

CRITICAL CLEANING IN PRECISION MANUFACTURING

Understanding the most

Plasma Cleaning

environmentally friendly

industrial

cleaning method

in use today.

of

Medical Devices

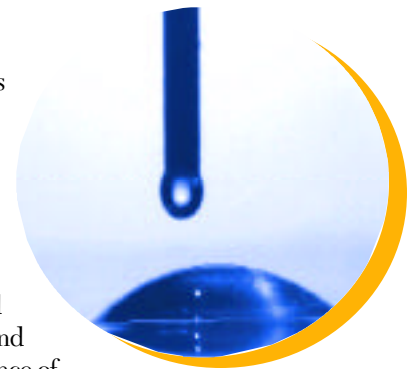
One of the trends affecting the medical device industry is the tightening of already stringent health and safety regulatory guidelines. A concurrent trend is the increasing design complexity of devices used in invasive medical procedures. Consideration of these trends is the impetus for medical device manufacturers to implement the latest technologies in contamination removal.

To most patients, the cleanliness of medical devices begins and ends at whether or not the “things” about to enter their bodies are free from “germs.” But to the medical device manufacturer, cleanliness is a far more complex issue. Not only is there concern about microbial contamination, but there is also the need to eliminate contaminants originating from manufacturing processes. These contaminants include, but are not necessarily limited to, cutting or polishing fluids used in machining, adhesives used to join polymer subassemblies, mold release agents, polymer processing aids, carbon residues from laser drilling and cutting, and airborne contamination from the factory environment. The presence of these contaminants on a finished medical device can negatively impact its biocompatibility to result in patient inflammation, infection, and systemic allergic responses.

Fouling of devices with even low levels of any of the above-mentioned contaminants can affect subsequent manufacturing processes as well, resulting in problems of adhesion, bonding or surface derivatization. The presence of surface films or particles, for example, interferes with the bonding of different parts in a medical device, and can lead to unacceptable levels of device failure. Thus, cleanliness of medical devices is critical not only for patient safety but also for manufacturability.

Conventional Cleaning Processes

Conventional cleaning processes generally employ wet chemical techniques. Of these, the gentler approach is the use of aqueous surfactant solutions to dissolve organic and inorganic contaminants. Acids are also used to assist cleaning and to etch bonding surfaces. Unfortunately, despite the use of aggressive surfactants, highly purified



deionized water¹, and several rinses, the solutions often leave residues in place of the original contamination. The new problem is to now remove the cleaner!

The use of organic solvents overcomes some of the limitations of aqueous systems but introduces a different set of problems. Medical devices made from polymers that are sensitive to organic solvents can deform and lose the close tolerances needed for proper operation. While organic systems tend to leave fewer residues than aqueous systems, trace amounts of the solvent can cling and, consequently, lead to adverse device biocompatibility. While requiring considerably less energy to evaporate than its aqueous counterpart, organic systems pose environmental hazards that must be addressed at a prohibitive cost.

for air and water sanitation, it has enjoyed less success in medical device cleaning because the high temperatures associated with the process are harmful to sensitive biomaterials.

Another alternative that not only offers better results but also does it consistently without device damage is low temperature or “cold” plasma cleaning .

What Is Plasma?

Plasma can be defined as a partially or wholly ionized gas with a roughly equal number of positively and negatively charged particles. Some scientists have dubbed plasma the “fourth state of matter” because while plasma is neither gas nor liquid, its properties are similar to those of both gases and liquids.³ An example of naturally occurring plasma is lightning. A familiar form of artificially generated plasma is the fluorescent light.

Plasma is artificially generated using a high voltage, high temperature arc, which is the basis for the corona discharge process and for the plasma torch used to vaporize and redeposit metals (Figure 1) .

To ionize the gas stream, most plasma system manufacturers use energy fields whose frequencies (13.56 MHz or 2.45 GHz) are in either the radio or microwave segment of the frequency spectrum, respectively. International agreements set these frequencies to prevent use of sources that could interfere with communication bands worldwide.

When gas atoms are ionized, the collision of high energy particles knocks electrons out of their orbits. This results in very reactive free electrons as well as the characteristic “glow” or light associated with plasma. Gas plasma’s activated species include atoms, molecules, ions, electrons, free radicals, metastables, and photons in the short wave ultraviolet (vacuum UV or VUV) range.

Under atmospheric pressure, the ionized gas is very hot and reactive. It could thus become extremely damaging to devices. Low temperature plasma processing is preferred for most industrial cleaning and surface treatment applications.

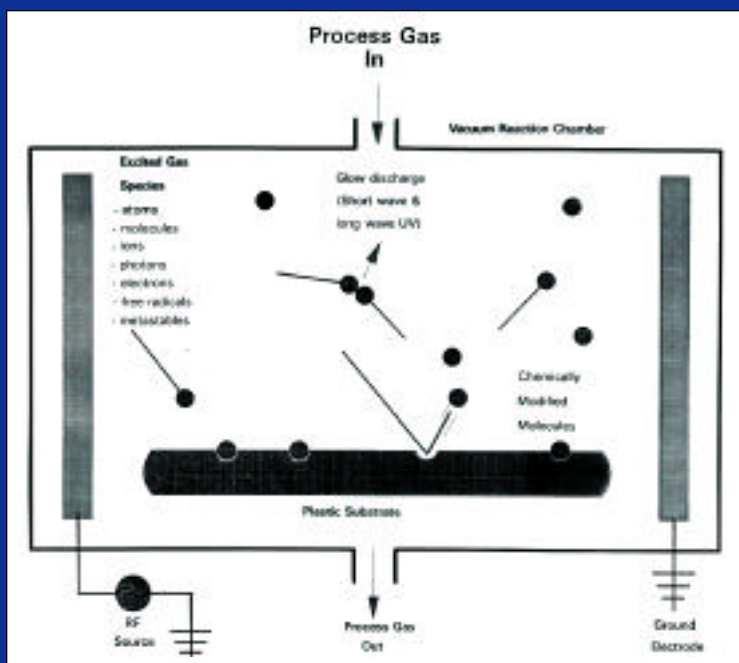
Low temperature plasmas are generated in closed reactors (Photo 1) at low pressures, typically 0.1 to 2.0 Torr. The low pressure results in a long free path of accelerated electrons and ions. While individual electrons have temperatures that can approach 100,000° K, the temperature of the ions and neutral particles remains relatively low between a few hundred to 1000° K. Because there are so few of these particles in a vacuum, the overall reactor temperature is close to ambient.

How Does It Clean?

If the gas used is oxygen, the plasma is an effective, economical, environmentally safe method for critical cleaning.⁴ The VUV energy is very effective in the breaking of most organic bonds (i.e., C-H, C-C, C=C, C-O, and C-N) of surface contaminants. This helps to begin to “chip apart” high molecular weight cont-

Figure 1.

Schematic of plasma processing within the plasma reactor.



When wet chemical methods are ineffective in the removal of tenacious contaminants, sonication may be used to assist the cleaning process. The residual contamination, waste handling, and device damage problems associated with wet chemical techniques remain.

Some manufacturers have turned to high-tech alternatives to achieve maximum cleanliness. One of these techniques is **corona discharge** , a process by which high voltage electricity is discharged into an air stream, producing high densities of Ozone (O₃). Ozone is a powerful oxidizing agent that essentially oxidizes the surfaces of the medical devices.² In the medical device industry, corona discharge is most often used as a method to enhance bonding; outside the industry, it is most commonly employed to purify air and water. Unfortunately, while the process is effective

aminants. A second cleaning action is carried out by the activated oxygen species (O_2^+ , O_2^- , O_3 , O , O^+ , O^- , ionized ozone, metastably-excited oxygen, and free electrons). These species combine with organic contaminants to form H_2O , CO , CO_2 , and low molecular weight hydrocarbons.⁵ These compounds have relatively high vapor pressures and are consequently evacuated from the chamber during processing, leaving a clean surface. Several independent tests have been conducted in industry and academia that show that increases in several orders of magnitude of particulate and gaseous emissions could be tolerated without exceeding government mandated or recommended limits. In most cases, the oxygen plasma does not affect the medical device substrate.⁶

Should the device consist of easily oxidized materials such as silver or copper, inert gases such as argon or helium are used. The activated atoms behave like a molecular sandblast and can break down organic contaminants. These contaminants are then vaporized and evacuated from the chamber during processing.

Whether or not organic removal is complete can be assessed with either Electron Spectroscopy for Chemical Analysis (ESCA, **Table 1**)⁵ or more conveniently via contact angle measurements (**Photo 2**).³ When an organic contaminant is present, the contact angle of water with the device will be high. After the removal of the contaminant, the contact angle will be reduced to that characteristic of contact with the pure substrate.

Plasma cleaning requires optimization of a number of inter-related variables, most notably gas species, pressure, time in reactor, nature of substrate and contaminant, and power. For instance, a device might be extremely heat-sensitive and it might therefore be desirable to minimize power input. While lower power densities will result in negligible device heating and do indeed remove contamination, overall organic removal can be impeded. While the top layers of organic material are removed, the underlying layers may be encouraged to crosslink in three dimensions to create a stable contaminating structure.³ Thus, a series of experiments designed to optimize processing conditions is recommended.

Advantages of Plasma Cleaning

Plasma cleaning of critical devices offers a number of advantages to medical device manufacturers. Chief among these is the fact

Photo 1.

Industrial scale plasma reactor.



that plasma cleaning leaves no organic residue. Since the process is effective at near-ambient temperature, no damage to most heat-sensitive biomaterials is expected.

Plasma treatment affects only the contaminants or near surface of treated substrates and does not change the bulk material properties.^{6,7} When combined with an initial aqueous cleaning step to remove any inorganic deposits, plasma processing can achieve complete contamination removal. Additionally, plasma exhibits no surface tension restrictions. While surface tension constraints can prevent aqueous cleaners from getting into small holes, plasma can easily penetrate small areas within the surface.

In addition to contaminant removal, plasma cleaning can result in surface modification since the ionized species interact with the device substrate in a number of ways. Oxygen plasma can lightly oxidize the substrate, giving the surface a hydrophilic character that is essential for many adhesives.

Plasma etching or **ablation** refers to the removal by evaporation of surface material. The plasma breaks covalent bonds of the polymer backbone by bombardment with the high-energy particles. As long molecules become shorter, their volatile oligomers and monomers boil off ("ablate") and are swept away with the exhaust. Plasma etching is used to roughen the surface consisting of polymer films or carbon deposition to improve bonding properties.^{8,9} Specific etching profiles can be developed using combinations of gas, pressure, power, and flow to match different etching criteria.

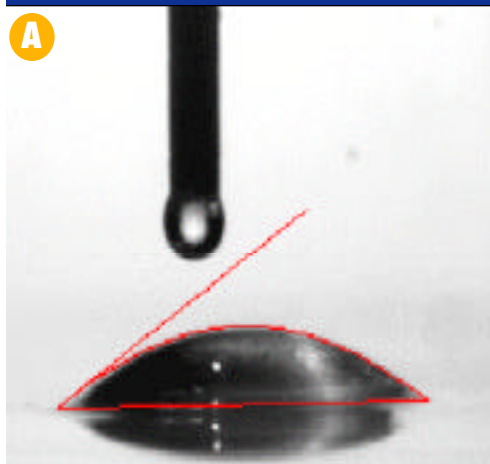
Table 1.

Using ESCA to assess contaminant removal.

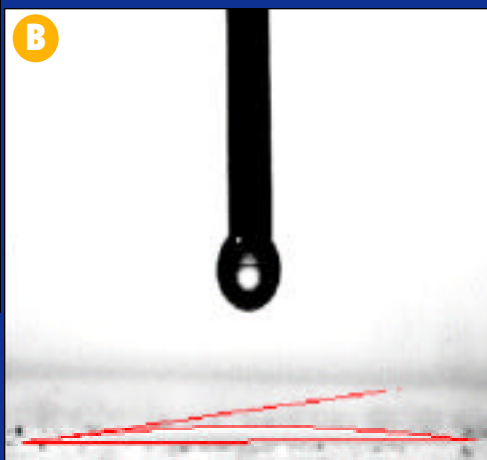
Cleaning Process	Atom % Carbon by ESCA
Control (contaminated stainless steel sample)	88
5 min. sonication in non-ionic surfactant	47
5 min. O_2 plasma	38
5 min. sonication in non-ionic surfactant + 5 min. in O_2 plasma	35
5 min. sonication in non-ionic surfactant + 5 min. in Ar/O_2 plasma	27

Photo 2.

Using contact angle to assess contamination removal.



A. Aluminum coupon with cutting oil contamination before plasma cleaning (contact angle = 57.54°).



B. Aluminum coupon with cutting oil contamination after plasma cleaning.

energy vacuum pumps and sophisticated process controls) and construction material costs. Since operating costs are not excessive, amortization of the capital expense may prove to be more attractive than the costs of other more conventional processes.

Conclusion

While the medical device industry continues to drive its manufacturers to higher and higher standards of cleanliness, many of the conventional cleaning options result in unacceptable levels of contamination. Plasma cleaning of medical devices, while still a relatively new approach to contamination removal for this market, offers advantages that far outweigh any disadvantages.

Another benefit of plasma cleaning is its safety. With short processing time, no hazardous chemicals, and no liquid waste disposal, plasma cleaning is an efficient and cost effective alternative to wet cleaning.¹⁰ The EPA has classified most plasma processes as “green” processes. It can even be said that plasma cleaning is the most environmentally friendly process currently in use.

Plasma processing is highly reproducible. Thus, the reliability required by the regulatory agencies is achievable. While not under the oversight of the FDA, the semiconductor industry nevertheless imposes stringent standards of cleanliness on its products. Plasma cleaning has been used successfully in that industry for many years.^{9,10}

Plasma technology has also been used for the disinfecting and sterilization of medical devices.¹¹ A search of Internet patent databases revealed more than 50 recent patents that used this particular technology. A simultaneous cleaning and sterilization step is very attractive to manufacturers. Additionally, plasma sterilization may be appropriate for medical implants and devices that are sensitive to high temperatures (autoclaving), chemical (ETO sterilization), or radiation (gamma sterilization).

Disadvantages of Plasma Processing

Most of the drawbacks to plasma processing are related to a high initial capital equipment investment (high

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