Supercritical Carbon Dioxide: A Non-Aqueous Cleaning Agent in Surface Preparation of Polymers by Increasing the Surface Energy

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ABSTRACT

Supercritical CO_2 is an organic solvent with all the desired chemical properties for micro to nano level cleaning that makes it one of the best non-aqueous cleaning agents. Its chemical stability, non-flammability, non-toxicity and low cost makes it very useful in today's industry. In this case, FTIR and Particle Counter microscope studies showed that supercritical CO_2 when accelerated along with a propellant stream (compressed air stream) under optimized thermodynamic parameters effectively cleans a surface specifically polymers at nano level. Several studies showed its role in raising surface energy as well. In this paper, the main goal is to demonstrate the cleaning capabilities of supercritical CO_2 and its role in increasing the surface energy when combined with plasma in polymers for surface preparation prior to painting or applying adhesives for reliable and long-lasting results.

INTRODUCTION

Supercritical CO_2 cleaning has been proven one of the best non-aqueous cleaning in wide-range of industries in past few decades. Unlike many organic solvents, supercritical CO_2 is non-flammable. It is inert, non-toxic, has a relatively low cost and has moderate critical constants. Its solvation strength can be fine-tuned by adjusting the density of the fluid. [1] As mentioned by Dorothy Lozowski, [1] this "green solvent" is an attractive alternative in place of traditional organic solvents. CO_2 is not considered a Volatile Organic Compound (VOC). Although CO_2 is a greenhouse gas, if it is withdrawn from the environment, used in a process, and then returned to the environment, it does not contribute to the greenhouse effect. [1] Using supercritical CO_2 and passing it through a compression chamber increases its pressure and temperature, and then a sudden expansion as dictated by Joule's Thomson, lowers its temperature drastically creating hard subcooled particles commonly known as 'dry ice particles'. These hard particles then get accelerated by a hot propellant stream, in this case a compressed air stream. This introduction of propellant stream gives two benefits to the dry ice particles, first it inserts extra kinetic force on the dry ice particles and increases their velocity, and second, it raises the temperature of solid dry ice particles and converts these particles into fine and sharp dry ice 'bullet particles' (BPs). This physical property helps these BPs to transfer their kinetic energy to the surface at collision. It also weakens the bonds between contaminants and the surface, shovels out the 'contaminant particles' (CPs) and sublimes quickly, leaving behind the surface clean and aqueous-free.

This contact of Bullet Particles (BPs) with the surface, not only cleans the surface by breaking down the bonds between contaminants and the surface but also increases the surface energy(γ). In the bulk solids, the cohesive forces between the atoms tend to balance as the atoms are evenly embedded. As temperature increases, the atoms start vibrating more. This vibration reduces the cohesive force binding the atoms. The surface energy (γ) depends on the net inward cohesive force, so surface energy (γ) decreases with an increase in temperature. [2] Having contamination on the surface also indicates a lower surface energy (γ). The contaminant particles change the balance of forces and reduce the net inward force that is directly proportional to the surface energy (γ) [2] as shown by a study conducted by T. Frolov and Y. Mishin in FIG. 1. [3] This indicates that higher temperatures decrease the surface energy, that decreases the bonding capability of that surface and vice versa which is not desirable in surface preparation for applying any adhesives. The most reliable technique to measure the surface energy is through wettability. The surface energy (γ) of the solid substrate directly affects how well a liquid wet the surface. The wettability, in turn, is easily demonstrated by contact angle measurements. The contact angle is the angle between the tangent line at the contact point and the horizontal line of the solid surface. If a substrate has a low surface energy, its wettability is poor and coating adhesion very scarce, and then needs a surface treatment to increase energy. When plasma gas is discharged on the polymer, effects of ablation, crosslinking and activation are produced on its surface. [4]

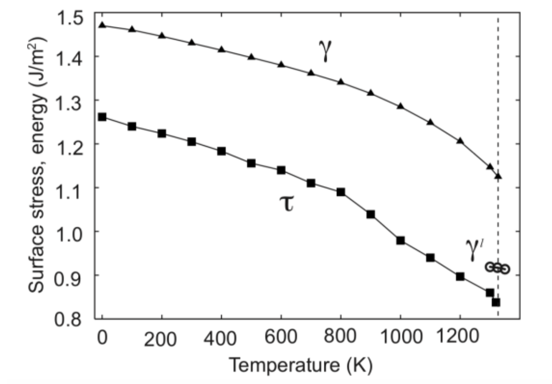

FIG. 1.

This technique has been proven very effective over the series of experiments. A Corona Plasma Generator was used to raise the surface energy along with supercritical CO_2 and proved to be a very effective combination for maximum performance and reliability.

MATERIALS AND METHODS

To achieve the best cleaning results, supercritical CO_2 by itself is not sufficient enough. The surface where the contaminant particles (CPs) are bonded by weak Van der Waals forces or in some cases strong hydrogen bonds, low temperature helps in breaking the bonds. For this very natural bond property, Dry Ice Bullet Particles play a very vital role in this technology. Dry CO_2 particles have a very low temperature of -109.3°F or -78.5°C that weakens the bonds between CPs and the surface dramatically. It also requires high speed particles that also holds super solvent properties to break these bonds and wipe off these CPs from the contaminated surface.

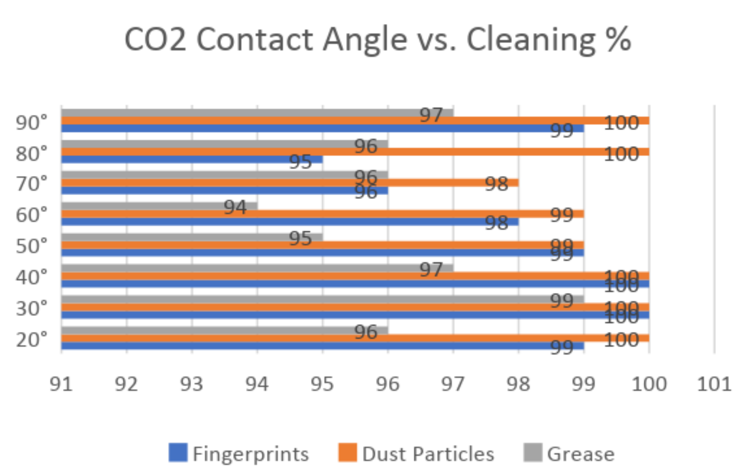

FIG. 2

The CO_2 cleaning nozzle and the supercritical CO_2 cleaning operational unit "M2" model, has been designed specifically to enhance the physical parameters like **temperature** of CO2 and the Propellant (Air)**,** **pressure** of CO2 and the Air, **velocity** of the outlet stream, and the **geometry** of the nozzles to maximize the yield. To design an efficient system or an efficient nozzle, all these parameters mentioned above have to be kept in mind. With all the optimizations and appropriate equipment, a perfect supercritical CO_2 cleaning module "M2" was developed. CO_2 gas is used as an input in the M2 unit. After series of experiments, it was found that the best cleaning result was obtained at around 30° nozzle to surface angle as shown in FIG. 2.

A series of experiments was conducted to prove the effectiveness of supercritical CO_2 cleaning for some daily based contaminants like fingerprints, dust particles and grease at different angles. Although all the results were positive, but from optimization point of view, cleaning at 30° turned out to be the most optimum cleaning angle. To validate the cleaning results, several optical and digital techniques have been used. Partsens particle counter is for solid particle counts and detection. It uses reflective light properties to count the particles up to 1000 microns. FTIR techniques were also used to detect contamination on the surface and validate the cleaning. To increase the surface energy, a portable Plasma Corona generator was used. Most of the experiments were integrated using KUKA robot arm KR-6 for better optimization. A full running system has 10 jets of subcooled CO_2 coming out of the nozzle manifold as shown in FIG. 3.

FIG. 3: M2 Cleaning Effector with CO_2 Streams

RESULTS

The cleaning validation has been done several times at different labs in different environments using different techniques. Each time the result was in favor of supercritical CO_2 cleaning. One of the experiments focused on CO_2 cleaning for plastic car parts. For that, some car parts were ordered from Honda motors and some were ordered from Subaru. First these parts were placed under traditional cleaning techniques using power wash and tack cloth for surface preparation. Later, these parts were placed under supercritical CO_2 treatment and the results were perfect. As shown in the graphs below (FIG. 4 & 5), the effectiveness of supercritical CO_2 cleaning is very clear.

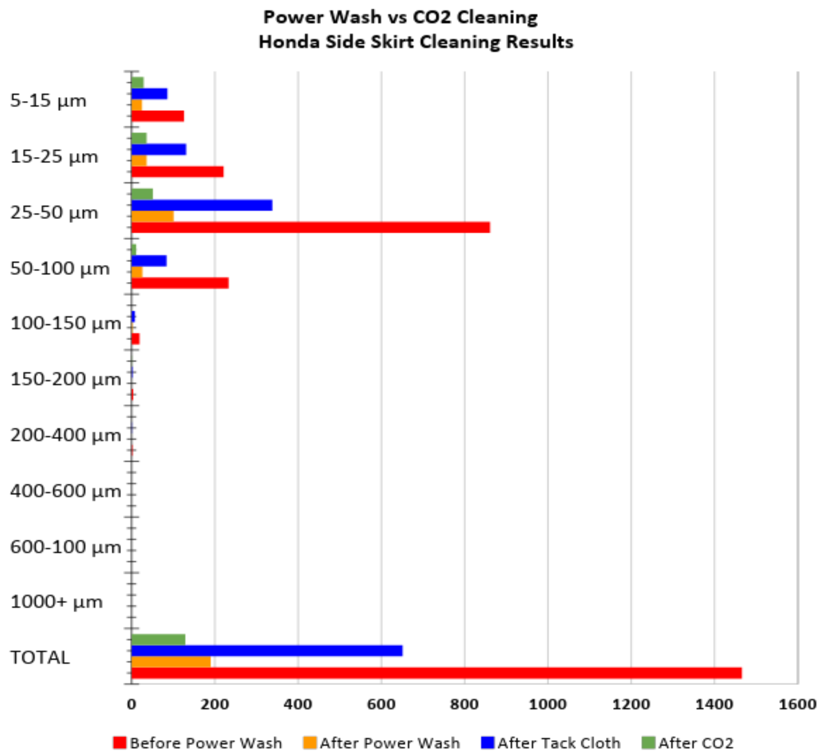

FIG. 4: Particle count for traditional cleaning vs. CO_2 cleaning for HONDA side skirts plastic parts

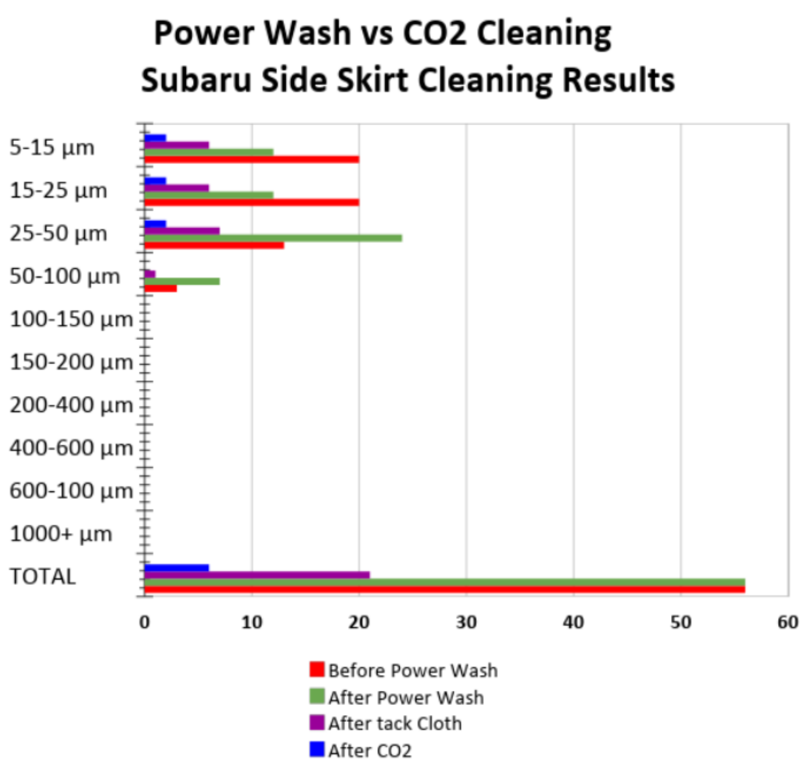

FIG. 5: Particle count for traditional cleaning vs. CO_2 cleaning for Subaru side skirts plastic parts

Another series of experiments were conducted where plastic parts were removed fresh from boxes and then stored for one day in normal ambient conditions and then cleaned with traditional Power Wash System, and then compared it with CO_2 cleaning. The data showed once again how effective supercritical CO_2 cleaning is and how much time and cost integrated CO_2 cleaning saves.

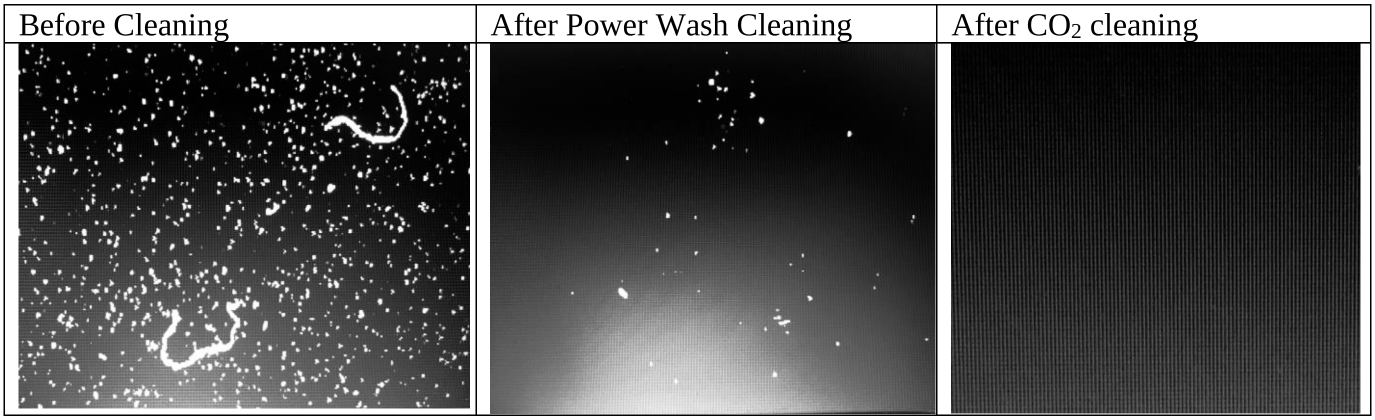

FIG. 6 Partsens Microscope Particle Counter images before after supercritical CO_2 cleaning

Following is a table showing the data points collected before and after cleaning. Partsens particle counter was used to validate CO_2 cleaning in this experiment.

Condition	**100-150 µm**	**150-200 µm**	**200-400 µm**	**400-600 µm**	**600-1000 µm**	**1000+ µm**	**TOTAL PARTICLES OVER 100 µm**
Fresh from Mold	35	12	13	8	7	1	76
Stored one day	273	61	39	6	3	2	384
After Prep	1014	287	183	38	22	10	1554
After Power Wash	69	16	6	2	3	0	96
After CO_2 cleaning	***1***	***0***	***0***	***0***	***0***	***0***	***1***

Table 1: Data points collected before and after cleaning using a Particle Counter

After the validation of CO_2 cleaning, the next step was taken towards proving how effective supercritical CO_2 is along with plasma to raise the surface energy of non-reactive surfaces like polymers. For this purpose, several tests were conducted with the collaboration of BTG Labs where they used their Surface Analyst™that instantly measures contact angle to determine the potential adhesive strength of bonds. In these experiments, first a plastic surface was observed using the wettability test that measures the contact angle by putting a water droplet on the surface. Then the same surface was treated with CO_2 alone, then a wire brush alone and then Plasma alone. These iterations indicated clearly that the order of increasing surface energy was with the following,

$$\text{Wire Brush} < CO_2 < \text{Plasma}$$

After treating the surface with these possible materials, a matrix was developed that included all possible combination of these three materials, wire brush, CO_2 and plasma. It can be seen from the following graph that CO_2 with plasma was the most optimum combination to raise the surface energy as shown in FIG. 7.

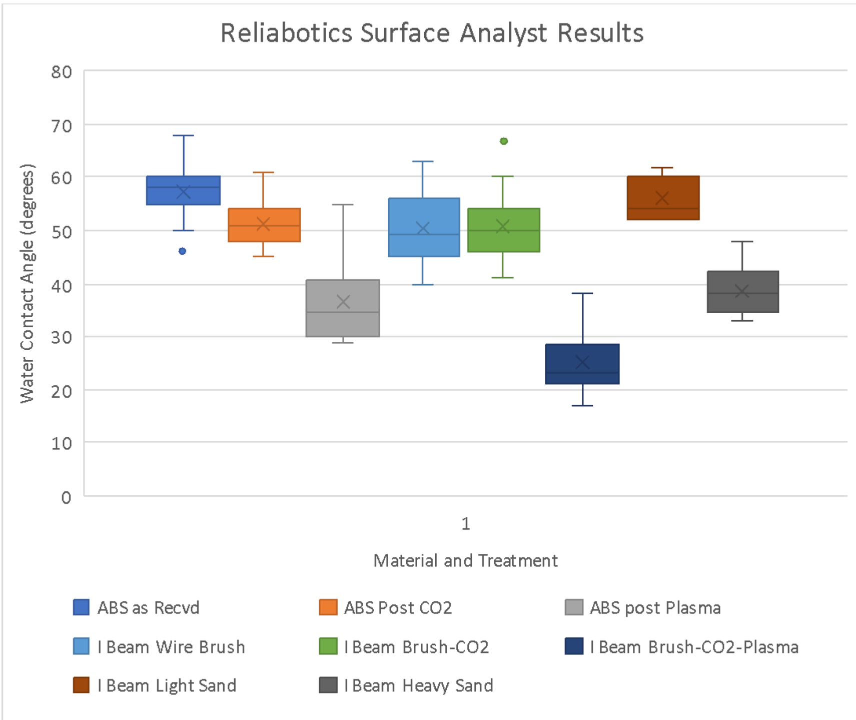

FIG. 7 Water contact angles using supercritical CO_2, Plasma, Wire brush and their combinations

CONCLUSION

After treating different plastic surfaces such as Polypropylene(PP), Polyurethane (PUR), Poly-Vinyl-Chloride (PVC), ABS, Polyamide (PA), Polystyrene (PS), Polyethylene (PE) and POM (polyoxymethylene) with a wide range of contaminants such as organic oils, molds, dust particles, ethylene glycol, grease etc., it was proved that supercritical CO_2 cleans the surface perfectly and without damaging or changing any chemistry. It can also be concluded from series of experiments and studies that supercritical CO_2 along with Plasma/Corona prepares a non-reactive surface like polymers for adhesive and paint bonding by raising their surface energy.

Several repeated experiments have also shown that the optimized supercritical CO_2 cleaning system M2 developed by RSTG is the most advanced and most economical CO_2 cleaning system. It utilizes at least 5x less CO_2 than any other CO_2 cleaning system and its full integration makes it one of the most accurate and optimized non-aqueous cleaning system in the world today.

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