CO_2 Clean Manufacturing Technology for Electronic Device Fabrication

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Abstract

CO_2 technology offers electronic device manufacturers a robust platform for a variety of precision cleaning and machining applications. Surface and substrate contamination such as flux residues, organics, particulate matter, outgassing residues, ionic residues, and laser and mechanical machining heat can be addressed (uniquely) with this technology. Available CO_2 processes include one or a combination of composite jet sprays, centrifugal liquid immersion, supercritical fluid extraction, and both vacuum and atmospheric plasma surface treatments.

CO_2 technology eliminates or significantly reduces both lean and green waste generation at the production operation level (source) by modifying manufacturing processes such as precision cleaning and machining. Because it is safe and dry, CO_2 technology can integrate directly into manufacturing processes and tools to provide in-situ cleaning and/or thermal control. CO_2 technology can be implemented in a variety of process configurations to meet the constraints of lean production layouts and product flow requirements, including direct integration into existing production lines and equipment where the surface contamination is being generated. CO_2 is a very unique manufacturing agent that affords multiple cost reduction and performance improvement opportunities for electronic device fabrication.

Exemplary applications include silicone contamination removal from a surface using a CO_2 composite spray, hybrid CO_2 particle-plasma pad surface preparation for gold wire bonding, ceramic flip chip defluxing using centrifugal liquid CO_2, surface residue removal using a CO_2 composite spray following laser processing, particle removal from a CMOS image sensor following wire bonding, and CO_2-enabled laser machining of organic and ceramic substrates.

I. Introduction

Over the past 25 years, CO_2 clean manufacturing technology (CO_2 CleanTech) has been used within many high technology, high reliability, and high capacity manufacturing operations. Industries have included aerospace, hard disk drive, microelectronics, and optoelectronics, among many others. CO_2 CleanTech has been used primarily as a means for increasing the cleanliness of components, assemblies, tools and fixtures to increase both capacity and quality. Possibly more significant, CO_2 CleanTech has proven itself to be a means for reducing the cost of manufacturing high reliability products [1].

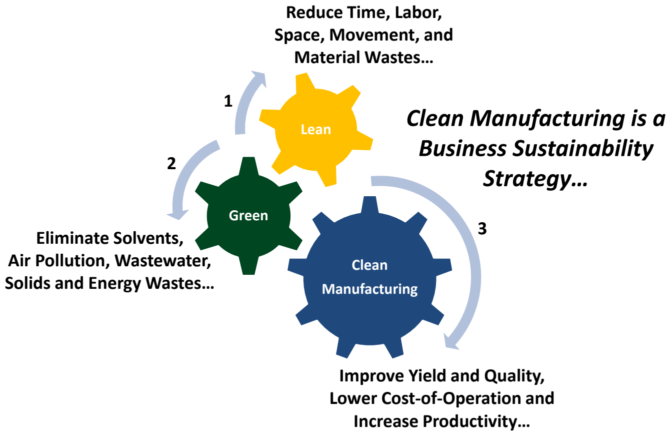


Figure 1 – Lean and Green Manufacturing

As described under Figure 1, in an environment of escalating manufacturing challenges such as intense global competitiveness, environmental regulation and energy supply issues, material and process engineers must have both lean and green manufacturing (aka “Clean Manufacturing”) technology to identify and eliminate multifaceted manufacturing wastes in their operations that stealthily steal away business profits. CO_2 CleanTech represents a significant business opportunity to adapt production tools and operations to meet the challenges. The merging of green practices such as CO_2 technology into manufacturing is delivering additional value in the form of less chemical, energy, labor, and water usage as well as the elimination of solid wastes, air and water pollution [2].

CO_2 CleanTech offers electronic device manufacturers, component suppliers and assembly equipment OEMs new ways to re-tool their factories and equipment for cleaner production. Assembly tool builders can develop and deliver clean-in-place assembly process-tool combinations to support sustainable manufacturing initiatives. Component suppliers can produce and supply better quality product at lower cost and device manufacturers can adapt dry clean-in-place capability throughout the factory. CO_2 CleanTech can uniquely address the composite opportunity to reduce both lean and green manufacturing waste throughout the production network; tool suppliers, component suppliers, and manufacturers.

II. CO_2 is a Unique Manufacturing Solution

CO_2 is a safe and abundant compound that plays a very important role in many commercial and industrial applications. CO_2 can be used in cleaning, cooling and machining applications. Many companies have implemented CO_2-based cleaning technology and have realized improved productivity and a lower cost-of-operation of their production operations. CO_2 CleanTech has also served as a strategy for complying with worker safety and environmental regulations. The CO_2 used in cleaning, machining and thermal control processes is the same CO_2 used to charge fire extinguishers, carbonate beverages, weld steel, cast metals, and refrigerate products, among many other important industrial uses. In fact it’s the same CO_2 that you are exhaling while reading this paper; about 1 kilogram of it every day.

CO_2 is an abundant (and recyclable) by-product of numerous industrial and natural processes. Recycled CO_2 is a valuable and renewable manufacturing resource that will never run out of supply. Unique benefits derived from using recycled CO_2 include the conservation of water, reduced energy consumption and a reduction in industrial CO_2 emissions. Moreover CO_2-based process technology is a positive contribution to Hazardous Air Pollutant (HAP), Volatile Organic Compound (VOC), and Greenhouse Gas (GHG) emissions reduction strategies.

Using recycled CO_2 to reduce pollution, conserve energy and eliminate wastes (both environmental and manufacturing) produces numerous tangible and measurable benefits. Major industrial sources of CO_2 emissions include:

1. Electrical power generation and usage,
2. Chemical generation and usage, and
3. Transportation.

The use of recycled CO_2 technology as a chemical/process substitute lowers electrical power usage, reduces manufacturing wastes, increases manufacturing productivity, and decreases the need for chemicals such as lubricants and solvents, among many other positive socioeconomic and environmental benefits. A reduction of manufacturing wastes or elimination of production chemical inputs of any kind decreases industrial CO_2 (carbon) footprint. Following are examples of how this works:

- ✓ Less CO_2 is produced if less electricity is consumed for processing.
- ✓ Less CO_2 is produced if less oil is refined, transported and consumed.
- ✓ Less CO_2 is produced if less cleaning solvents are produced, transported and consumed.
- ✓ Less CO_2 is produced if more products can be manufactured for the same energy, labor and space inputs.
- ✓ Less CO_2 is produced if products don’t have to be cleaned using hot deionized water or dried using solvents or other drying agents.

Thus from a GHG emissions perspective, using recycled CO_2 significantly offsets new CO_2 gas production and emission from both the industrial supply and consumption sides of the equation. Pending USEPA CO_2 emissions reporting legislation is intended to impact the "generators" of CO_2. A user of recycled CO_2 is not considered a generator of CO_2. The CO_2 used in commercial and industrial processes is already accounted for in the GHG emissions inventory.

With regards to smog generation, CO_2 is not a VOC and is not regulated as such. From a worker health and safety perspective, CO_2 is non-toxic. From a building safety and equipment protection perspective, CO_2 is non-flammable and noncorrosive. CO_2 is a perfect solution for protecting the environment and improving the health and safety of both workers and communities, while improving the performance and cost-of-operation of high reliability product manufacturing operations.

III. CO_2 is Many Manufacturing Agents in One

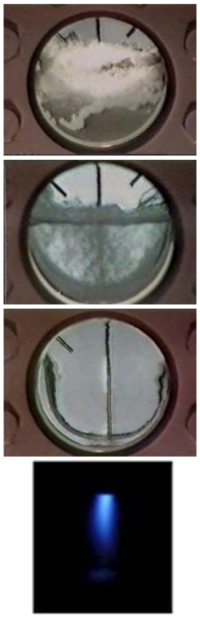


Figure 2 – Phases of CO_2

As shown in Figure 2, CO_2 is a very versatile manufacturing agent; 5 manufacturing agents in 1. It can be used as a solid, liquid, supercritical fluid, and both atmospheric and low-pressure plasma. CO_2 is useful as a spray treatment agent [3], immersion and extraction solvent [4], as well as in the form of many hybrid or combinational substrate processing possibilities. In addition, CO_2 fluids purification and management systems have been developed to support these various capabilities. Manufacturing applications for CO_2 CleanTech are diverse as well. Applications include precision degreasing, departiculation, outgassing, precision drying, disinfection, surface modification and functionalization, cooling and lubrication, among many others.

CO_2 solvent properties are similar to halogenated solvents such as Freon® 113 and HFE-7100. CO_2 possesses a Hildebrand solubility parameter in the adjustable range between 14 $MPa^{1/2}$ to 22 $MPa^{1/2}$ depending upon phase, temperature and pressure. CO_2 can be compressed to a range of liquid-like densities, yet it will retain the diffusivity of a gas with extremely low viscosity. Supercritical and liquid CO_2 cleaning agent densities may be adjusted between 0.5 g/cm^3 and 0.9 g/cm^3. Solid phase CO_2 has a density of 1.6 g/cm^3, identical to Freon® 113. High density provides significant and controllable impact shear stresses of between 10kPa (i.e., using fine CO_2 particles at low velocity) and 300 MPa (i.e., using CO_2 pellets at high velocity) when projected against a non-compliant substrate surface. Surface tensions for CO_2 fluids range from 0 dynes/cm (supercritical) to 5 dynes/cm (liquid). Practical benefits derived from these unique properties include rapid penetration and wetting, hydrocarbon solubility, and energetic cleaning, cooling and dry lubrication effects.

IV. CO_2 Technology Reduces or Eliminates Manufacturing Waste

CO_2 CleanTech eliminates or significantly reduces waste generation at the production operation level (i.e., at the source) by modifying manufacturing processes, and in particular precision cleaning, assembly processes requiring critical cleaning, and precision machining operations. CO_2 modifies conventional manufacturing processes and tools in several dimensions, described as follows;

1. Physically; shape, size, space, application and configuration;
2. Chemically*;* solvency, toxicity, and dryness;
3. Quality; defects, rework, scrap; and
4. Time; productivity.

Table 1 - Examples of CO_2 CleanTech Utilization and Benefits

Equipment and Process Configuration	Waste Reduction Benefits
Integrate CO_2 CleanTech with automation and environmental control to produce custom stand-alone automated cleaning cells or islands to replace aqueous and solvent cleaners.	Eliminate aqueous cleaning and rinsing fluids, drying equipment and related waste-producing operations.
Integrate CO_2 CleanTech into existing production lines and processes.	Enables in-line cleaning where none existed and without an increase in floor space.
Hybridize CO_2 CleanTech with one or more manufacturing processes such as dispensing, bonding, welding, coating, curing, soldering, machining and inspection.	Eliminate the need for separate and additional cleaning equipment, processes and related waste-producing operations.

CO_2 CleanTech may be implemented in a variety of production equipment and process configurations to meet the needs of lean production schemes and product flow constraints, including both existing and new production line and tool implementations. Examples of unique CO_2-enabled production configurations and manufacturing waste reduction benefits are summarized in Table 1.

V. Applications

CO_2 CleanTech provides material and process engineers with a robust surface treatment platform and window for challenging substrates having complex or microscopic geometries. As shown in Figure 3, many different types of devices can be processed to address numerous contamination challenges including particulate matter, organic residues, outgassing residues, oxides, ionic residues, as well as process heat during machining processes. Shown in Figure 3: [A] Removal of laser welding oxides (alloys) from titanium neurostimulator electrodes, [B] Removal braze weld debris from electronic package, [C] Removal of fingerprint from CMOS image sensor, and [D] Removal of built-up aluminum and aluminum oxide particles from test probe contact. CO_2 treatment processes include composite jet sprays, centrifugal immersion, supercritical fluid extraction, precision drying (i.e. critical point drying), and vacuum and atmospheric plasma treatments – and hybrid processes using combinations of these.

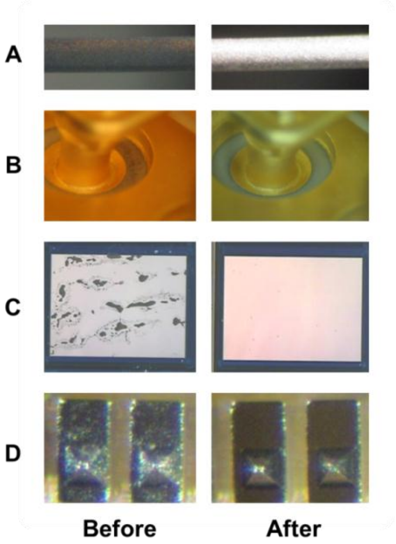


Figure 3 – CO_2-Processed Devices

Many different hybrid processes comprising the various CO_2 treatment processes are possible. Numerous combinations of CO_2 treatments with other advanced substrate processing techniques such as Laser, UV, micromachining, ozone, microabrasives, plasma, robotics, among many others are uniquely possible. The inherent compatibilities and synergies generated between these systems create numerous and varying manufacturing benefits, including the creation of new intellectual property.

CO_2 CleanTech is used in a variety of microelectronic device manufacturing and assembly processes, and in manual, mobile, and automated production configurations. Examples include:

- Adhesive Bonding,
- Functional Coating
- Encapsulation/Sealing

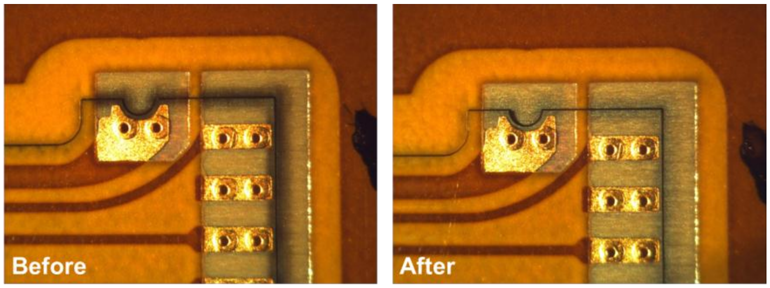


Figure 4 – Removing Laser Cutting Residues

- Wire Bonding
- Welding
- Ceramic, Glass and Crystal Polishing
- Optical Device Assembly (and Test)
- Laser and Diamond Machining
- Microfluidic Device Fabrication
- Precision Device Assembly

CO_2 CleanTech applications have included many types of passive, electro-mechanical and electro-optical substrates with varying end-product performance requirements, and for many different markets including Biomedical, Military, HDD, and Aerospace. Examples of materials and applications relevant to microelectronic device manufacturing are summarized in Table 2.

Microelectronic assemblies require high-volume and cost-effective cleaning during various stages of assembly or rework operations. Due to component compatibility problems and drying challenges, partially assembled devices cannot be immersed in or sprayed with aqueous cleaners or solvents. CO_2 CleanTech overcomes these constraints by providing high capacity, dry solvent-like spray cleaning capability [5]. In many electronic device fabrication applications, selective cleaning of the surface is needed to remove localized contamination generated by processes such as pad preparation, cutting, and drilling. Figure 4 shows an example of selective removal of laser residues from a portion of a polyimide flexible circuit following cutting using a CO_2 Composite Spray cleaning process. This process can be further enhanced using combinational or hybrid processes such as CO_2 particle-plasma treatments, described under the case study below.

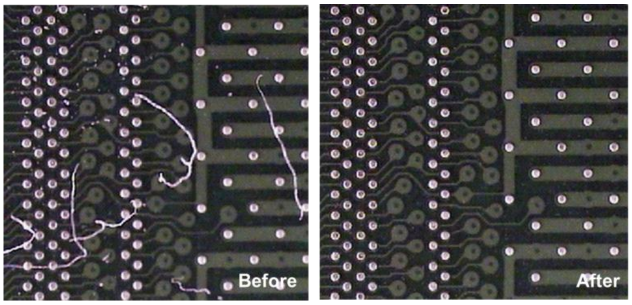


Figure 5 – Removing Particles and Fibers

CO_2 CleanTech can remove microscopic thin film residues, particles and fibers from the functional surfaces of electronic devices, including sub-micron particles. For example, this is evidenced by electronic performance changes noted during the treatment of quartz crystal resonators [6]. Figure 5 shows the removal of typical airborne manufacturing debris such as fibers and particles from a circuit board.

Table 2 – Materials and Applications

Material	Application
Quartz Crystal Resonator	Drive-Level-Dependence (DLD) reduction
Fiber Optical Device	Removal of polishing residues
Optoelectronic Device	Build clean protocol
Ceramic Substrate	Removal of Laser and diamond cutting residues during or following machining (clean cutting)
Polymeric Substrate	Removal of residues during or following machining
Metallic Bond Pads	Bond pad preparation for wire bonding
Low-Energy Polymer	Improved adhesion
Flexible Printed Circuit Board	Removal of residues from laser-processed devices
Acrylic Polymer	Improved adhesion for Light-cure acrylic bond
RF/Microwave Packages	Particle and residue removal following brazing
Ceramic-Metal Composites	Improved adhesion
Patterned Wafer	Photoresist and processing residue removal

VI. Case Study

Bond Pad Surface Preparation for Wire Bonding

Background

A statistically significant study was performed to determine the effectiveness of a dry, selective CO_2 particle-plasma surface treatment process for preparing bond pads for gold wire bonding operations [7]. The study compared and contrasted the performance of the CO_2 surface treatment method with that of a conventional solvent-plasma method. The two treatment methods were used to prepare the surface of a metalized ceramic wafer that simulated bond pad surfaces and treatment areas representative of the actual high-reliability electronic board. Robust surface treatment of bond pads is required in this particular application to insure complete removal of a variety of possible surface contaminants for strong and reliable wire bonds following gold ribbon bonding operations.

As shown in Figure 6, the conventional solvent-plasma method used in this study comprised four sequential steps (proprietary processing parameters), as follows: 1) manual solvent wipe cleaning (i.e., acetone) to remove any thick films and gross manufacturing debris, 2) ultrasonic immersion cleaning (i.e., aqueous) and deionized water rinsing to remove thin film and inorganic contamination, 3) precision drying to remove residual rinsate, and 4) Ar/O_2 low pressure plasma treatment to precision clean, micro-etch, and activate surfaces. Issues associated with the solvent-plasma method include surface contaminant smearing and re-deposition of residues, contamination accumulation within the treatment solvents, and an inability of low-pressure plasma treatment to reliably remove various inorganic residues and particulate matter from the bonding pads. Contaminant transfer, solvent-contaminant build-up, and manual cleaning operations are known to introduce cleaning process variability that result in wire bonding defects. Another constraint associated with the solvent-plasma process is a lack of selectivity. The entire electronic assembly must be immersed into cleaning solvents and plasma, which can introduce contamination or compatibility issues with other electronic components and materials co-located on the electronic assembly. Finally, the solvent-plasma process prevents the implementation of a lean and continuous high-capacity cleaning in this application.

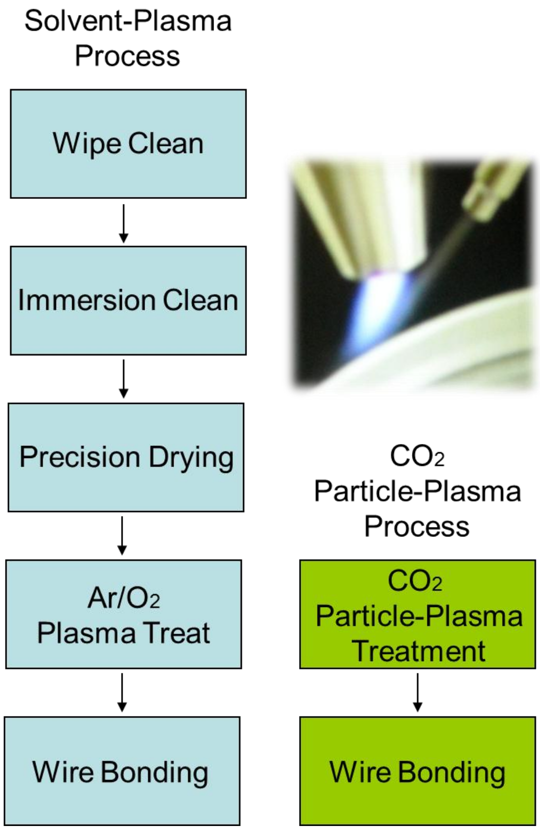


Figure 6 – Solvent-Plasma compared to CO_2 Particle-Plasma Process

The CO_2 particle-plasma process used in this study involved a patented and patents-pending hybrid CO_2 particle-plasma spray process called CO_2 particle-plasma cleaning [8]. The CO_2 particle-plasma process is a single-step process derived by mixing CO_2 particles and CO_2 plasma into a composite atmospheric treatment stream. A blown ion spray (Plasma Component) is directed into the CO_2 Composite Spray (Particle Component); the composition of which is directed against the surface as shown in the picture under Figure 6. Using this hybrid spray composition, the CO_2 particles (and propellant) are doped with beneficial ions, radicals, UV light, and ozone from the blown ion plasma stream through both fluid shearing and vortical mixing actions. The CO_2 Composite Spray further serves as a chemical and physical cleaning and cooling barrier stream, transmitting and transporting beneficial UV radiation and reactants (i.e., ozone, oxygen radical, nitrate ions, hydroxyl, heat, etc..), respectively, to the surface – simultaneously removing plasma-surface reaction by-products including excess heat and ablated, oxidized, or decomposed contaminants.

Metalized ceramic surfaces were doped with thick layers of various common contaminants as well as a mixture of same. An example of a doped test coupon is shown in Figure 7. Gold ribbon wire bonding was performed following surface cleaning operations. The CO_2 particle-plasma cleaning process was developed and performed under the direction of the author. Solvent-plasma cleaning and treated-coupon wire bonding, pull testing and statistical analysis were performed by the co-investigator. The experimental testing and results are summarized and discussed below.

Experimental

106 ceramic wafers (Al_2O_3), designated as sample numbers SN1-SN106, each containing a surface layer comprising vapor-deposited TiW, Ni, and Au, were divided into 5 test groups. These composite substrates represented the bonding pad characteristics (surface chemistry and area) of the actual hybrid electronic board and bond pads in various states of cleanliness, described as follows:

Figure 7 – Example of Contaminated Test Sample

<u>Solvent-Plasma Cleaning Process Test Group (SN1-5, SN16-20, SN31-35, SN45-50 and SN85-89)</u>
25 samples, designated as SN1-5, SN16-20, SN31-35, SN45-50 and SN85-89, were subdivided into 5 sample sets, contaminated as described below and cleaned using the proprietary solvent-plasma process described above.

<u>CO_2 Particle-Plasma Cleaning Process Test Group (SN6-15, SN21-30, SN36-45, SN51-60, and SN90-99)</u>
25 samples, designated as SN6-15, SN21-30, SN36-45, SN51-60 and SN90-99, were subdivided into 5 sample sets, contaminated as described below and cleaned using the CO_2 Particle-Plasma cleaning process described below.

<u>OSEE Inspection Baseline Test Group (SN61–65)</u>
5 samples (SN61-65) were retained for establishing a baseline photocurrent using a non-contact surface inspection method called Optically Stimulated Electron Emission (OSEE). The OSEE photocurrent of the OSEE baseline testing group was compared to the contaminated and CO_2 cleaned coupons.

<u>Bonding Parameter Test Group (SN101, SN102, SN101-105)</u>
7 samples, SN101, SN102, SN101-SN105, were used to establish the ribbon bonding and pull test criteria for all test groups.

<u>Control Test Group (SN66-84, SN106, SN100)</u>

A total of 21 samples, designated as SN66-84, SN106 and SN 100, were retained as sample controls. Following wafer metalization processes, control samples were vacuum plasma treated (Ar/O_2), gold ribbon bonded, and pull tested to establish clean surface baseline bond strength.

Surface Contamination Challenge

Both the solvent-plasma and CO_2 particle-plasma process test groups (50 sample coupons total) were doped using a brush with a particular contaminant type, described as follows:

- Tape Adhesive (SN1-15)
- Finger Oils (SN16-30)
- Flux (SN31-45)
- Silicone Oil (SN46-60)
- Combination of adhesive, finger oils, flux and silicone oil (SN85-99)

Each type of contamination was brushed onto the metalized wafer surfaces using an acetone solvent carrier and dried.

Note: The simulated surface contamination produced was a very thick film. This level of contamination is not a normal manufacturing surface contamination level and thus represented a worst-case challenge test for both treatment processes.

CO_2 Particle-Plasma Cleaning Test Apparatus

Shown in Figure 8, the CO_2 Particle-Plasma treatment test apparatus comprised a programmable Cartesian robot with moveable x, y and z axes. An end-of-arm tool (EOAT) connected to the z-axis comprised a CO_2 Composite Spray nozzle (45 degree angle), and CO_2 Plasma nozzle (shown with OSEE surface inspection probe in 90 degree position). Doped wafers were affixed to the x axis using double-sided tape, whereupon the same (optimized) CO_2 Particle-Plasma surface cleaning and treatment recipe was executed for each test sample.

Figure 8 – Experimental Cleaning Test Apparatus

Optimized CO_2 Particle-Plasma Cleaning Process Variables

Propellant Gas:
Type: Nitrogen Gas
Pressure: 80 psi (552 kPa)
Temperature: 120° C (393 K)

CO_2 Particle Generator:
Condenser Diameter (I.D.): 0.030 inches (8 mm)
Condenser Length: 8 feet (244 cm)
Spray Nozzle: Coaxial 2:2 Straight
Spray Angle: 45 Degrees

CO_2 Plasma:
Treatment Gas: Carbon Dioxide
Plasma Type: Blown Ion
Spray Pressure: 80 psi (552 kPa)
Spray Angle: 90 Degrees

Robot/EOAT:
Robot Type: Cartesian, 3-axis
Treatment Scan rate: 10 mm/sec
Treatment Sequence: X-Y Scan, 10 mm Step
EOAT distance from surface: 1.27 cm

CO_2 Particle-Plasma Treatment Process Description

CO_2 Particle-Plasma is sprayed over the entire topside surface of the test sample, which simulated the actual surface area of the electronic board bonding pad strips. The treated surface area was 2 inch x 1 inch (5 cm x 2.5 cm) portion of a 2 inch x 3 inch (5 cm x 8 cm) test substrate. A total of three (3) treatment passes were performed on each strip.

CO_2 Cleaning Method and Packaging

1. Test sample was mounted to robot fixture using tack tape (un-treated side).
2. CO_2 Particle-Plasma spray was projected at test sample surface using optimized treatment spray and robotic scan cleaning parameters described above.
3. Treated test substrates removed from the mounting fixture and heat-sealed in clean nylon packaging.

An example of surface condition before and after CO_2 treatment is shown in Figure 9.

Gold Ribbon Bonding Process

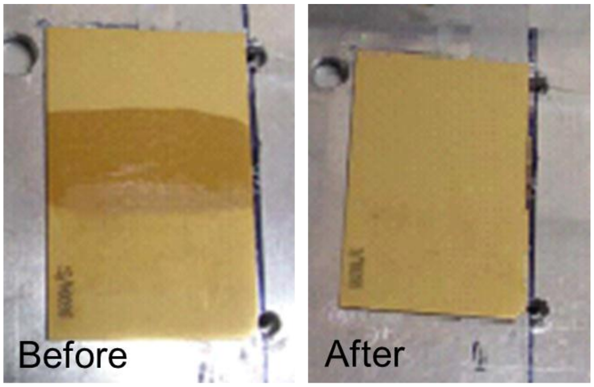


Figure 9 – Before and After CO_2 Cleaning (Coupon SN096)

The gold wire bonding equipment and process parameters used are described as follows:

Ribbon Bonder: Westbond Model Number 4630E
Au Ribbon: 0.005” x 0.007”
Ribbon Bonding Tool: Deweyl MRCSVD-1/16-1-52-CG-.5X7-M

Gold ribbon bonding was performed with tool heat and work holder temperature at 150° C. Following wire bonding, all wire bonds were pull-tested using a procedure detailed in MIL-STD-883E [8].

Results and Discussion

Bond Pull Failure Modes; Number of Bond Lifts
Control Group: 0
Solvent-Plasma: 10
CO_2 Particle-Plasma: 6

As shown in Figure 10, the CO_2 particle-plasma process showed a lower aggregate number of bond lifts as compared to the solvent-plasma cleaning group. Within the variance of the process, the CO_2 particle-plasma cleaning process performance was equivalent to the solvent-plasma cleaning process for finger oils, flux, and silicone oil and for contaminant mix coupons.

Average Bond Pull Strength
Control Group: 58 g

Shown in the Figure 11, all ribbon bond pull strength test measurements for both solvent-plasma and CO_2 particle-plasma cleaning for each type of contaminant were a magnitude higher than the 6.8 g minimum pull strength per MIL-STD-883, Method 2011.7.

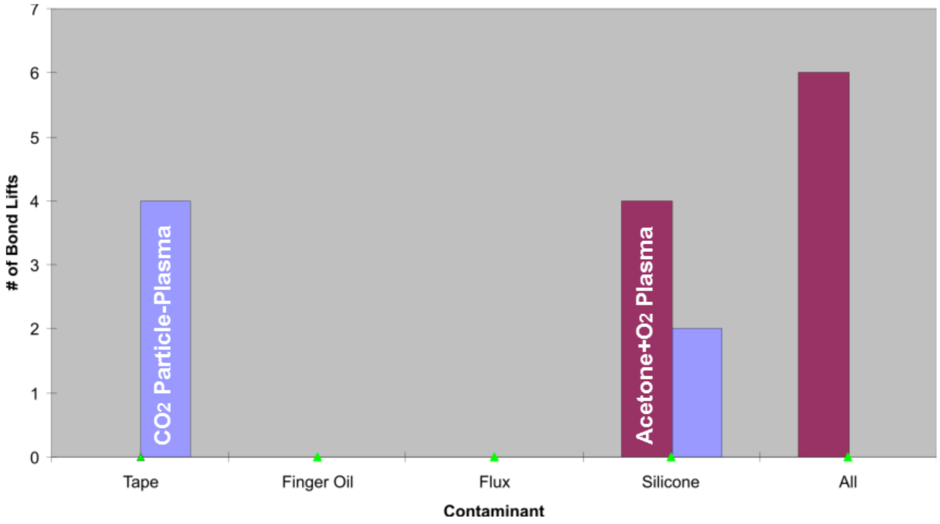


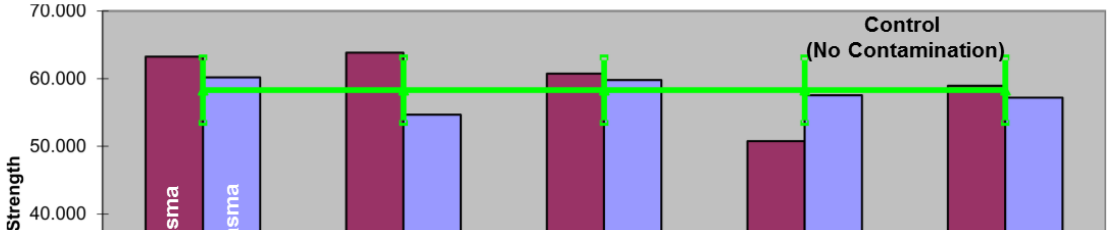
Figure 10 – Number of Bond Lifts

Bond Pull Defects; Calculated Defects per Million (DPM)
Control Group: 233 DPM

The solvent-plasma treatment group showed a higher aggregate DPM compared to the CO_2 particle-plasma treatment group.

Solvent-Plasma: 117664.7 DPM
CO_2 Particle-Plasma: 17051.8 DPM

Shown in Figure 12, the data also showed that CO_2 particle-plasma treatment represents only 2% of the DPM as compared to



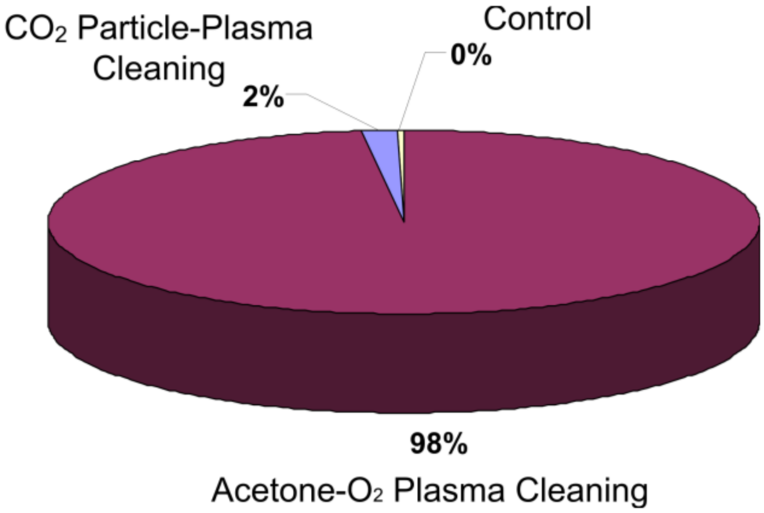


Figure 12 – Defects-Per-Million (DPM)

solvent-plasma cleaning which represents 98% of the DPM.

Bond Pull Strength Variance; Coefficient of Variance (CpK)

Shown in Figure 13, the CO_2 particle-plasma cleaned coupons showed a tighter distribution within the established control limits as compared to the solvent-plasma treatment group. The CpK data for silicone contamination indicated that the CO_2 particle-plasma cleaning process is slightly more effective, with the solvent-plasma CpK data falling below the Lower Safety Limit (LSL).

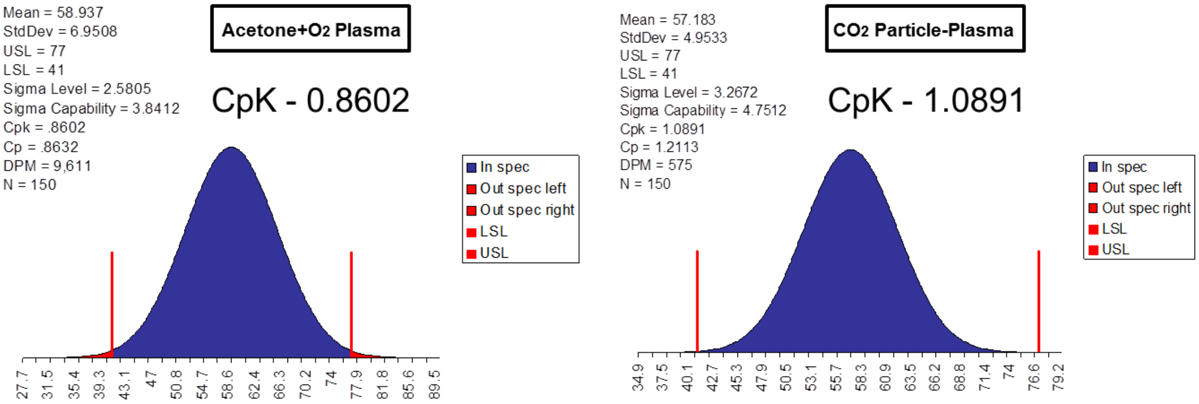


Figure 13 – CpK Analysis

Conclusion

The test results of this evaluation demonstrated that the CO_2 particle-plasma surface treatment process is statistically similar to or sometimes better than the solvent-plasma cleaning process. CO_2 cleaning was determined to be better for some types of contaminants as well – and in particular the more relevant mixed-contaminant challenge tests. The CO_2 cleaning process demonstrates a lower defect-per-million (DPM) level and an improved CpK.

Compared to the solvent-plasma process, the CO_2 cleaning process does not produce waste by-products such as spent cleaning solvents, wipers and associated cleaning residues. The CO_2 cleaning process is easily automated and can be integrated into existing fabrication lines. CO_2 cleaning process is robust, less susceptible to cleaning process (i.e., chemistry) variation, selective, and more efficient - requiring much less labor. Moreover, the CO_2 cleaning process is a lean and green operation, producing a dry and clean surface in a single-step without cleaning waste by-products.

VII. Conclusion

CO_2 CleanTech transforms electronic device manufacturing operations in a variety of unique ways. CO_2 CleanTech addresses challenging contamination constraints with cleaner production solutions and a lower cost-of-operation (CoO). CO_2 CleanTech serves as an alternative to conventional immersion, extraction, spray and plasma treatment processes. CO_2 CleanTech is uniquely versatile and adaptable to the production of a diverse array of high-reliability products including flexible and hybrid printed circuit boards, CMOS image sensors, optoelectronic devices, microfluidic devices, guidance systems, fuel injection devices, spacecraft components, and disk drive assemblies, among many other examples. Finally, CO_2 CleanTech is proving to be a superior option in material cleaning and modification processes such as the preparation of bond pads for wire bonding operations. CO_2 cleaning processes produce as good as or better wire bond strength with fewer defects as compared to conventional methods – and without the labor, space, chemical, and energy waste constraints associated with same.

VIII. References

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CO_2 Clean Manufacturing Technology for Electronic Device Fabrication

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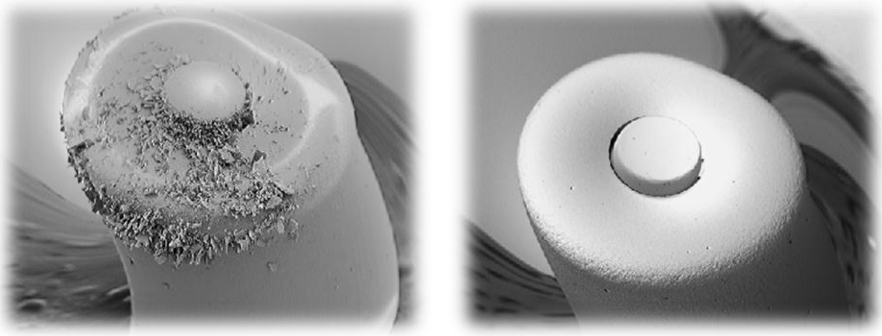
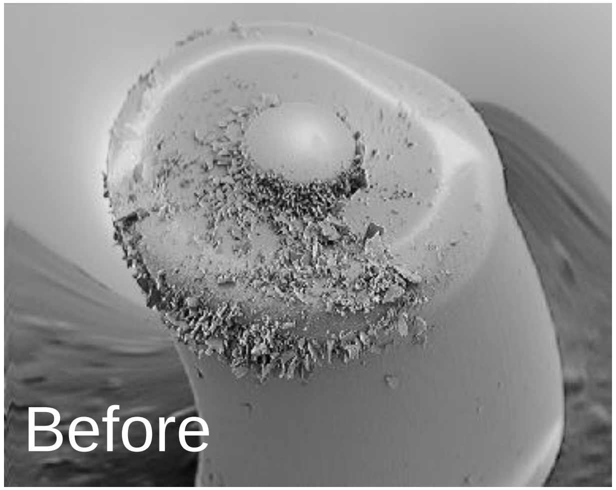
Part I

Need for Better Cleaning Technology



Need for better cleaning technology…

- More complex hardware
- Higher performance standards
- Smaller geometries
- Better selectivity
- Need for improved productivity
- More adaptive to production line, tools, processes and flow
- Smaller footprint
- Less waste by-products
- Desire for dry processing
- Lower cost of operation
- Cleaner air and work environment



Before

After

Part II

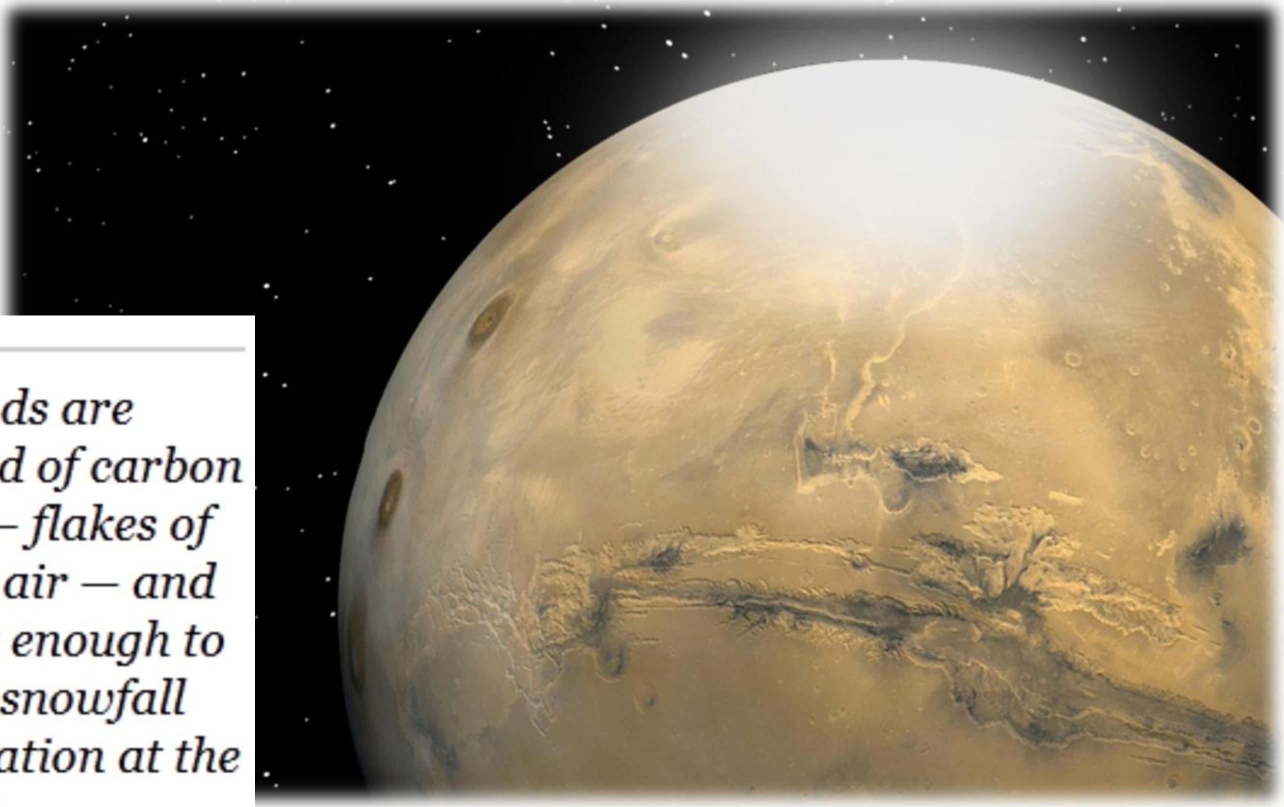
CO_2 Cleaning Technology

Carbon dioxide (CO_2)…

Ozone Depleting Potential (ODP)	OSHA PEL	VOC
None	5,000 ppm	No

Fire Hazard	Corrosive	Price $/lb
No	No	$0.05 - $0.15

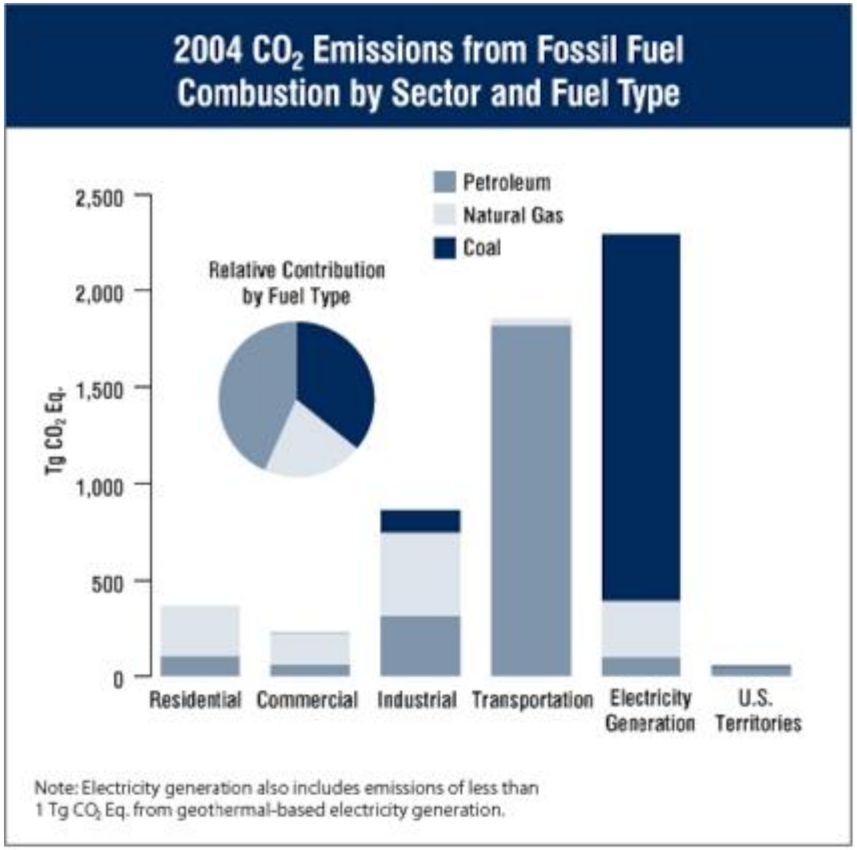
CO_2 is abundant …



'The clouds are composed of carbon dioxide — flakes of Martian air — and are thick enough to result in snowfall accumulation at the surface.'

- Paul Hayne of NASA's Jet Propulsion Laboratory

Carbon footprint…



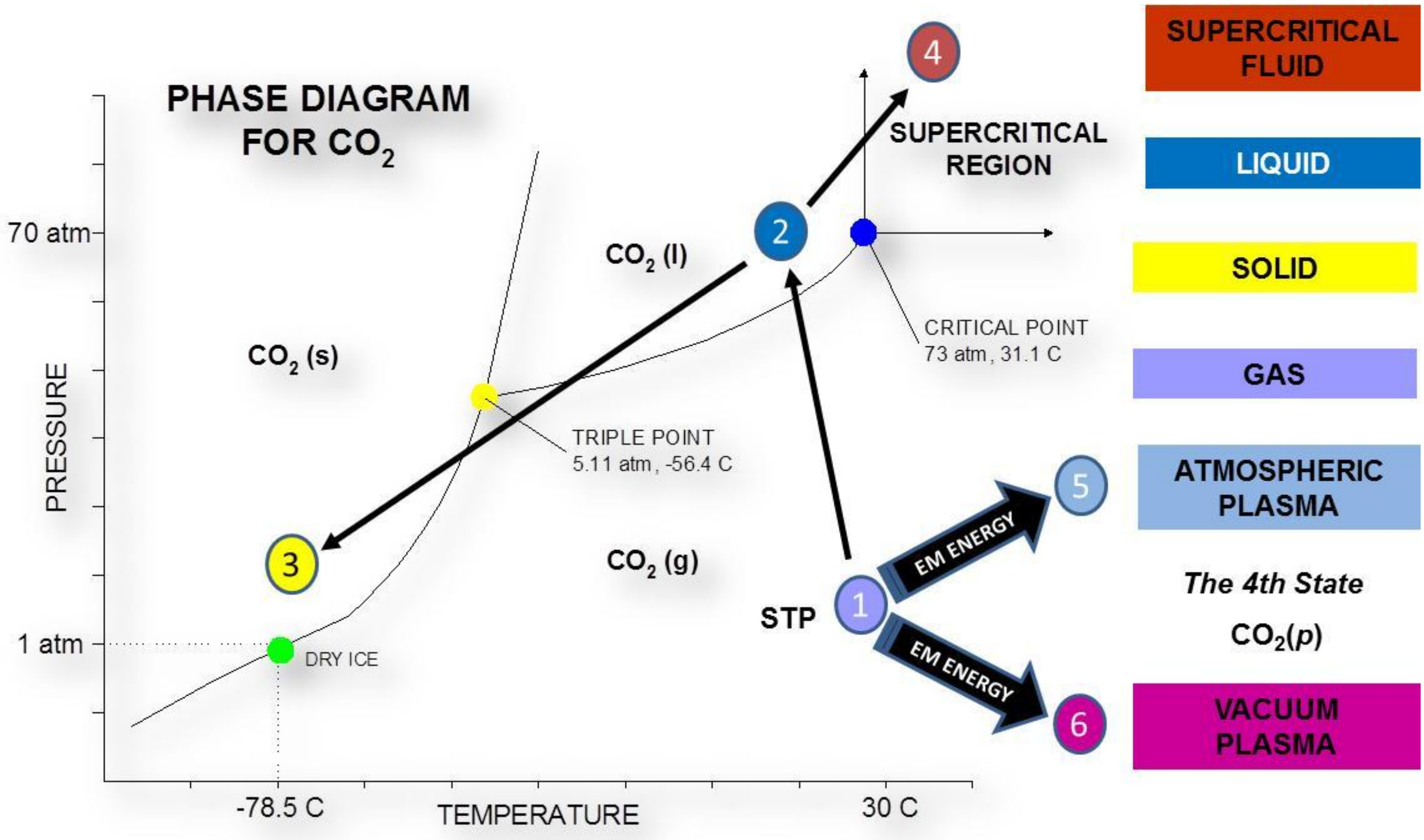
2004 CO_2 Emissions from Fossil Fuel Combustion by Sector and Fuel Type

Note: Electricity generation also includes emissions of less than 1 Tg CO_2 Eq. from geothermal-based electricity generation.

- ✓ Less CO_2 is produced if less oil is refined, transported and consumed as cleaning, machining and thermal control agents.
- ✓ Less CO_2 is produced if products can be manufactured with lower energy, labor, material, time and space inputs.
- ✓ Less CO_2 is produced if products don't have to be cleaned and rinsed with water, and dried with hot air.

Replacing water and solvents with recycled CO_2 technology reduces the carbon footprint….

Many useful agents in one chemistry…



CO_2 cleaning processes…

CO_2 technology offers robust methods for cleaning, modifying, and treating surfaces (selectively or collectively) during the manufacture of products such as aerospace parts, optical devices, automobile sensors, integrated circuits, hard disk drives, air bags, medical devices, among many others.

A diversity of dry treatment schemes:

- Selective Spray
- Immersion Solvent
- Extraction Solvent
- Atmospheric Plasma
- Low Pressure Plasma
- UV-Ozone Treatment
- Microabrasive-Snow

Combinational Treatments

Hybridized Processes

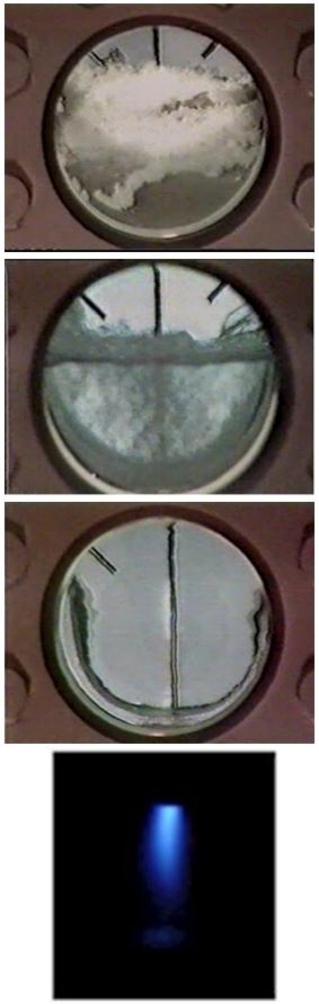
Manufacturing Equipment And Processes

CO_2 cleaning agents and applications…

- Five process agents in one chemistry.

1. Solid (Spray)
2. Liquid (Immersion)
3. Supercritical (Extraction)
4. Atm. Plasma (Surface Mod.)
5. L.P. Plasma (Surface Mod.)

- Multiple hybrid processes possible.
- Multiple uses in manufacturing operations.



Manufacturing Application
Polymer Extraction
Outgassing
Surface Modification
Resist Stripping
Machining
Precision Drying
Cooling
Selective Disinfection
Selective Cleaning
Liquid-Liquid Extraction
Defluxing
Fabric/Textile Cleaning
Degreasing / Deoiling
Departiculation
Thick Film Removal
Stripping
Expansion
Thin Film Deposition

CO_2 cleaning agent chemistry…

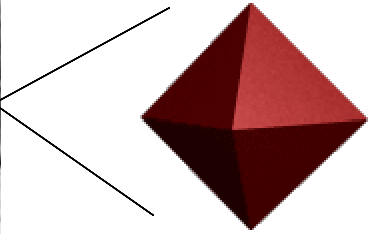
	Carbon Dioxide			HFE-7100	CFC 113
	Solid	Liquid[1]	SCF[2]	Liquid[3]	Liquid[4]
DENSITY g/ml	1.6	0.8	0.5	1.5	1.6
VISCOSITY $mN\text{-}s/m^2$	0.07 (S-L Interface)	0.07	0.03	0.58	0.75
SURFACE TENSION dynes/cm	5 (S-L Interface)	5	0	19	19
SOLUBILITY $MPa^{1/2}$	22 (S-L Interface)	22	14	13	15
KB VALUE	20-30 (S-L Interface)	20-30	10-20	10	14

1. 20 C, 60 atm (Liquid CO_2)
2. 35 C, 100 atm (Supercritical Fluid CO_2)
3. 25 C, 1 atm
4. 25 C, 1 atm

CO_2 spray cleaning agent…

Solid Carbon Dioxide Particles

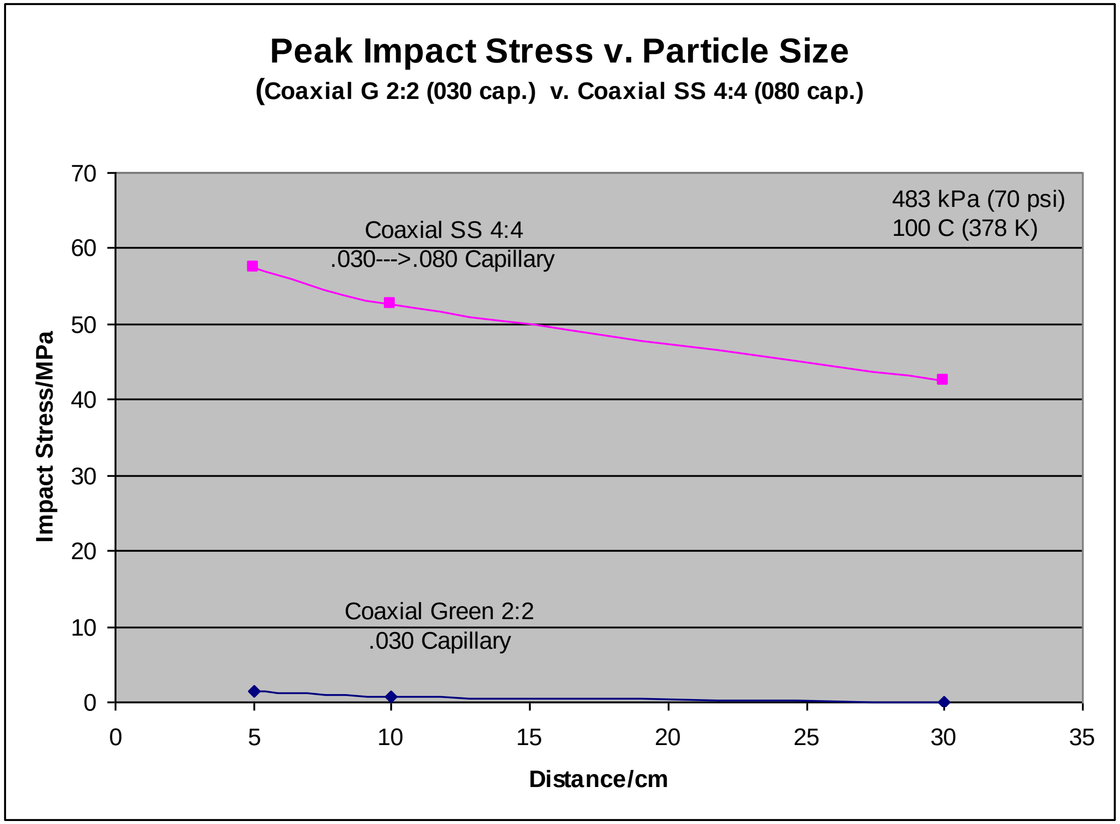
SEM Photomicrograph

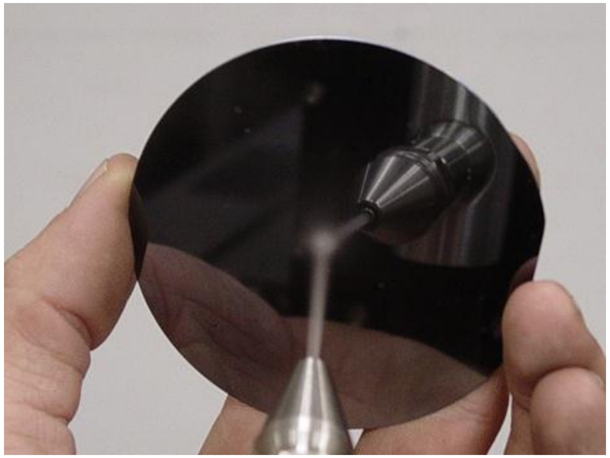


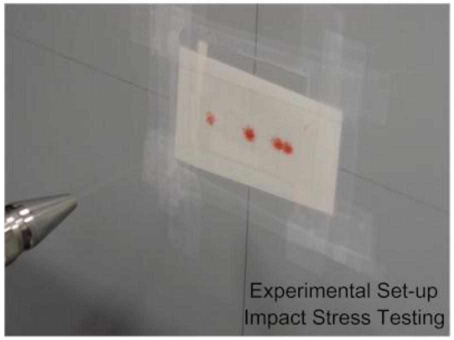
Octahedron

- Structure - molecular crystal, angular, octahedron
- Solvency– hydrocarbon-like, 22 $MPa^{1/2}$
- Impact phenomenon – ablation and phase change (solid->gas, solid->liquid->gas)
- Co-solvency – can be modified with plasmas, liquids, solids, vapor-phase additives
- Compressibility - practically incompressible
- Density - 1.6 g/cm^3
- Hardness – 0.3 Hm (8 Hv)
- Particle Size – < 0.5 microns to > 500 microns, range adjustable (fine-to-coarse)
- Impact Stress - up to 60 MPa, pressure/particle size/distance dependent

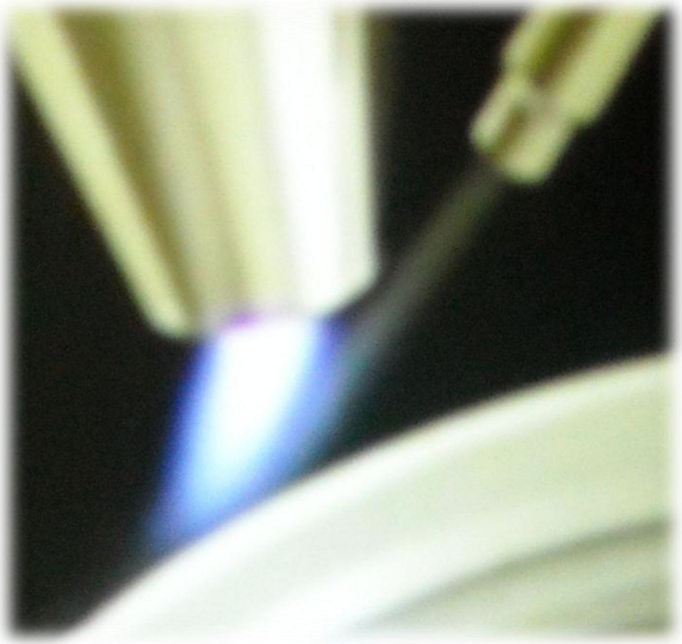
CO_2 spray cleaning…



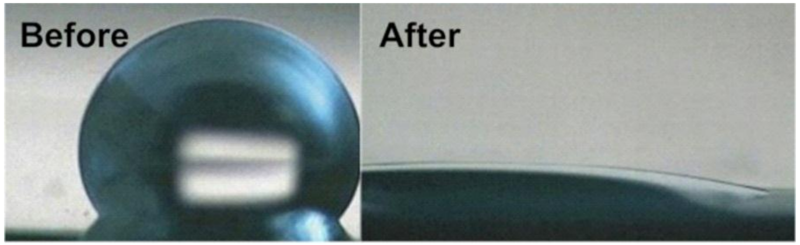




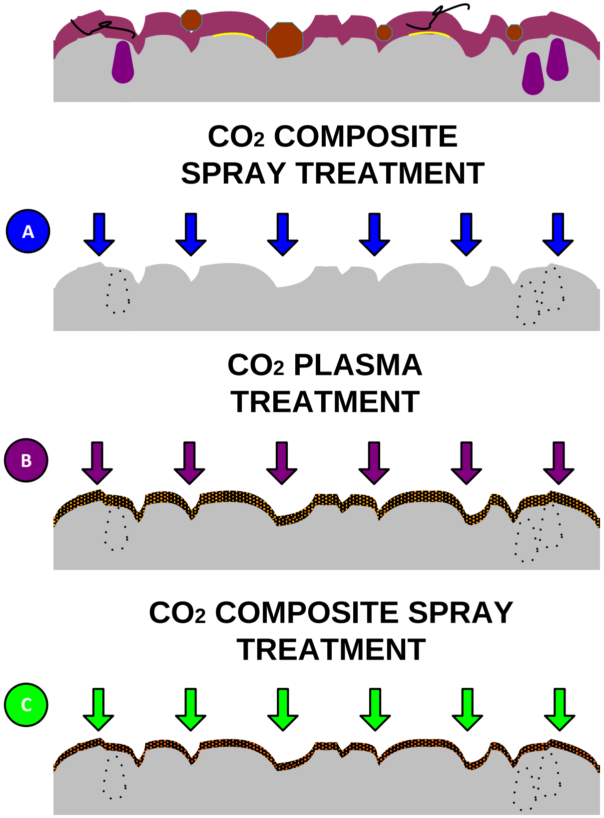
Hybrid particle-plasma process…



Atmospheric CO₂ Particle-Plasma Hybrid Process



Hybrid Cleaning Process



CO_2 COMPOSITE SPRAY TREATMENT

CO_2 PLASMA TREATMENT

CO_2 COMPOSITE SPRAY TREATMENT

Surface ready for adhesive bonding, coating, potting, encapsulating, welding, wire bonding, soldering, printing, plating...

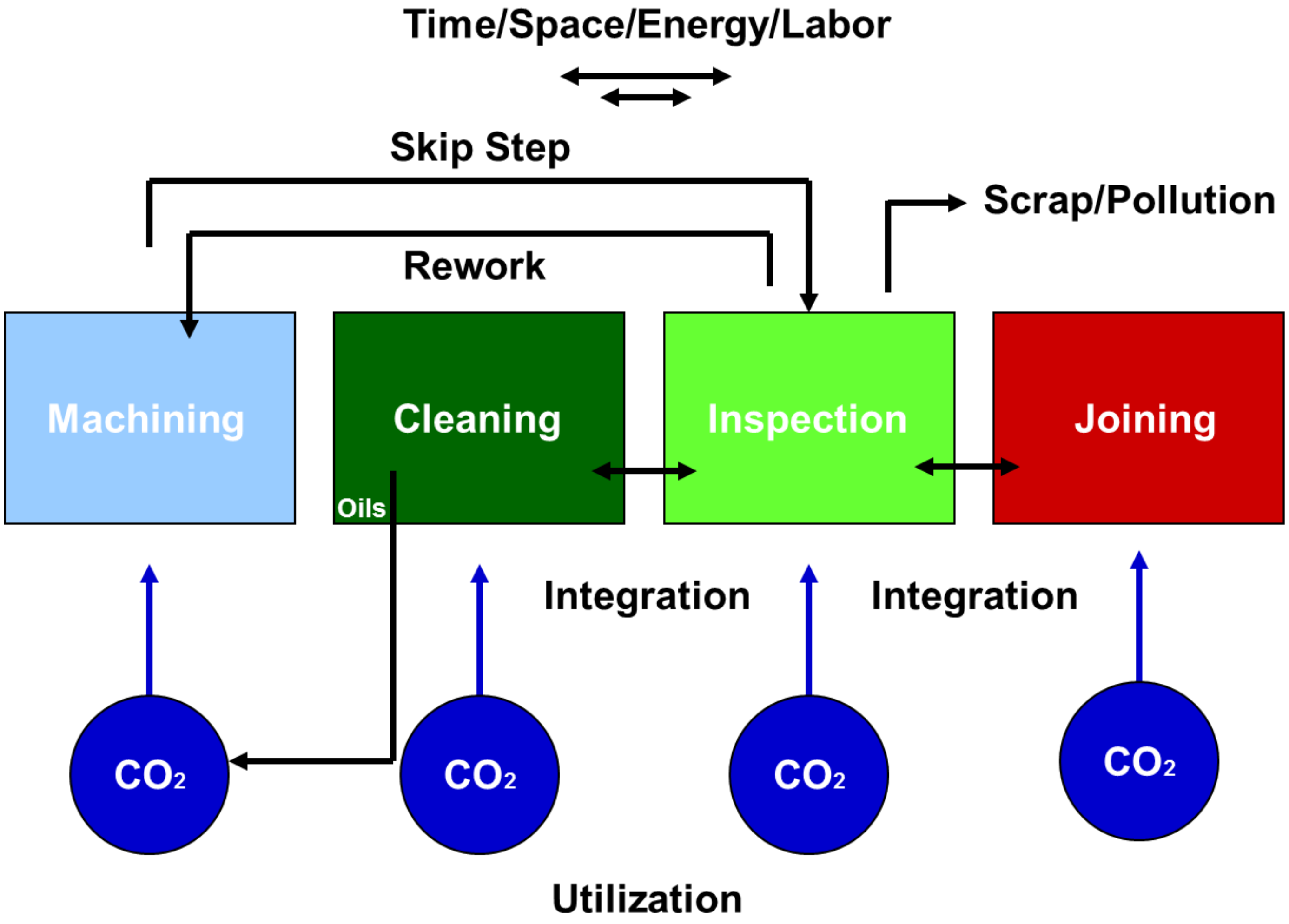
Part III

CO_2 Transforms Manufacturing

CO_2 Tech transforms manufacturing operations…

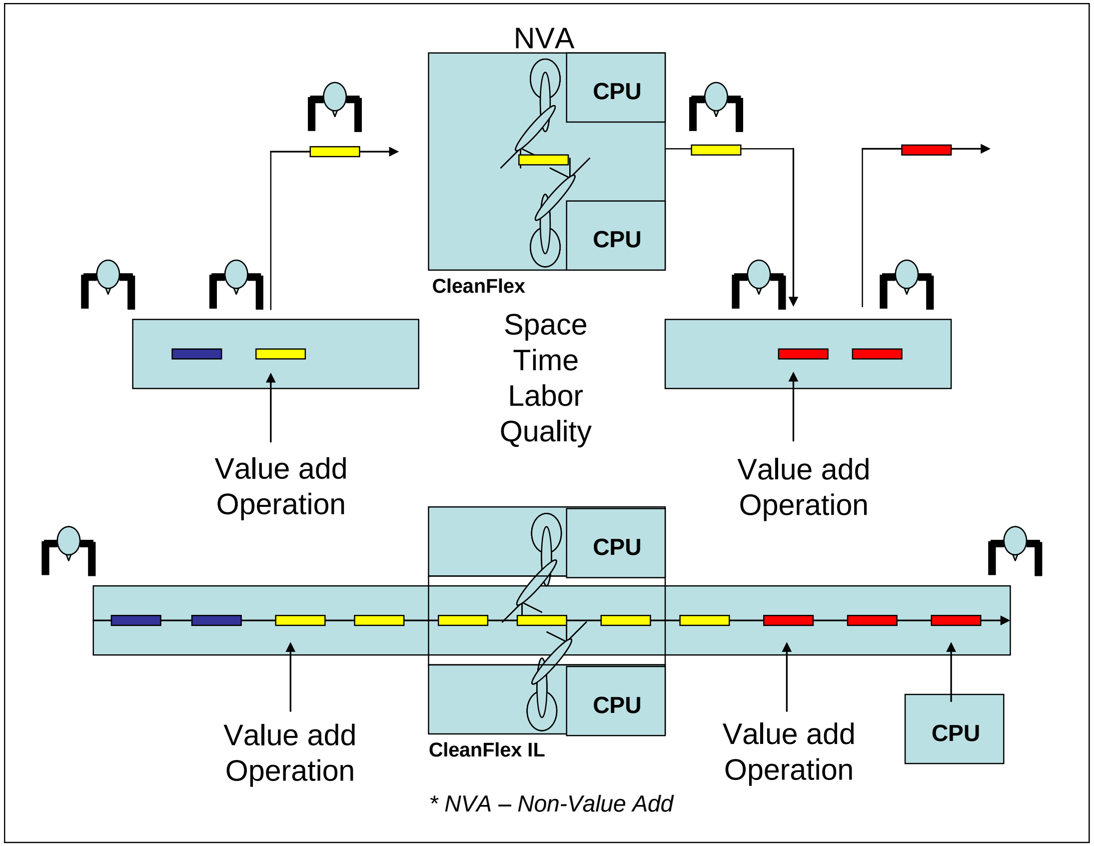
Aspect	Examples
Processes	Fastening, Welding, Machining, Stamping, Thermal Spray, Coating, Molding, Testing, Inspection, Wire Bonding, Adhesive Bonding, Polishing, and Microabrasive Blast…
Wastes	Motion, Space, Energy, Inventory, Transport, Tool Life/Changes, Safety, Scrap, Environmental Permitting, Pollution, Water, Labor, Capital, and Rework…
Contaminations	Particles, Ionic Residues, Heat, Outgas Compounds, Organic Residues, Biological Residues, Flux Residues, and Resistive Residues…
Functions	Degreasing, Thermal Control, Disinfection, Deoiling, Defluxing, Bioburden Reduction, Outgas Removal, Surface Modification, and Dry/Near-Dry Cooling-Lubrication, Precision Drying, and Pressure Impregnation…
Implementations	Integrated with a process tool, Integrated with a conveyor, Stand-alone tool, Cluster tool, Mobile tool, and Robotic tool…
Quality	Higher Yields, Cleaner Environment, Safer Environment, Better Surface Finish, Higher CpK, Improved Product Performance, and Improved Dimensional Control…

CO_2 Tech transforms manufacturing…



CO_2 Tech transforms manufacturing…

Adapt CPU® (CO_2 Processer Units) to flow-through islands, cells and production lines.



** NVA – Non-Value Add*

Part IV

CO_2 Value

(Return-on-Investment)

CO_2 value…

Increased Yield in the form of reduced part rejects, improved cleanliness, lower process variability, better surface finish, or improved product performance…

Increased Productivity in the form of reduced manpower, faster cutting, reduced cleaning process steps, longer tool life, or adaptability to conventional assembly automation processes…

Increased Environmental Quality through the elimination of solvents and waste cleaning by-products, less air pollution, and the elimination of permitting tasks and pollution management facilities…

CO_2 value…

Hard Disk Drive Component Cleaning

Cleaning Cost Comparison

Between DI/US Immersion and CO_2 Composite Spray Cleaning

Deionized Water (Immersion/Drying)	**CO_2** (Dry Spray)
$0.12-$0.13/part	**$0.015-$0.06/part**

50% - 88% cost reduction - fully burdened

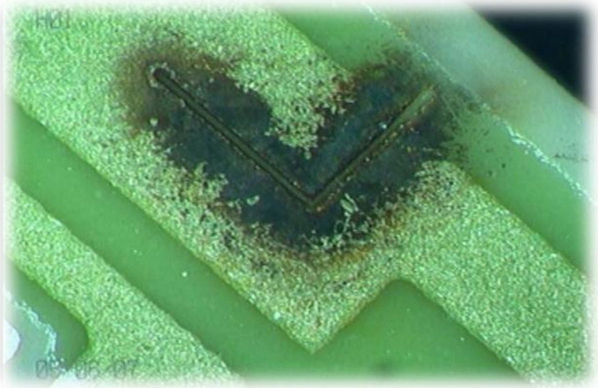
CO_2 value…

Screw Machined Parts Cleaning

		PERC		CO2	
Utilities		$41,100		$7,400	**Energy**
natural gas (boiler)	$32,500				
water treatment costs (boiler/water treatment)	$2,500		$100		
electricity	$6,100		$7,300		
Materials		$33,700		$10,800	**Materials**
perchloroethylene	$29,600				
cutting oil make-up (oil in waste perk)	$4,100				
CO2			$6,400		
HOP oil			$4,400		
Maintenance		$31,500		$5,400	**Labor**
boiler	$3,500				
carbon adsorption/distillation unit/ degreaser	$27,500				
centrifuge and elevator	$500				
air comperssor/ chiller			$500		
CO2 unit/ chip removal/ HOP			$4,400		
filters			$500		
Environmental Costs		$47,700		$0	**Permitting**
hazardous waste disposal (waste perk)	$5,300				
hazardous waste disposal regulation fees	$5,000				
hazardous waste disposal (activated carbon)	$6,500				
air pollution permits	$2,600				
air emission fees	$1,500				
air toxics "hot spots" fees	$1,800				
carbon canisters (water treatment to sewer)	$7,000				
lab costs	$18,000				
Total	**$154,000**	**$154,000**	**$23,600**	**$23,600**	
Cost Savings	**$130,400**				

Part V

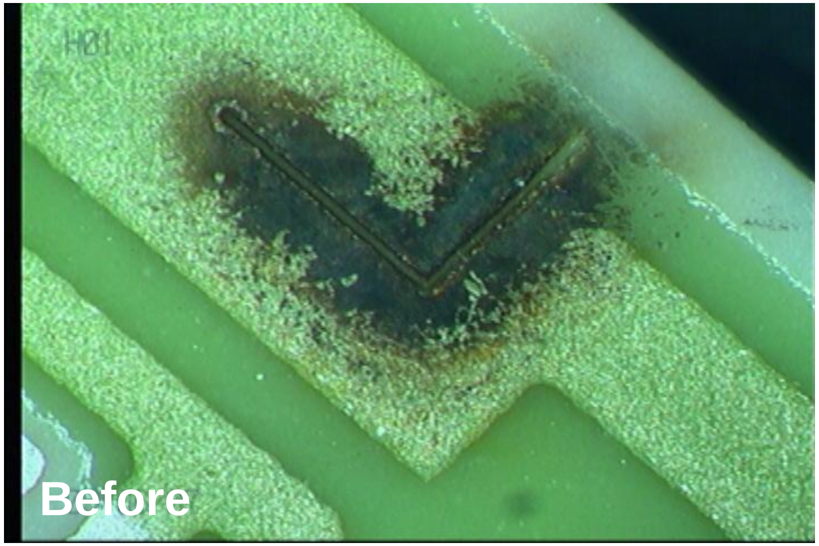
CO_2 Applications (and Performance)

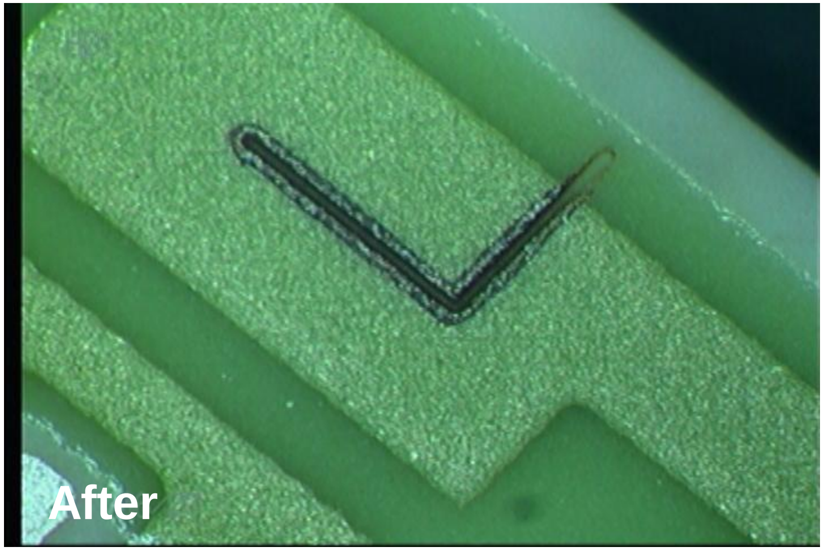


CO_2 applications…

Ceramic Circuit Board

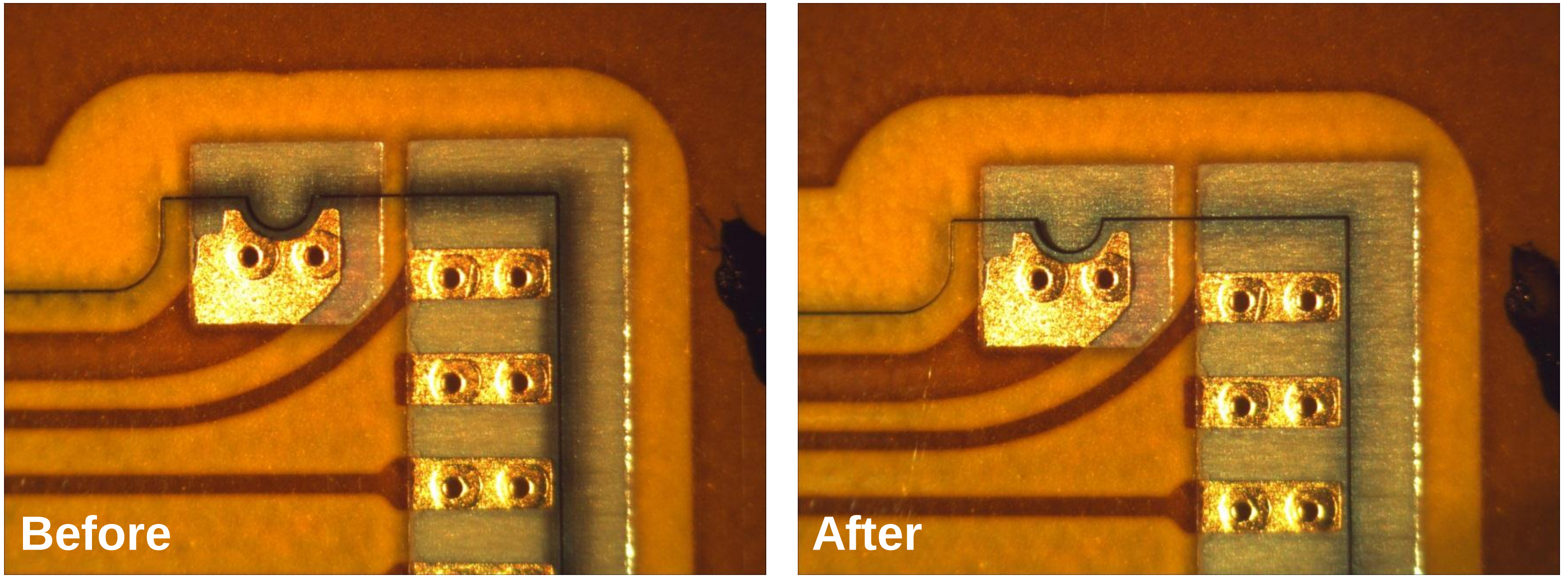
Laser Processing Debris Removal





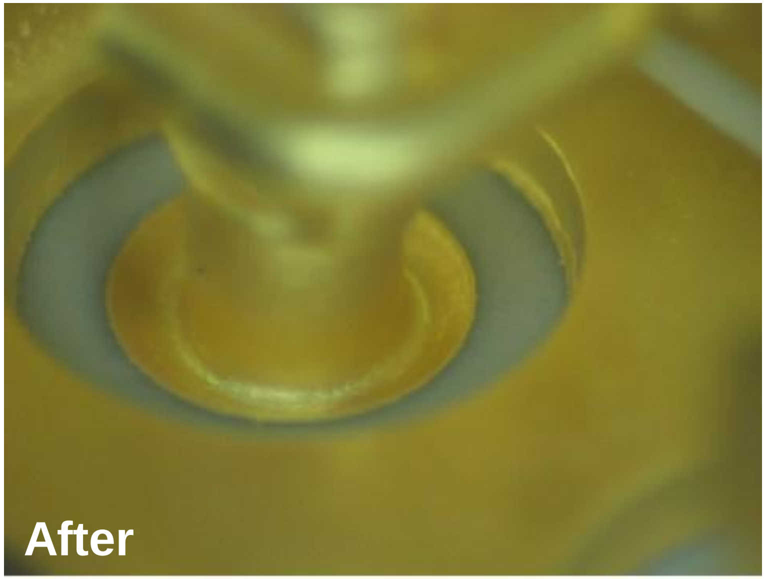
CO_2 applications…

Flexible Circuits
Laser Cutting Residue Removal



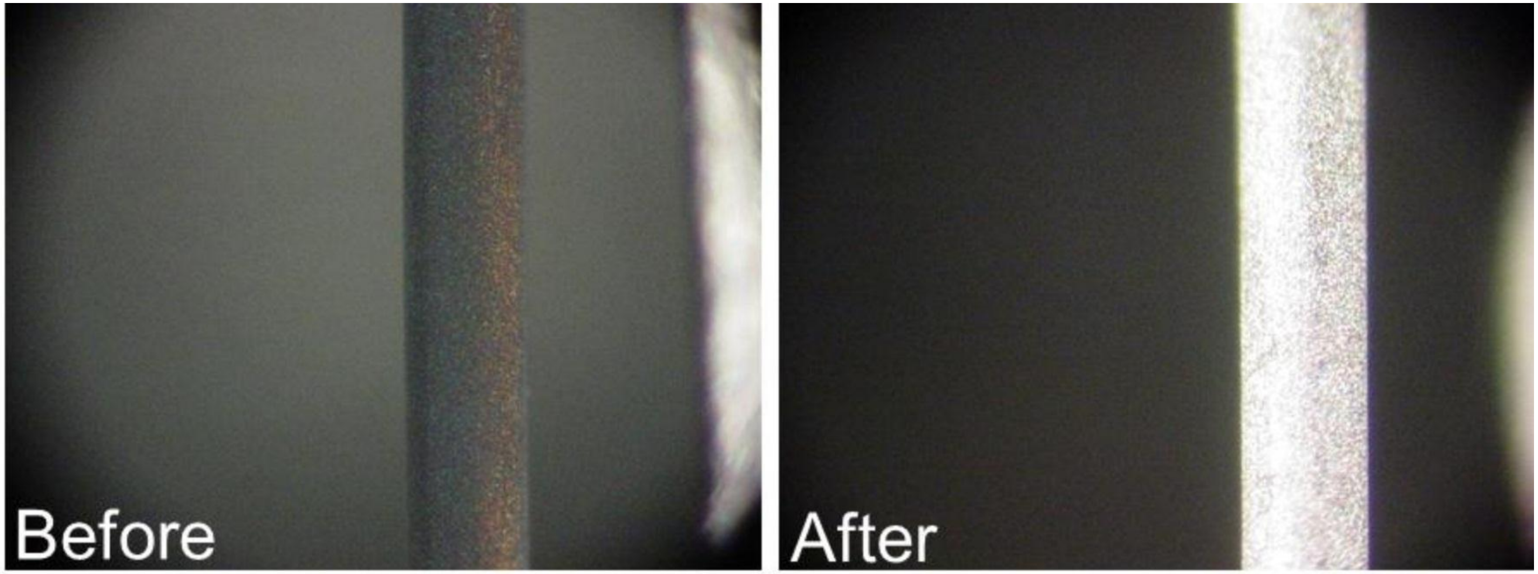
CO_2 applications…

Microelectronic Device
Laser Brazing Residue Removal



CO_2 applications…

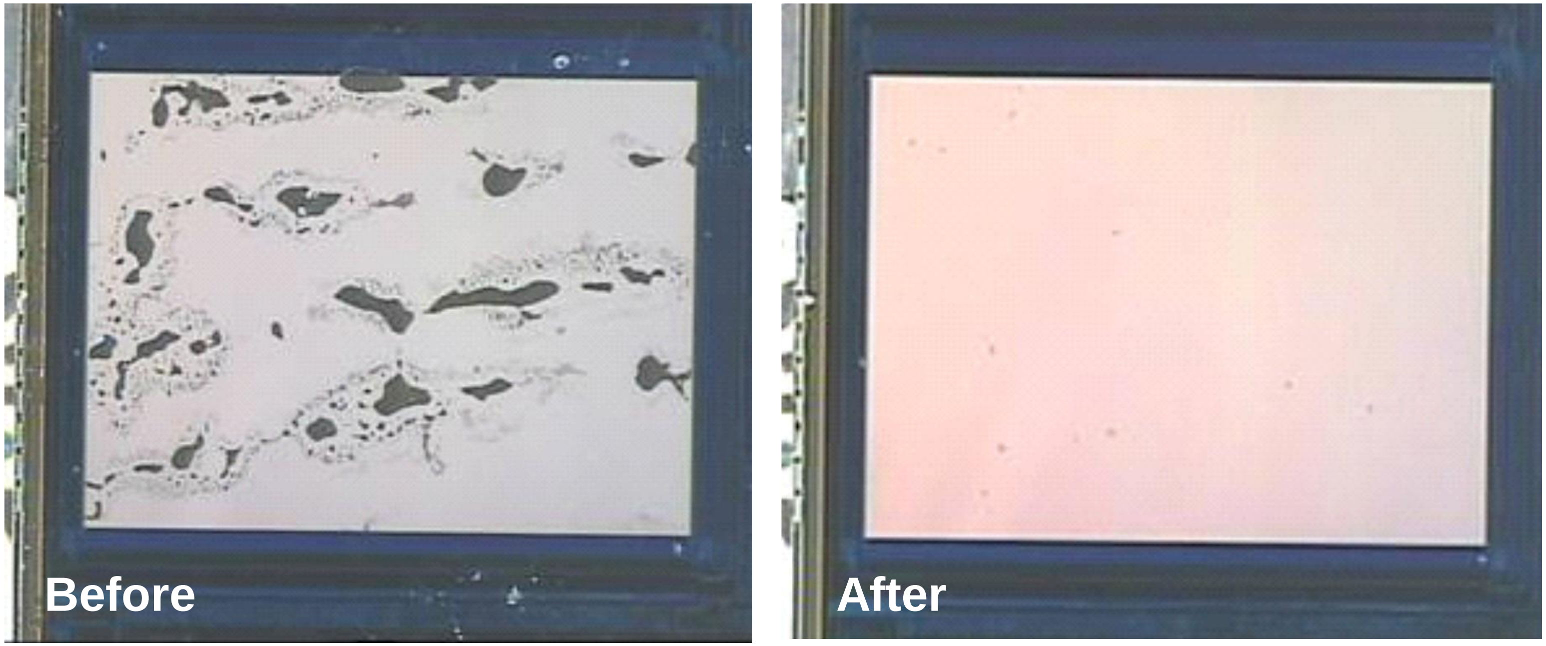
Titanium Leads
Laser Welding - Alloy Oxide Removal



Ti-Mx → TiO_2-MOx (soot)

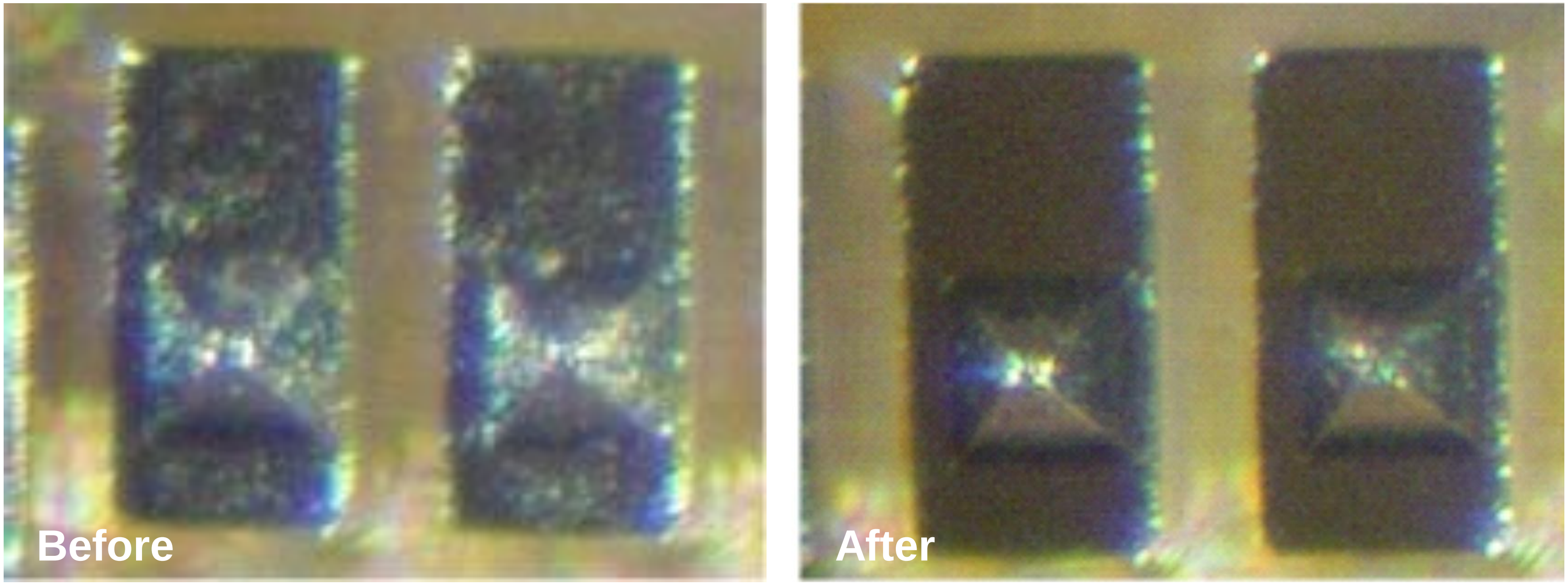
CO_2 applications…

CMOS Image Sensor
Fingerprint Removal



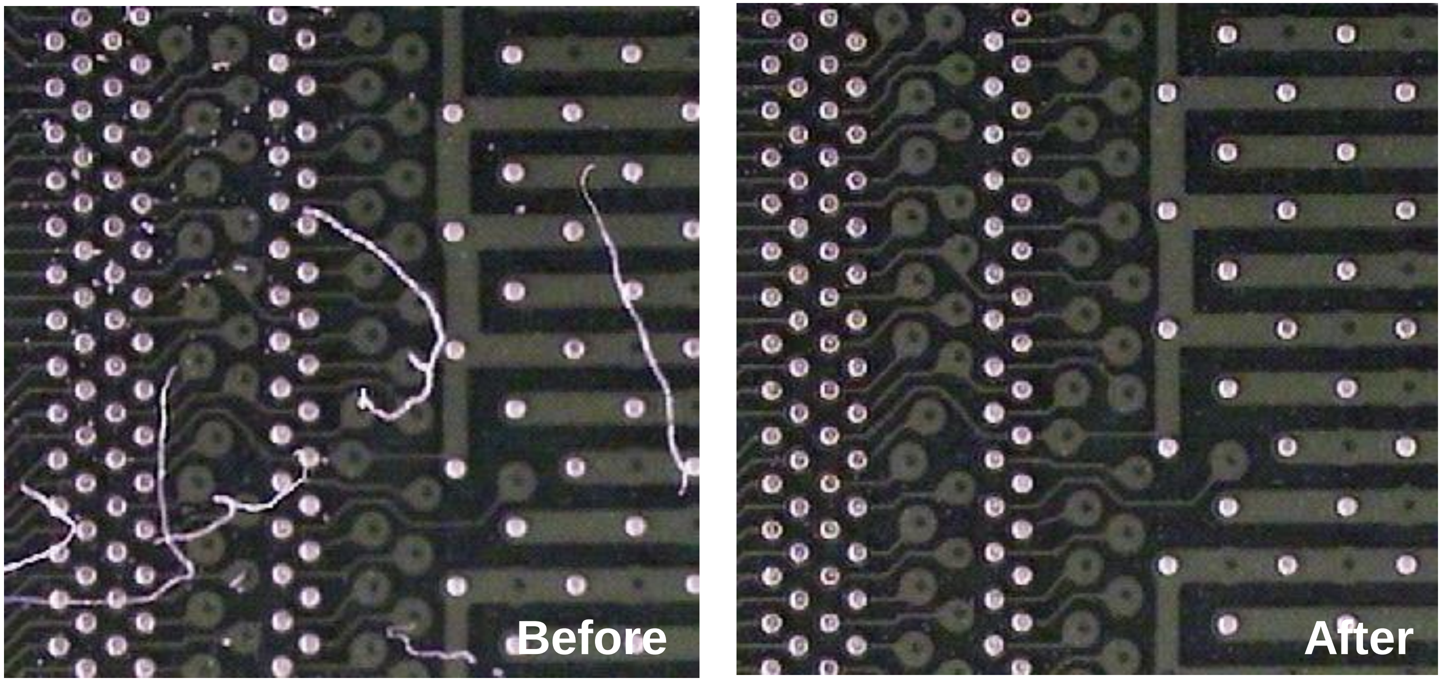
CO_2 applications…

Probe Card Contacts
Aluminum Metal/Oxide Removal



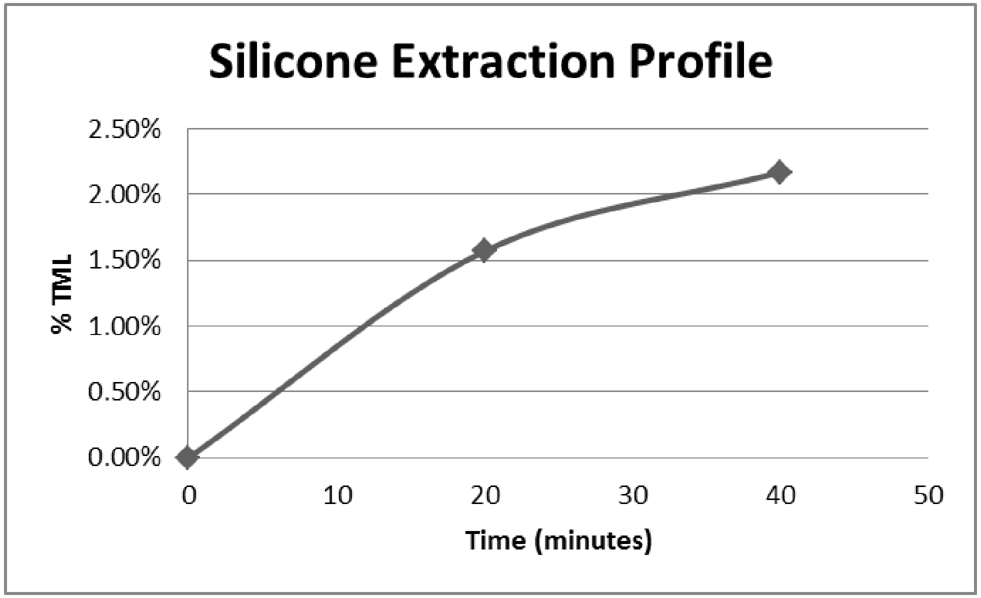
CO_2 applications…

Circuit Board
Manufacturing Debris Removal



CO$_2$ performance…

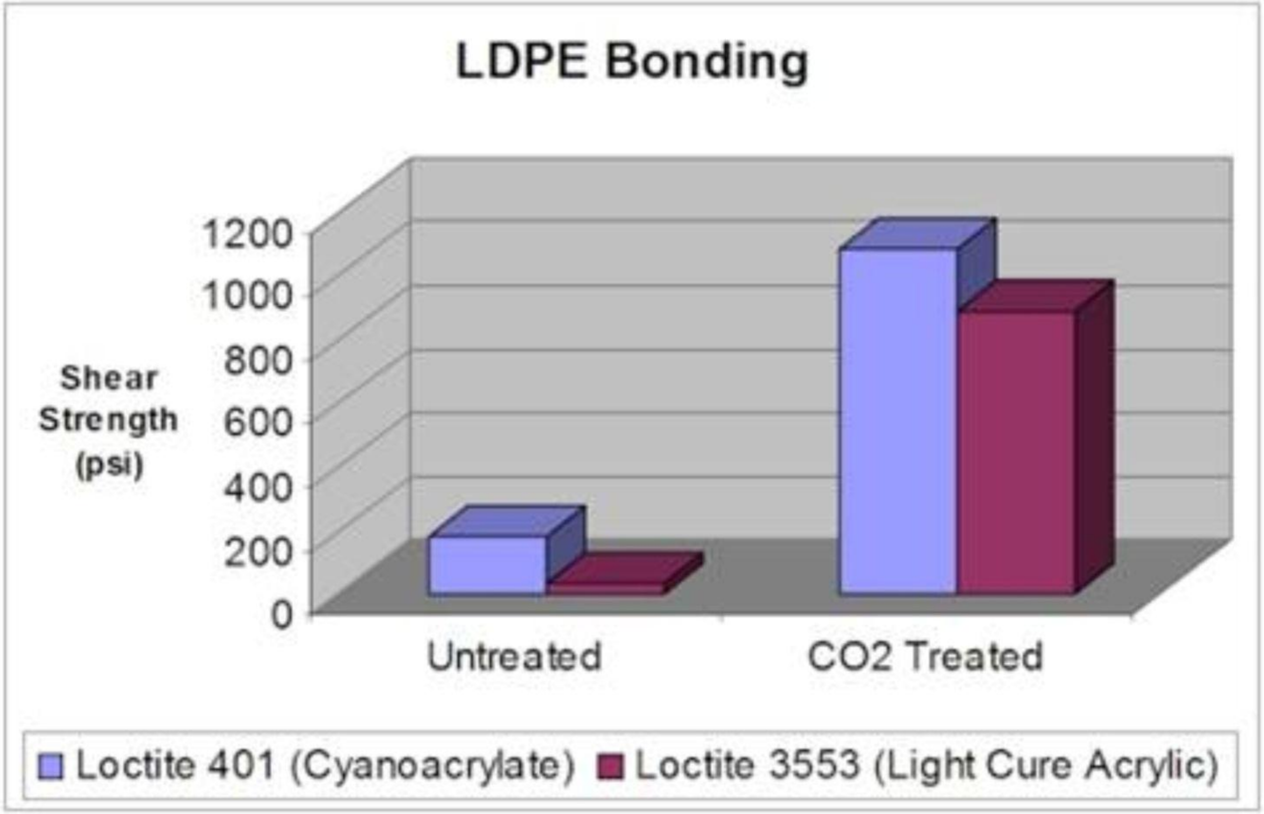
Spacecraft and Cleanroom Cabling
Silicone Oil Removal



Silicone Rubber ZZ-R-765	Before	After
Hardness (A)	44	48
Tensile Strength (PSI)	758	834
Elongation (%)	345	411
Compression (%)	3.4	10.6

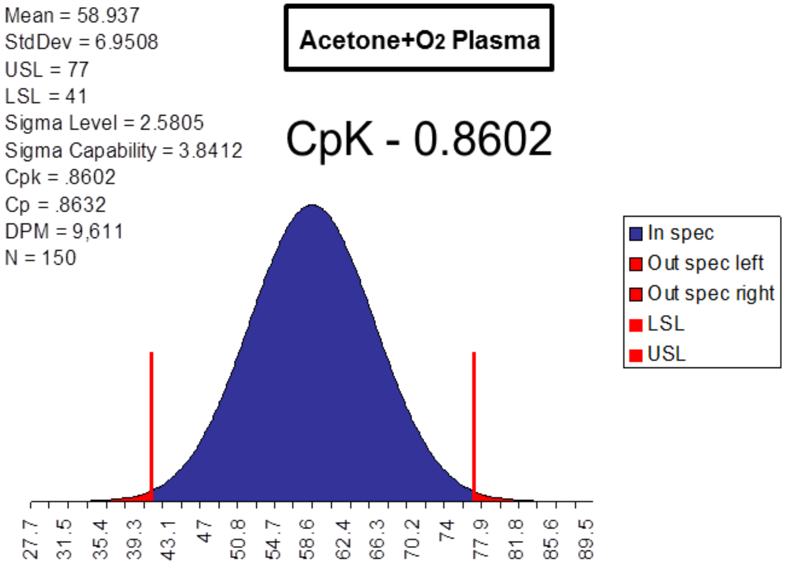
CO_2 performance…

Low Energy Polymer
Surface Cleaning and Activation



CO_2 performance…

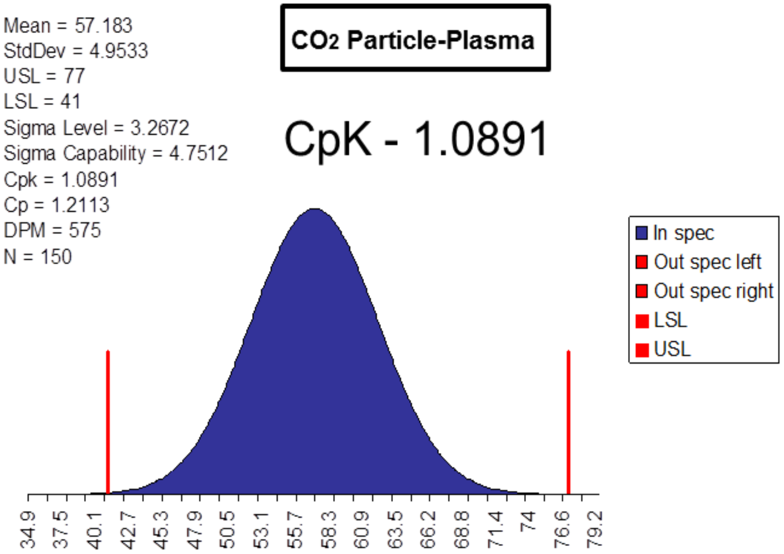
Wire Bonding
Case Study
(IPC Paper)



Acetone+O2 Plasma

Mean = 58.937
StdDev = 6.9508
USL = 77
LSL = 41
Sigma Level = 2.5805
Sigma Capability = 3.8412
Cpk = .8602
Cp = .8632
DPM = 9,611
N = 150

CpK - 0.8602



CO2 Particle-Plasma

Mean = 57.183
StdDev = 4.9533
USL = 77
LSL = 41
Sigma Level = 3.2672
Sigma Capability = 4.7512
Cpk = 1.0891
Cp = 1.2113
DPM = 575
N = 150

CpK - 1.0891

Statistically significant evaluation determined that the 1-step CO_2 cleaning process was as good as a 4-step solvent and plasma treatment process…

CO_2 performance…

Device	Application	Performance
Flip Chips	 Defluxing for underfill	JEDEC Level 3 testing, no delaminating, acoustic microscopy
Bearings	 Degreasing for repack	Visually clean under blacklight
Connectors	 Extraction for space	Meet NASA TML/VCM spec
Wipers	 Extraction for cleaning	Removal of organic/ionic extractables to BDL/Soxhlet)
Ball Points	 Cleaning for assembly	Removal of machining oils and particles to < 1.6 ug/part

Questions?

Contact:
David Jackson
CLEANLOGIX
david.jackson@cleanlogix.com

For more detail and discussion, please refer to IPC paper entitled:

CO$_2$ Clean Manufacturing Technology for Electronic Device Fabrication