, thin droplets, most of which are less than 0.5 microns in diameter. The droplets are not easily seen with a light microscope because they are small and widely dispersed on the surface, however Nomarski polarization is helpful.

Atmospheric Plasma

Among the “combinational” dry surface treatment schemes mentioned above, atmospheric plasma regimes present an intriguingly cost-effective technology to pair with CO₂ phase cleaning technologies to clean both particle and organic contaminations at attractive processing speeds because of their low capital and operating expense, in addition to their high density surface reaction capabilities.

The so-called “dielectric barrier” discharge (DBD) atmospheric plasmas utilize a dielectric covering over one or both of the electrodes of which one is typically radio-frequency (rf) driven while the other is grounded. The purpose of the dielectric is to rapidly terminate the arcs that form in the potential field between the two electrodes. The discharge consists of a multitude of rapidly forming and equally rapidly terminated arcs that fill the volume between the electrodes. Materials processing is done by passing the substrate material within the discharge region between the electrodes.

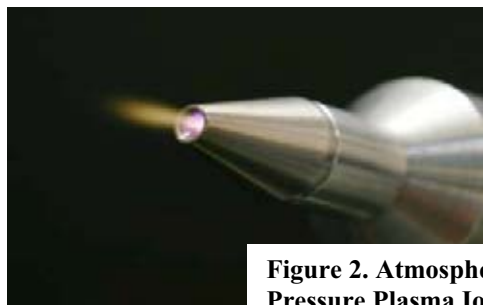


Figure 2. Atmospheric Pressure Plasma Ion Bombardment Device

Atmospheric pressure plasma ion bombardment devices (Figure 2) are true non-thermal plasma systems which deliver a stream of high velocity ions to substrate surfaces. The source discharge produces a stable, homogeneous and uniform plasma stream using air or various gases under pressure, passing between electrodes which are well upstream of the discharge orifice. Hence, discharge arcs forming the plasma are contained within the device and only high energy ions discharge to the material surface at atmospheric pressure. The discharge is free of filaments, streamers, and arcing. The gas temperature of the discharge is typically between 50 and 300° C, depending on the gas used.

When exposed to the high energy discharge field, oxygen (O₂) is broken down into monatomic oxygen (O), O⁺ and O⁻. The oxygen combines with hydrocarbons at atmospheric pressure. Following volatilization, the resultant byproduct is water vapor, CO and CO₂, which is carried away in the exhaust stream. The reaction takes place at the atomic and molecular level and is by its nature complete with no residual surface products.

The purpose of this study is to examine one promising combinational approach, specifically capitalizing on the particle cleaning advantage of CO₂ with the efficient atomic and molecular level cleaning capabilities of atmospheric plasma ionic discharges. The use of combinational treatments is critical for several reasons:

- 1) Bonding surfaces are heterogeneous, with contaminations varying in type, thickness, and among different base materials.
- 2) Contaminants can be complex, ranging from acids/oils and particles to process residues and mold release agents.

Methodology / Experimental

A device embodied by affixing an atmospheric pressure plasma ion bombardment treater with an atmospheric CO₂ composite “snow” spray cleaning module (see Figure 3) was positioned above an un-

Figure 3. Atmospheric Pressure Plasma Ion Bombardment Device (center) mounted to CO₂ Spray Cleaning Module (right).



treated low density polyethylene (LDPE) material used in microelectronic devices (for use within military and aerospace electronic systems) for surface pre-treatment prior to application of a Loctite 401 cyanoacrylate adhesive, and separately a Loctite 3553 light-cure acrylic adhesive. The 401 cyanoacrylate adhesive was chosen specifically since it is designed for the assembly of difficult-to-bond materials which require uniform stress distribution and strong tension and/or shear strength. The product provides rapid bonding of a wide range of materials, including metals, plastics and elastomers. The 3553 light-cure acrylic adhesive adequately represents the class of adhesives which cure at a higher wavelength than visible light for cure-on-demand workflows.

The ion bombardment device ionized a CO₂ gas flow rate of between 15-40 lpm and projected a surface treatment band of 19mm. The CO₂ spray cleaning module featured a pendant-style spray applicator with a coaxial hose and was capable of delivering an 8mm to 19mm surface treatment band.

Results and Discussion

After a dwell time of five seconds under the device,

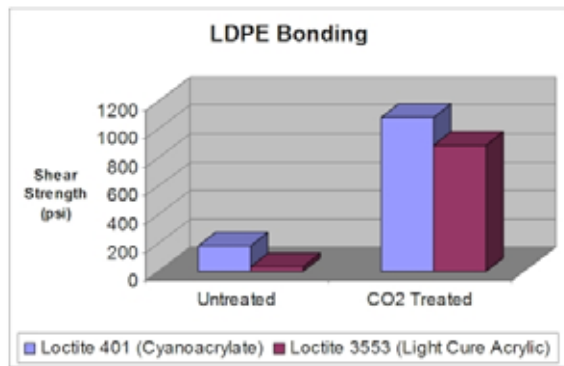


Figure 4. LDPE Bond Shear Strength After CO₂ Pre-Treatment

it can be seen in Figure 4 that the shear strength of the bond between the LPDE sample and cyanoacrylate adhesive increased ten-fold, and the shear strength of the bond between the LPDE sample and the light cure acrylic adhesive increased forty-fold. Subsequently, MIL-STD-883 Method 2011.7 was applied as a destructive bond pull test to evaluate bond strength and bond strength distribution of various surface contaminations after CO₂ treatment. The apparatus used had an accuracy of ± 5% and performed at a 90° peel angle.

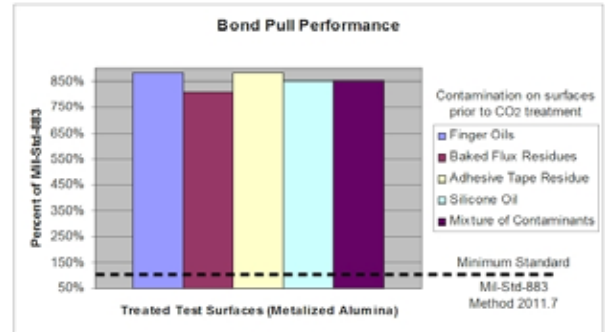


Figure 5. LDPE Bond Pull Performance After CO₂ Pre-Treatment

As can be seen in Figure 5, the minimum bond pull standard was dramatically exceeded after pretreatment removal of both organic and inorganic contaminations. The average % of the MIL-STD-883 achieved ranged from 820% to 880%, an 8-fold increase above the minimum standard requirement.

Conclusion

The cleaning process is based upon the expansion of either liquid or gaseous carbon dioxide through an orifice. This expansion leads to the nucleation of small dry ice particles and a high velocity gas carrier stream. Upon impact with a contaminated surface, the dry ice media removes particles by momentum transfer and some hydrocarbons via a transient solvent or a freeze fracture mechanism. It appears that the combinational use of atmospheric plasma ion bombardment discharges significantly increases the surface tension of base substrates as opposed to the use of snow cleaning processes alone. Bonding strength of adhesives are commensurately improved with the combinational approach. The combinational approach would seem to be suitable for either initial or final cleaning, and for numerous critical and non-critical cleaning applications in the semiconductor, disk drive, research, aerospace, military, surface science, surface analysis, optical, medical, automotive, analytical instrument, and manufacturing communities.

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