



CHAPTER 3

CLEANING PROCESS AND MANUFACTURING PROCESS

3.1 CARBON DIOXIDE (CO₂)

Carbon dioxide, CO₂, is one of the gases in our atmosphere, being uniformly distributed over the earth's surface at a concentration of about 0.033% or 330 ppm. Commercially, CO₂ finds uses as a refrigerant (ft ice is solid CO₂), in beverage carbonation, and in fire extinguishers. In the United States, 10.89 billion pounds of carbon dioxide were produced by the chemical industry in 1995, ranking it 22nd on the list of top chemicals produced. Because the concentration of carbon dioxide in the atmosphere is low, it is not practical to obtain the gas by extracting it from air. Most commercial carbon dioxide is recovered as a by-product of other processes, such as the production of ethanol by fermentation and the manufacture of ammonia. Some CO₂ is obtained from the combustion of coke or other carbon-containing fuels.



Carbon dioxide is released into our atmosphere when carbon-containing fossil fuels such as oil, natural gas, and coal are burned in air. As a result of the tremendous worldwide consumption of such fossil fuels, the amount of CO₂ in the atmosphere has increased over the past century, now rising at a rate of about 1 ppm per year. Major changes in global climate could result from a continued increase in CO₂ concentration.

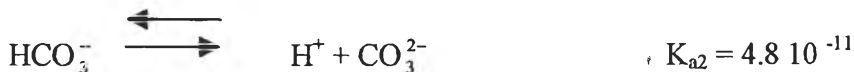
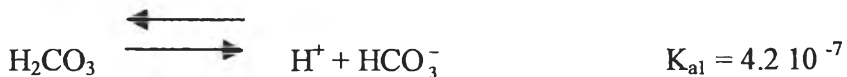
In addition to being a component of the atmosphere, carbon dioxide also dissolves in the water of the oceans. At room temperature, the solubility of carbon dioxide is about 90 cm³ of CO₂ per 100 mL of water. In aqueous solution, carbon dioxide exists in many forms. First, it simply dissolves.



Then, equilibrium is established between the dissolved CO₂ and H₂CO₃, carbonic acid.



Only about 1% of the dissolved CO₂ exists as H₂CO₃. Carbonic acid is a weak acid, which dissociates in two steps.



As carbon dioxide dissolves in seawater, equilibrium is established involving the carbonate ion, CO₃²⁻.

The carbonate anion interacts with cations in seawater. According to the solubility rules, "all carbonates are insoluble except those of ammonium and Group IA elements." Therefore, the carbonate ions cause the precipitation of certain ions. For example, Ca^{2+} and Mg^{2+} ions precipitate from large bodies of water as carbonates. For CaCO_3 , the value of K_{sp} is 5×10^{-9} , and for MgCO_3 , K_{sp} is 2×10^{-3} . Extensive deposits of limestone (CaCO_3) and dolomite (mixed CaCO_3 and MgCO_3) have been formed in this way. Calcium carbonate is also the main constituent of marble, chalk, pearls, coral reefs, and clamshells.

Although "insoluble" in water, calcium carbonate dissolves in acidic solutions. The carbonate ion behaves as a Brønsted base.



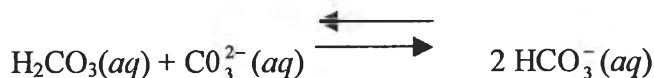
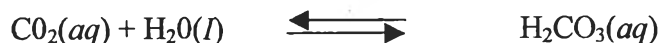
The aqueous carbonic acid dissociates, producing carbon dioxide gas.



In nature, surface water often becomes acidic because atmospheric CO_2 dissolves in it. This acidic water can dissolve limestone.



This reaction occurs in three steps.

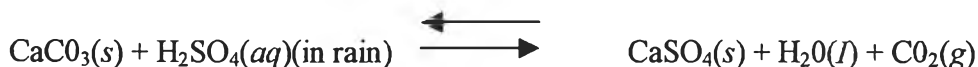


In the third step, carbonate ions accept hydrogen ions from carbonic acid. This reaction often occurs underground, when rainwater saturated with CO_2 seeps through a layer of limestone. As the water dissolves calcium carbonate, it forms openings in the limestone. Caves from which the limestone has been dissolved are often prevalent in areas where there are large deposits of CaCO_3 (e.g., Mammoth Cave, Carlsbad Caverns, and Cave of the Mounds). If the water containing dissolved Ca (HCO_3)₂ reaches the ceiling of a cavern, the water will evaporate. As it evaporates, carbon dioxide escapes, and calcium carbonate deposits on the ceiling.

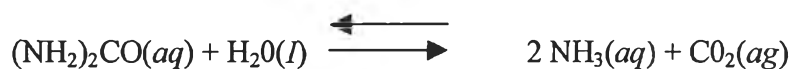


Similar chemical reactions are also responsible for the erosion of marble and limestone monuments of historical and cultural importance, such as the Taj Mahal in India, the

Mayan temples in Mexico and Guatemala, and the Rock Churches of Ethiopia. Here, the acid involved is likely to be H_2SO_3 or H_2SO_4 , formed when the atmospheric Pollutants SO_2 and SO_3 dissolve in rainwater. The carbonate stone is damaged by the conversion of the relatively insoluble carbonate to the more soluble sulfate.



The calcium sulfate is eroded away as it slowly dissolves in rainwater (the K_{sp} of CaSO_4 is 3×10^{-5}). The life of these monuments is now being extended by treating them with a mixture of barium hydroxide, $\text{Ba}(\text{OH})_2$, and urea, $(\text{NH}_2)_2\text{CO}$. This mixture soaks into the porous marble or limestone. Gradually, the urea decomposes to ammonia and carbon dioxide.



This carbon dioxide combines with the barium hydroxide to form barium carbonate.



Barium carbonate is more resistant to erosion because it is less soluble than calcium carbonate. For BaCO_3 the K_{sp} is 2×10^{-9} . Furthermore, barium sulfate is even less soluble, with a K_{sp} of 1×10^{-10} . When barium carbonate on the surface of the treated monument reacts with sulfur dioxide in the air, it forms a layer of barium sulfate, which protects the monument.

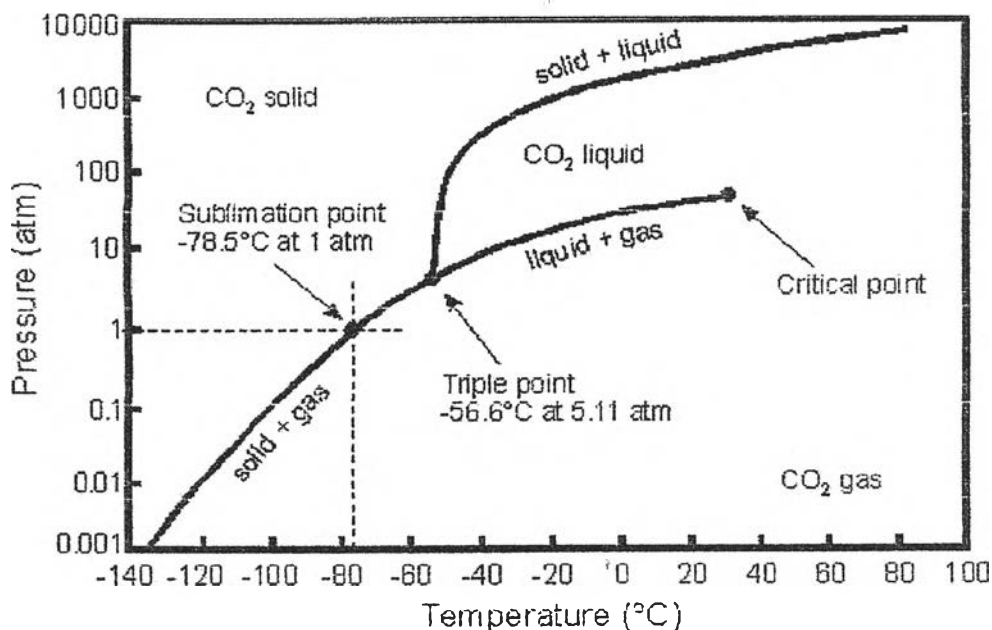


Figure 8 illustrated Pressure-Temperature Phase diagram for CO_2

Source : <http://scifun.chem.wise.edu/chemweek/CO2/CO2.html>

A new use for liquid carbon dioxide currently under development is as a dry-cleaning solvent. Currently, most laundries use chlorinated hydrocarbons as dry-cleaning solvents. These chlorinated hydrocarbons are probable human carcinogens, so the search is on for replacements. Carbon dioxide does not exist in liquid form at atmospheric pressure at any temperature. The pressure-temperature phase diagram of CO₂ shows that liquid carbon dioxide at 20°C requires a pressure of 30 atmospheres. The lowest pressure at which liquid CO₂ exists is at the triple point, namely 5.11 atm at -56.6°C. The high pressures needed for liquid CO₂ require specialized washing machines. Like chlorinated hydrocarbons, liquid carbon dioxide is an effective solvent for grease and oils. Liquid CO₂ has some advantages over chlorinated hydrocarbons--items that cannot be dry cleaned with chlorinated hydrocarbons, such as leather, fur, and some synthetics, can be safely cleaned with liquid carbon dioxide.

Physical and Chemical Properties of CO₂

Molecular Formula	CO ₂
Molecular Weight	44.01
Appearance and odor	(1)Gas: colorless; odorless. (2)Liquid: volatile; Colorless; odorless.
Density	
-Solid	97.5189 lb/ft ³ @-109.3° F
-Liquid	63.69 lb/ft ³ @ 0° F
-Gas	0.1234 lb/ft ³ @ 32° F
Specific Gravity	1.522 at 21.1°C and 1 atmosphere
Melting Point	-69.9° 75.1 psia
Boiling Point	-109.3° F volatile
Triple Point	-69.9° F 75.1 psia
Critical Temp	87.8° F
Critical Press	1069.4 psia
Critical Pressure	28.9519 lb /ft ³
Viscosity	
-Liquid	0.14 Centipoises (0°F)
-Gas	0.015 Centipoises (32° F)
Thermal Conductivity	
-Liquid	0.11 Btu ft / ft ² F hr (0° F)
-Gas	0.0085 Btu ft / ft ² F hr (32° F)
Surface Tension	8.23 Dynes / cm (0° F)
Solubility in Water	1.79 ft ³ CO ₂ / ft ³ H ₂ O (32° F)
(P ^H)	3.7

Table 4 illustrated Physical and Chemical Properties of CO₂.

Source :*Condensed Chemical Dictionary*

3.2 Snow formation

Thermodynamics of CO₂ Snow Formation

The carbon dioxide phase diagram 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. See figure 9 for reference.

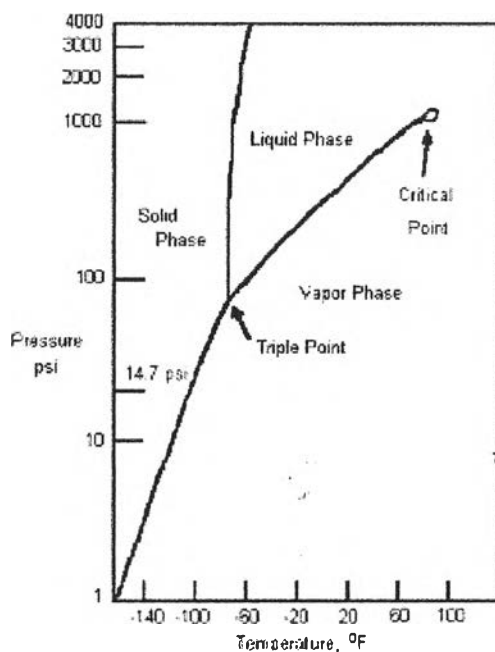


Figure 9 illustrated gas, liquid and solid phase boundary.

Source : <http://www.co2clean.com/snowform.htm>

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.

The key physical property of the Carbon Dioxide system is its excellent solvent properties 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. Please note, 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.

The phase diagram tells us little regarding dry ice formation or aid in understanding organic removal process; instead, the CO₂ pressure – enthalpy diagram below provides insight to the phase changes that occur during snow formation. The features include the same 3 phases along with the region of pressure and enthalpy where these phases co-exist. These regions were phase boundaries in the above figure. In using this diagram, it is imperative to understand that the expansion of CO₂ through an orifice is ideally a constant enthalpy process. Therefore, as the pressure drops in an orifice, the pressure decreases vertically along a constant enthalpy line.

Carbon Dioxide Pressure-Enthalpy Diagram

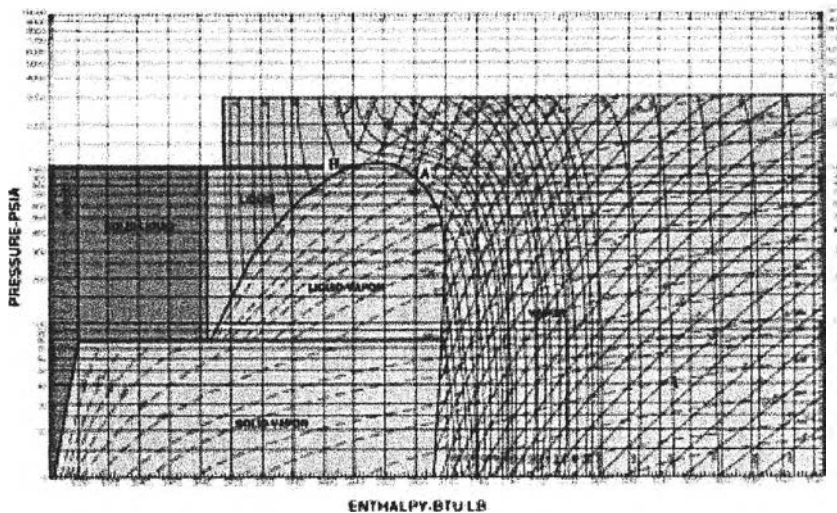


Figure 10 illustrated Carbon Dioxide Pressure-Enthalpy Diagram.

Source : <http://www.co2clean.com/snowform.htm>

A CO₂ cylinder filled with liquid CO₂ at room temperature has a gas pressure of about 800 psi. above the liquid. The enthalpy available to the cylinder contents are those values in the liquid-gas two phase region at about 800 psi., in the spots labeled "A" for the gaseous CO₂ and "B" for liquid CO₂. As the gas or liquid enters the orifice, the pressure drops from these two points with constant enthalpy values (under ideal conditions) into the two phase liquid-gas region.

With a gas fed source (starting from point A) as the pressure drops in an orifice, liquid droplets nucleate and the percentage of liquid increases. At the interface between the liquid-gas and gas-solid regions (near 80 psi.), all the liquid converts to solid - yielding about 6 % dry ice. With a liquid fed source (starting at point B) as the pressure drops in the orifice, gas bubbles form and the percentage of gas increases until the gas-solid boundary is met. Here, the remaining liquid is transformed into solid - yielding about 45% dry ice. The percentage of snow depends on the chosen feed phase and is influenced

by the source pressure and temperature. This diagram gives us information on the initial and final states and the phase changes that occur during snow formation and cleaning. Actual dry ice size, velocity, and percentage formed are based upon the above considerations and also orifice and nozzle designs.

From the above, we see that snow cleaning can be done with either a liquid or gas CO₂ source. Each feed has its advantages and disadvantages. Gas fed systems 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 produce more snow, allow for faster cleaning, but at a higher consumption rate. If the cleaning is occasional or a "small" area, a gas feed system is recommended, while for continuous high speed leaning or large areas, a liquid source is recommended.

In our snow cleaning equipment, we chose the asymmetric Venturi nozzle design for our nozzles. This selection maintains the constant enthalpy conditions the longest, yielding more snow, maximize velocity, and a focused cleaning stream. Please note that straight tube nozzles violate the constant enthalpy condition and usually do not produce adequate snow unless the orifice diameter is larger. This is quite dramatic with gas fed sources. With liquid fed sources, it is also seen at small orifice diameters. This limitation implies an inherent inefficiency in the straight tube designs.

3.3 CO₂ Snow Cleaning Technology

Figure 11 is a phase diagram for CO₂, which shows that CO₂ exists as a low-density gas at standard temperature and pressure (STP) conditions.

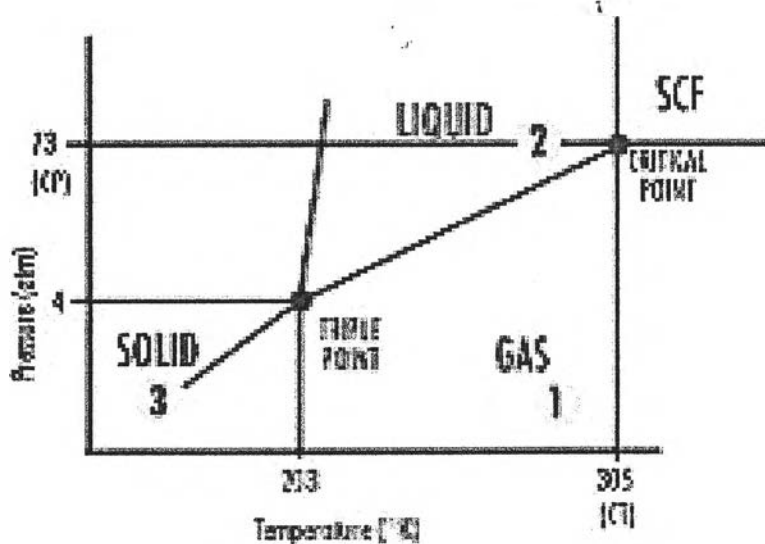


Figure 11 illustrated phase diagram for CO₂

Source : <http://www.precisioncleaningweb.com>

Compressing CO₂ at a temperature and pressure just below its critical temperature liquefies the gas at approximately 60 atmospheres. Cooling liquid-state CO₂ to below its triple point (the conditions of temperature and pressure under which a liquid, solid, and gas coexist in equilibrium) causes a phase transition to solid-state CO₂. The solid-state density is approximately 1.6 g/cm³. The resultant substance resembles a powdery, white spray-or “snow” –as it is propelled through the air.

Cleaning Media Hardness

One way to describe the physical characteristics of solid-state cleaning agents is through a comparison of hardness values. Media hardness, in combination with mass and velocity, determine the aggressiveness of the cleaning action. One scale used to describe the hardness of solid cleaning media is Moh’s 10-point scale of Hardness, where 1 is a talc-like substance and 10 is diamond.

In a comparison between solid CO₂ and common abrasive cleaning agents, solid CO₂ has the lowest hardness value (2 Mohs) of all solid cleaning agents, which make it an ideal choice for solid-state cleaning of sensitive substrates.

Cleaning Action: Theories on Separation

Media separation is analogous to solid-state CO₂ cleaning. It entails the removal of a contaminant from a substrate by the forceful impact of small solid CO₂ particles, either dry or mixed with a small quantity of liquid or another solid additive.

Unlike immersion cleaning, solid-state cleaning action is highly directional, and contaminant removal is line-of-sight in nature. The type of cleaning action, energy, and efficiency-whether removing polymeric coatings or removing hydrocarbon residues-is determined by particle density, particle speed, and substrate topography. Particulate CO₂ cleaning is very useful for removing small particulates and trace organic residues from substrates; palletize CO₂ cleaning is useful for coating removal.

The cleaning power offered by solid-state CO₂ can also be described in terms of physical and chemical traits, including kinetic energy transfer, viscous drag, cohesion energy, and electrostatic energy transfer mechanisms described below.

Kinetic Energy Separation

Carbon dioxide snow is able to remove small particles from a surface through a kinetic energy transfer process called “linear momentum transfer.”

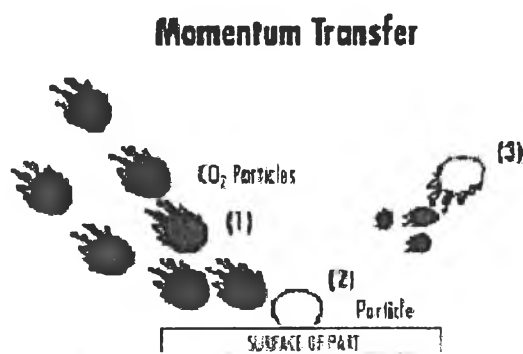


Figure 12 illustrated how a stream of solid CO₂ particles

Source : <http://www.precisioncleaningweb.com>

(1) imparts a significant mass and velocity on a stationary surface particle (2), causing the surface particle to accelerate away from the surface (3).

Viscous Drag Separation

The energy required to remove small particles rises exponentially as the diameter of the particle decreases; consequently, sub micron particles can require an energy output of several million g-forces. This adhesive energy is a combination of gravitational, electrostatic, and molecular attraction forces between the particle and substrate. This adhesion level is also influenced by energy interactions between the particle and substrate coatings (e.g., hydrocarbon films or other viscous surface coatings) and physical entrapment within complex surface topography.

The fluid velocity parameter contributes the most significant impact on viscous drag. Fluid velocities rapidly decrease from turbulent flow (high energy) to laminar flow (low energy) close to the surface. This is where small particles “hide out.” To overcome this energy barrier, commonly called “the wall,” high fluid velocities must be achieved (Figure 13)

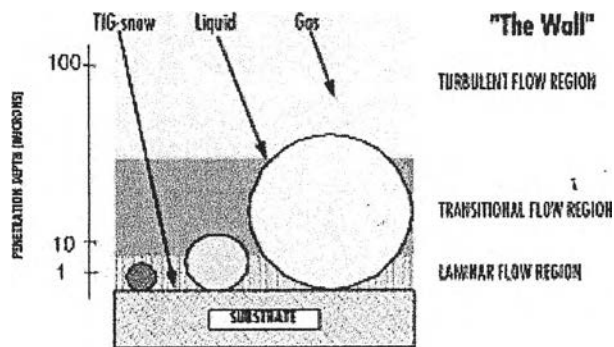


Figure 13 illustrated the methods by which CO₂ snow cleaning overcomes the energy barrier created by a rapid drop in fluid velocity.

Source : <http://www.precisioncleaningweb.com>

Higher surface fluid velocities (and fluid mass) increase fluid flow from laminar to turbulent, which increases viscous drag (also called shear stress) on the particle. The higher the near-surface fluid velocity, the more energy is delivered and hence the smaller the particle that can be dislodged. As show in the figure, TIG snow cleaning can offer better particle removal compared with conventional high-pressure spray cleaning applications (using Freon or other liquid solvents) and high-pressure blow-off gases. Microscopic snow particles have significant density and can penetrate completely through the laminar flow region, impacting the surface at high velocity.

Given that the viscous drag force parameters-density, particle surface area, and coefficient of drag-are similar between conventional liquid cleaning agents and snow, high snow velocity at the surface produces much higher viscous drag on surface particle. As a result, snow particle energy is usually sufficient to overcome very strong electrostatic and intermolecular adhesive forces, commonly referred to as Van der Waal's forces that hold small particles to the surface.

Chemical Separation

Trace organic films on surfaces can also be removed using solid CO₂; however, the mechanism by which this is accomplished is not fully understood. It has been postulated to be a combination of momentum transfer and a phase change of minute solid CO₂ particles from solid state to liquid state. This results in rapid microsoluting of trace surface residues in liquid CO₂.

According to the phase diagram for CO₂, a minimum isostatic pressure of approximately 6 atm (88 psi) at 195 K is required to produce a liquid-solid interphase. Energy transformations are possible (other than the formation of a liquid phase), including particle fragmentation or shearing, gas phase transition, and temperature rise in the solid during impact.

In Figure 12, another chemical separation mechanism is proposed, which involves the formation of microscopic combinations of micro particulate CO₂ (1) and hydrocarbon residues (2). The snow-hydrocarbon interface is theorized to be the formation of a lyophilic crystalline gel or colloid, called "snow-gel" (3). Snow-gels are comprised of trace organic surface residues (treated as solvents or solutes) dispersed in solid-phase CO₂ particles (treated as a sub cooled solvent-solute matrix). Subsequent bombardment by micro- particulate CO₂ entrains and ejects snow-gels from the substrate.

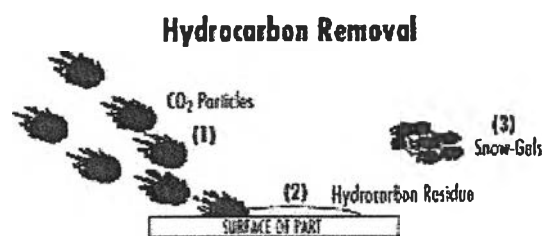


Figure 14 illustrated Hydrocarbon removal

Source : <http://www.precisioncleaningweb.com>

This proposed mechanism is supported by solubility research performed by Myers and Prausnitz⁶ in which they treated solid CO₂ (solid-state xenon has also, been studied) as a

sub cooled liquid to determine cohesive energy values. Test data showed high solubility of solid CO₂ with several hydrocarbon systems.

Solid CO₂ possesses electron acceptor (Lewis acid) and molecular quadruple moment properties, which contribute to a hydrocarbon-like cohesion energy and complex forming ability with hydrocarbons.

Electrostatic Separation

Another possible separation mechanism might involve electrostatic energy transfer. According to this theory, charged solid CO₂ particles act as electrostatic magnets," which collide and combine with small charged surface particles. The resulting interaction is an electrical charge transfer from one body to another called "electro coagulation." The coagulated particle mass is swept from the surface under continuous snow particle bombardment.

3.4 Equipment Concept Design

Very important to the CO₂ snow cleaning process is the design and application the CO₂ snow cleaning equipment. Conventional CO₂ snow cleaning is based on an expansion process where compressed CO₂, liquid is rapidly expanded to ambient pressure, creating a mixture of vapor and solid particles of CO₂. The expansion process-combined with a suitable nozzle design-accelerates the snow particle to near sonic velocities near the nozzle tip. When targeted at a substrate these high velocity projectiles remove particle contamination from the surface through momentum transfer.

Conventional CO₂ snow cleaning equipment is generally self-similar and, in many cases, additional cleaning energy is required to achieve cleanliness standards beyond the capability of conventional alternatives. A modification of the technology that employs TIG-snow offers an exclusive coaxial thrust enhancement design (Figure 3), which provides additional and controllable surface cleaning energy as well as substrate temperature and ionization control.

3.5 Return to Cleaning Technology Profiles

Carbon dioxide (CO₂) can be used in three distinct states in precision cleaning applications: in liquid form, where CO₂ acts to perform surface cleaning and degreasing; as a gas, which is ejected as "snow" from specialized nozzles; and in a "super" critical form for chemical extraction cleaning.

Carbon dioxide is a nontoxic, non-hazardous, nonflammable material, with no ozone depleting potential. CO₂ cleaning methods are commonly applied to those contaminants that dissolve in CO₂, which include most organic soils. This method of cleaning is generally not applicable to rust, scale, and most inorganic compounds.

Employing CO₂ methods in the workplace offers reduced worker exposure to hazardous chemicals, less regulatory considerations, and reduced permitting requirements. However, direct contact with CO₂ can cause skin damage (frostbite). Also, adequate ventilation should be maintained to ensure that the CO₂ does not displace oxygen necessary to breathe.

Due to cost and labor time constraints, CO₂ is generally not recommended for gross contaminant removal but is more appropriate for removing thin coatings and residues.

Liquid CO₂

Analogous to cold cleaning with liquid CO₂ (LCO₂) involves dipping contaminated parts into a cleaning chamber, where the contaminants are then dissolved. Cleaning is enhanced by the low surface tension and low viscosity of CO₂. Agitation systems can be added to increase the effectiveness of the cleaning process.

LCO₂ is effective in removing loosely bound dust, lint, fingerprints, light-to-medium hydrocarbon, oils, select particulate contamination, drawing compounds, and other machining fluids.

High pressures are needed to maintain CO₂ as a liquid (it has a boiling point of -78.5°C). Standard process equipment includes a pressure vessel, gas/liquid pumps, and a recycle system. LCO₂ systems are primarily manually based, though batch automation is possible. A cleaning cycle requires approximately 10 to 20 minutes. LCO₂ is not available as a continuous or conveyor process.

SELECTION CRITERIA

- Mechanical agitation (Ultrasonic, Megasonics, spray systems) can be used to improve the cleaning process.
- LCO₂ is ineffective in removing most inorganic contaminants.
- High pressures are required to maintain CO₂ as liquid.

CO₂ snow

With specialized nozzles, CO₂ can pass through a “triple point,” where solid, liquid, and gaseous CO₂ meet in one phase, forming snowflakes.

CO₂ snow is commonly used to remove hydrocarbon oils, fluxes, fingerprints, dust, lint, fine fibers, fingerprints and other particulates as small as 0.1 microns. Contaminant removal using CO₂ snow is performed via one of two mechanisms: momentum transfer from the solid CO₂ snow that dislodges the small, particulate matter; or the dissolution of organic oils into the liquid CO₂ formed by the instantaneous liquefaction of dry CO₂ on contact with the surface.

Operating equipment includes a CO₂ source, a nozzle, and a delivery mechanism to transfer CO₂ from the source to the nozzle. Most cleaning applications are performed by

2 to 3 second bursts with at least 10 seconds between bursts. Snow systems can be automated.

Nozzle design is a current technology focus for CO₂ snow systems. Nozzle design can affect the shape and velocity of the spray, which has to be adapted to the degree of aggressiveness needed for individual cleaning applications.

SELECTION CRITERIA

- This cleaning method is ineffective in reducing heavy oil contamination.
- The characteristics of the snow produced, which may depend on the application, are highly dependent on the nozzle design.
- CO₂ snow systems can be automated.

Supercritical CO₂

At temperatures above 31°C (87°F) and a pressure of 72.8 atmospheres, the liquid and gaseous phases of CO₂ combine to form supercritical CO₂ (SCCO₂).

SCCO₂ is the oldest CO₂ cleaning method and is used to decaffeinate coffee.

Due to its low viscosity and surface tension, SCCO₂ is able to penetrate small pores and crevices and is thus commonly used for specialized precision applications. This type of cleaning is a dissolution process: The contaminants solvate within the SCCO₂ and are evacuated into a low-pressure chamber; they then become insoluble and precipitated from the LCO₂.

SCCO₂ can remove silicon, dielectric, and machine oils, plasticizers, monomers, fluorinated oils, lubricants, and organic extractable adhesive expansion value, separator, and a condenser. Cycle times vary from 15 minutes to two hours.

Research into future applications of SCCO₂ includes design of a standard model to meet multiple needs, development of a method capable of contributing to a particle-removal mechanism.

SELECTION CRITERIA

- This cleaning method is well suited for cleaning complex parts and penetrating small pores and crevices.
- High start-up costs due to high-pressure equipment.
- Operating costs are relatively low.
- High pressures may cause damage to delicate parts and cause safety considerations.
- Cannot be used as an in-line process.