Effectiveness of Metals to Control the Pathogens in Drinking Water

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***Abstract*—Good drinking water quality is essential to the health and well-being of all people. The most serious water pollutants in terms of human health worldwide are pathogenic organisms.Oligodynamic action is the ability of small amounts ofheavy metals to exert a lethal effect on bacterial cells.Definite metals and metal compounds confer in minutequantity of water solutions the ability to change andfinally kill cells of microorganisms in a characteristic way.Many metallic elements have beenobserved to inhibit the growth of bacteria and toinactivate enzymes. Practical applicationof such activityof metals has been made in the purification of water andin the preservation of tomato juice, cider and hides. Thisantimicrobial effect is shown by metals such asmercury, silver, copper, lead, zinc, gold, aluminum andother metals, and the concentration of the metal neededfor this antimicrobial effect is extremely small.The exact mechanism of this action is stillunknown but some data suggest that the metal ionsdenature protein of the target cells by binding toreactive groups resulting in their precipitation andinactivation. The high affinity of cellular proteins forthe metallic ions results in the death of the cells due tocumulative effects of the ion within the cells. The main focus of this study is the promotionof use of oligodynamic metals such as silver and copper, to control thepathogens in drinking water.**

***IndexTerms*—Disinfectant, Heavy metals, Microorganism, Pathogenic bacteria**

I. INTRODUCTION

Pathogen-free drinking water is a priority for the safety of human health concerned with waterborne infectious diseases. Increasing urbanization has aggravated the problem of microbial contamination in most of drinking water sources resulting into outbreaks and sporadic incidences of water transmitted diseases mainly gastroenteritis, cholera, dysentery, typhoid, poliomyelitis and hepatitis. Although there are a number of popular methods such as filtration, ozonisation, reverse osmosis and UV radiation, chlorination is the most popular globally used method for drinking water disinfection, particularly in piped supplies at community level. Recent analytical studies have revealed that chlorination of water produces numerous disinfection by-products (DBPs) after the reaction of residual chlorine with natural organic compounds such as humic and fulvic acids in water. Many of such DBPs have been reported to be mutagenic/ carcinogenic. To overcome this problem, there is a pressing need to replace chlorination with a safer and appropriate alternative process.

Certain metals like mercury, silver and copper with an oligodynamic property have been found to be biocidal with the capability to disinfect the water. Among these, silver is more appropriate as it is non-toxic and an efficient water disinfectant. Silver has been known as an effective biocide against viruses, bacteria, protozoa, algae, yeasts and moulds. Silver has strength, malleability, ductility, high reflectance of light, temperature resistance and electrical as well as thermal conductivity. Silver is used for electroplating, currency, ornaments, utensils, mirror plating, sweet coating, photography, electrical/electronic instrumentation, solar energy, medical (dental) applications and scientific research. The use of pots and pitchers made up of silver for storage of drinking water is an age-old tradition which indicates that its bactericidal property was well known to our ancestors.

Oligodynamic metals, such as silver and copper, havelong been utilized as disinfectants for non-spore-formingbacteria and viruses (Thurman &Gerba 1988). Silver canserve as a disinfectant at concentrations about 1,000times lower than the toxic level to mammalian life(Warrington 1996).

II. SILVER AS DISINFECTANT

The antimicrobial effects of silver (Ag) have been recognized for thousands of years. In ancient times, it was used in water containers and to prevent putrefaction of liquids and foods. In ancient times in Mexico, water and milk were kept in silver containers. Silver was also mentioned in the Roman pharmacopoeia of 69 B.C.

In 1884, silver nitrate drops were introduced as a prophylactic treatment for the eyes of new-borns, and this became a common practice in many countries throughout the world to prevent infections caused by Neisseria gonorrhoeae transmitted from infected mothers during childbirth. In 1928, the “Katadyn Process” based on the use of silver in water at low concentrations, was introduced.

Silver ions have the highest level of antimicrobial activity of all the heavy metals. Gram-negative bacteria appear to be more sensitive than gram-positive species. Kawahara et al. posited that some silver binds to the negatively charged peptidoglycan of the bacterial cell wall. Because gram-positive species have a thicker peptidoglycan layer than do gram-positive species, perhaps more of the silver is prevented from entering the cell.

Generally speaking, the observed bactericidal efficacy of silver and its associated ions is through the strong binding with disulphide (S–S) and sulfhydryl (–SH) groups found in the proteins of microbial cell walls. Through this binding event, normal metabolic processes are disrupted, leading to cell death. The antimicrobial metals silver (Ag), copper (Cu), and zinc (Zn) have thus found their way into a number of applications.

- **APPLICATIONS AND USES**

a) **Drinking Water**

Chlorine has been used as the principal disinfectant for drinking water since the early 1900s. In the 1970s, it was discovered that chlorination caused the formation of numerous chlorinated compounds in water, including trihalo-methanes and other disinfection by-products (DPB), that are known to be hazardous to human health. There is therefore a need to assess alternative disinfectants.

Silver electrochemistry experiments suggest that silver may have potential as a chlorine alternative in drinking water disinfection in applications in which chlorine may be considered too hazardous. Silver has been used as an effective water disinfectant for many decades, primarily in Europe. It has also been used to treat recycled water aboard the MIR space station and aboard NASA space shuttles.

Both the Environmental Protection Agency (EPA) and the World Health Organization (WHO) regard silver as safe for human consumption. Only argyria (irreversible skin discoloration) occurs with the ingestion of gram quantities of silver over several years or by the administration of high concentrations to ill individuals. There have been no reports of argyria or other toxic effects caused by silver in healthy persons (World Health Organization 1996). Based on epidemiological and pharmacokinetic data, a lifetime limit of 10 grams of silver can be considered a No Observable Adverse Effect Level (NOAEL) for humans (World Health Organization 1996). In the United States, no primary standards exist for silver as a component in drinking water. The EPA recommends a secondary non-enforceable standard of 0.1 mg/L (100 ppb) (Environmental Protection Agency 2002). The World Health Organization (1996) has stated this amount of silver in water disinfection could easily be tolerated because the total absorbed dose would only be half of the NOAEL after 70 years. Silver has been used as an integral part of EPA- and National Sanitation Foundation (NSF)-approved point-of-use (POU) water filters to prevent bacterial growth. Home water purification units (e.g., faucet-mounted devices and water pitchers) in the United States contain silverized activated carbon filters along with ion-exchange resins (Gupta et al. 1998). Today, some 50 million consumers obtain drinking water from POU devices that utilize silver (Water Quality Association 2001). These products leach silver at low levels (1–50 ppb) with no known observable adverse health effects. Such filters have been shown to prevent the growth of Pseudomonas flu-rescens and Pseudomonas aeruginosa in water; however, several studies have raised questions about their efficacy. Reasoner et al. (1987) established that bacterial colonization of such devices occurs within a matter of days and may result in a large number of bacteria in the product water.

b) **Cooling Towers/Large Building Water Distribution Systems**

Cooling towers provide cooling water for air compressors and industrial processes that generate heat. They provide an ideal environment and a suitable balance of nutrients for microbial multiplication. Chlorine is a popular method for controlling such bacterial growth, but there are difficulties in maintaining disinfection efficacy, particularly at a high temperature or pH. Chlorination can also cause corrosion of cooling tower facilities.

Ag/Cu ionization has been used in cooling towers to control bacterial growth. In a study by Martinez et al. (2004), an appreciably reduced chlorine concentration of 0.3 parts per million (ppm or mg/L) was combined with 200 ppb Ag and 1.2 ppm Cu. This method had an appreciable impact on levels of coliform bacteria, iron-related bacteria, sulphate-reducing bacteria and slime-forming bacteria in a cooling tower.

Large hot water distribution systems in hospitals and hotels have also often been attributed as a source of contaminating bacteria. Contaminated systems are usually treated by either superheating the water with flushing of the distal sites (heat-flush), by hyper chlorination, or by installing Ag/Cu ionization units. Greater bacterial reductions have been observed with Ag/Cu ionization than with the heat-flush method. Ag/Cu ionization is known to provide long-term control and may be used in older buildings in which the pipes could be damaged by hyper chlorination. Such systems are easy to install and maintain, are relatively inexpensive, and do not produce toxic by-products.

One microorganism that has been commonly isolated from cooling towers is Legionella pneumophila, the causative agent of Legionnaires' disease. Many outbreaks have been linked to cooling towers and evaporative condensers. L. pneumophila is also commonly isolated from the periphery of hot water systems in large buildings such as hospitals, hotels, and apartment buildings where temperatures tend to be lower. Ag/Cu systems have been in common use in hospitals to control Legionella for more than a decade. Mietzner et al. reported that one such ionization system maintained effective control of L. pneu-mophila for at least 22 mon. Legionella may develop a tolerance to silver after a period of years, requiring higher concentrations to achieve the same effect.

c) **Recreational Waters**

Bacteria, protozoa, and viruses may occur naturally in recreational waters or be introduced into swimming pools by bathers or through faulty connections between the filtration and sewer systems. Species carried by bathers include the intestinal Streptococcus faecalis and Escherichia coli, as well as skin, ear, nose, and throat organisms such as Staphylococcus aureus, Staphylococcus epidermidis, Streptococcus salivarius, Pseudomonas aeruginosa, and Mycobacterium marinum (Singer 1990). Mild to serious illnesses caused by ingestion of or contact with contaminated water can be the result of improperly maintained pools, spas, and hot tubs.

In recent years, there has been a rapid increase in the number of public, semipublic, and private pools built in Europe and America. Adequate disinfection of such waters is becoming an increasingly important health issue. Traditionally, chlorine-based products are used for disinfection of swimming pools. Chlorine produces harmful DBPs caused by the halogenation of organic compounds

(urine, mucus, skin particles, hair, etc.) released into the water by swimmers. Thus, there is also a need for alternative disinfectants for recreational waters.
Silver (Ag_2SO_4) at a low concentration (10 ppb) has been shown to kill more than 99.9% of heterotrophic bacteria in swimming pools within 30 min. Silver has been used commercially in pools, but it is too slow to be used as a primary disinfectant. Regulatory agencies in some countries have recommended its use only in combination with another disinfectant. Electrolytic generation of Ag and Cu ions allows ppb concentrations to be maintained in a convenient and reproducible manner.

d) **Food and Dietary Supplements**

Silver has been used to treat vinegar, fruit juices, and effervescent drinks and wine. It is also available in Mexico as col-loidal silver in gelatin (‘Microdyn’) for use as a consumer fruit and vegetable wash and in the U.S. as an alternative health supplement or in silver citrate complexes as food additives.

e) **Medical Applications**

Silver has been used in numerous medical applications. In dentistry, silver nitrate is effective against a number of oral bacteria including gram-negative periodontal pathogens and gram-positive streptococci that cause. Dental amalgams contain approximately 35% Ag(0) and 50% Hg(0). It is unclear whether sufficient Ag(0) is released and oxidized to Ag(I) to produce an antimicrobial effect; however, the release of Hg(II) selects for metal-resistant bacteria. New amalgams have therefore been introduced that contain silver alone.
Silver salts have traditionally been administered to the eyes of new born infants to prevent neonatal eye. Silver ions are the most commonly used topical antimicrobial agents used in burn wound care in the Western world. Both silver nitrate and silver sulphadiazine have also been used as topical antiseptics for cutaneous wounds. A topical cream containing 1.0% silver sulphadiazine and 0.2% chlorhexidinedigluconate has been marketed as Silvazine in the U.S.

Silver sulphadiazine has recently been incorporated directly into bandages used on burns and large open wounds. Unlike silver nitrate, silver sulphadiazine does not react with sulfhydryl groups or proteins. Thus, its action is not diminished in the wound. Nevertheless, the silver is still the antimicrobial portion of the molecule. Two commercial silver-coated dressings (Acticoat and Silverdin) prevented muscular invasion by P. aeru-ginosa in experimental burns in rats. P. aeruginosa and S. aureus populations were similarly affected by Silverlon, an FDA-approved wound dressing.
Silver has also been used to coat vascular, urinary, and peritoneal catheters, prosthetic heart valve sewing rings, vascular grafts, sutures, and fracture fixation devices. Plastic indwelling catheters coated with silver compounds retard the formation of microbial biofilms. Manal et al. (1996) determined that the adherence of four strains of E. coli was decreased by 50%–99% in comparison to silicone and latex catheters. In two separate clinical studies, 10%–12% of patients with silver-treated catheters developed bacteriuria (>100 microorganisms/mL) versus 34%–37% of patients with standard Foley catheters after 3 d. The onset of bacteria was thus delayed in comparison to latex catheters. Gentry and Cope (2005) also found a 33.5% reduction in catheter-associated urinary tract infections following the introduction of silver-coated catheters.
The complex of silver with antibiotics on the surfaces of polytetrafluoro ethylene vascular grafts has been examined in a number of studies. Silver increased the elution and prolonged the duration of ciprofloxacin release in one such study.

f) **Antimicrobial Surfaces/Materials**

Silver may be added to polymers to confer antimicrobial activity. The result is consumer products such as washing machines, refrigerators, and ice machines that have incorporated silver. Silver has been added to plastics to produce items such as public telephones and public toilets (in Japan), toys, and infant pacifiers. Johnson Matthey Chemicals (UK) utilizes an inorganic composite with immobilized slow-release silver as a preservative in their cosmetics. Synthetic fabrics with silver are popular in items such as sportswear, sleeping bags, bed sheets, and dishcloths. These fabrics are believed to reduce the level of bacterial contamination and thus odors.
Silver may also be added to inorganic ceramics (e.g., zirconium phosphate, zeolite) that are able to trap metal ions and may then be added to other materials (e.g., paints, plastics, waxes, polyesters) to confer antimicrobial properties. Zeolite ceramic (Sodium aluminosilicate) has a porous three-dimensional crystalline structure in which ions can reside; it has a strong affinity for silver ions and can electrostatically bind up to 40% silver (wt/wt). Zeolites act as ion exchangers, releasing silver into the environment in exchange for other. The amount of silver released is dependent upon the concentration of cations in the environment (Kawahara et al. 2000). The bactericidal activity of Ag-zeolite appears to result from both the effect of silver ions (Matsumura et al. 2003) and the generation of reactive oxygen species, under aerated conditions, such as superoxide anions, hydroxyl radicals, hydrogen peroxide, and singlet oxygen.
Studies on stainless steel surfaces coated with zeolites containing 2.5%Ag and 14% Zn ions demonstrated significant reductions in L. pneumophila (Rusin et al. 2003), S. aureus (Bright et al. 2002), Campylobacter jejuni, Salmonella typhimurium, Listeria monocytogenes, and Escherichia coli O157:H7 (Bright KR, Gerba CP, unpublished data). Vegetative cells of Bacillus subtilis, B. anthracis, and B. cereus were also inactivated by at least three orders of magnitude within 24 hr by a Ag/Zn-zeolite whereas Bacillus spores were completely resistant under the same conditions.

- **ANTIMICROBIAL EFFICACY**

The antimicrobial effect of silver has been demonstrated in numerous and varied applications against many different types of microorganisms including bacteria, viruses, and protozoa.

III. COPPER AS DISINFECTANT

In the last few decades, work has been done on the antimicrobial properties of copper and its alloys against a range of micro-organisms threatening public health in food processing and healthcare applications. The use of copper and copper alloys for frequently touched surfaces such as door and furniture hardware, bed rails, light switches and food preparation surfaces can help limit microbial infections in hospitals and food dispensing organizations. Michel's, et al. show that increasing the copper content of alloys increases antimicrobial effectiveness. The contact killing is so rapid that the production of protective biofilms is not possible. The specific mechanism by which copper affects cellular structures is not yet proven, but the active agent of cell destruction is generally considered to be the copper ion. Recent studies showed that large amounts of copper ions were taken up by E. coli over 90 min, when cells were applied to copper coupons via an aqueous suspension (a standing drop). When cells were plated on copper using minimum liquid and a drying time of 5 seconds, the accumulation of copper ions by cells was even more dramatic, reaching a high concentration in a fraction of the time.

The copper ion level of cells remained high throughout the killing phase, suggesting that cells become overwhelmed by their intracellular copper. The grain structure of the copper material affects ion diffusion and hence affects bacterial destruction by copper ions. The US Environmental Protection Agency (EPA) registers five copper alloys with public health claims. All of the alloys have minimum nominal copper concentrations of 60%. Registration of copper and certain copper alloys such as brass and bronze means that the EPA recognizes these solid materials' antimicrobial properties. Products made from any of the registered alloys are legally permitted to make public health claims relating to the control of organisms that pose a threat to human health. Laboratory studies conducted under EPA-approved protocols have proven copper's ability to kill, within 2 hours of contact time, more than 99.9% of the following disease-causing bacteria: Staphylococcus aureus, Enterobacteraerogenes, Escherichia coli O157:H7, Pseudomonas aeruginosa, Vancomycin-resistant Enterococcus faecalis (VRE) and MRSA.

- **Copper Surface Generation**

In order to make use of the antimicrobial ability of copper, surfaces that contact skin and foods should be composed of copper or copper alloy. This can be accomplished with solid copper equipment or by means of copper surface coating. In general, cost considerations favor copper coatings over solid structural copper. Various metal spray techniques are available for the purpose of depositing a copper surface onto implements that can transmit microorganisms, and it is desired to identify an optimal deposition method. Accordingly, three metal spray techniques are evaluated with respect to the anti-microbial activity of the copper surfaces produced by each.

- **Plasma Spray**

The plasma spray process shown in Figure 1 uses a DC electric arc to generate a stream of high temperature ionized plasma gas, which acts as the spraying heat source. The coating material, in powder form and carried by an inert gas, is injected into the plasma jet where it is melted and propelled towards the substrate.

The plasma spray gun includes a copper anode and tungsten cathode, which are both water cooled. Plasma gas (argon, nitrogen, hydrogen, helium) flows around the cathode and through the anode, which is shaped as a constricting nozzle. The plasma, containing suspended metal droplets, exits in the anode nozzle and is directed toward a surface, where the particles deposit.

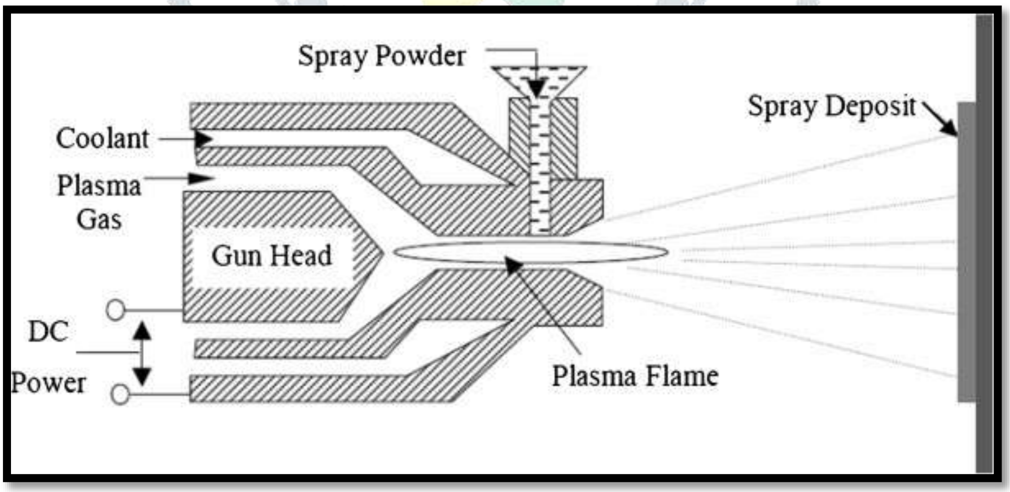

Figure 1:Plasma spray

- **Arc spray**

The arc spray process shown in Figure 2 creates an arc between two metallic wires acting as consumable electrodes. A DC voltage is applied between the wires, and an arc discharge is created at the contact of the wires. The wire electrodes are melted by the electric arc and a compressed air jet disperses the molten droplets and propels them onto a surface.

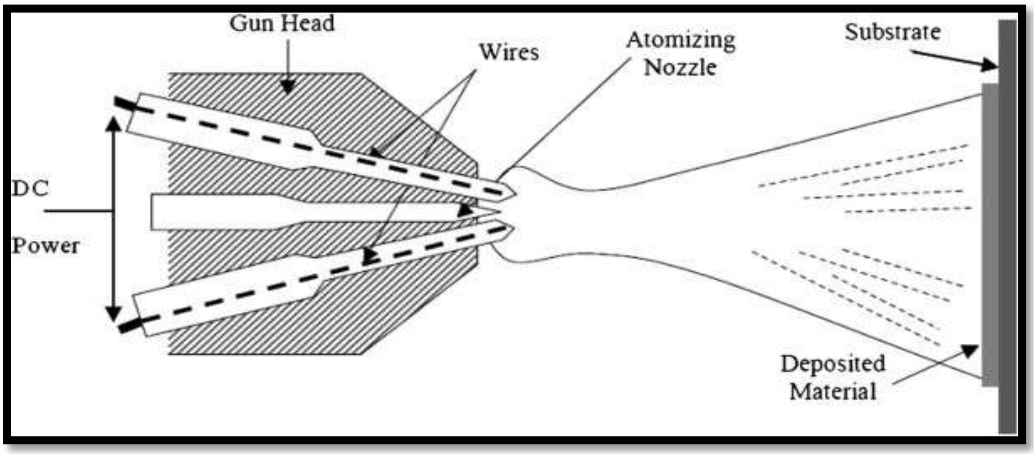

Figure 2:Arc spray

- **Cold spray**

The cold spray process shown in Figure 3 imparts super-sonic velocities to metal particles by placing them in a heated nitrogen or helium gas stream that is expanded through a converging–diverging nozzle. The powder feed is inserted at high pressure at the nozzle entrance. The particles, entrained within the gas, are directed towards a surface, where they are embedded on impact, forming a strong bond with the surface. The term "cold spray" has been used to describe this process due to the relatively low temperatures (100-500°C) of the expanded gas stream that exits the nozzle. Subsequent spray passes increase the structure thickness. The adhesion of the metal powder to the substrate, as well as the cohesion of the deposited material, is accomplished in the solid state.

The relatively low porosity of the cold spray coating results from particle packing caused by high velocity impact. Another characteristic of high velocity impacts is the creation of grain dislocations and work hardening. The low oxide content of cold sprayed deposits occurs because the particle temperature remains low and thus inhibits oxidation.

The spray techniques described each produce impacting metal particles in distinct temperature and velocity ranges. These temperatures and velocities create metal coatings with different characteristics with respect to the presence of oxides, porosity, grain dislocations, and hardness.

Because of these metallurgic differences, it is reason-able to assume that the coatings will exhibit differences in antimicrobial efficiency.

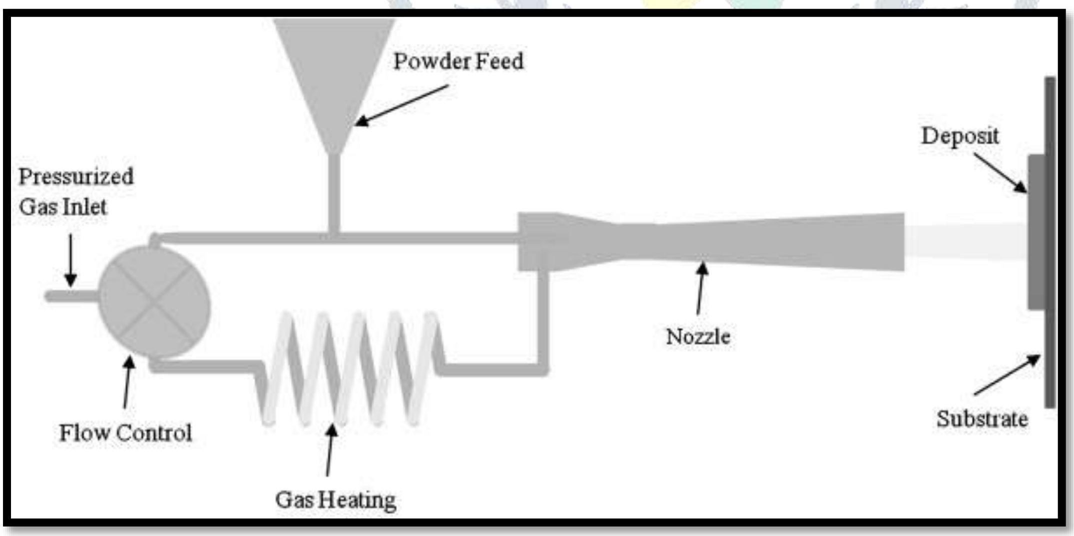

Figure 3: Cold spray

IV. CONCLUSION

Both the EPA and the WHO regard silver as safe for human consumption. It does not pose a risk to human health (World Health Organization 1996) and, in contrast to numerous other commonly utilized disinfectants, is not considered a hazardous substance. Silver inactivates a wide variety of micro-organisms such as bacteria, viruses, and protozoa, alone or in combination with other disinfectants, although this effect is not instantaneous.

The significant anti-microbiologic differences between coatings produced by different spray techniques demonstrate the importance of the copper application technique and of the resulting deposition structure. The cold spray technique showed superior anti-microbial effectiveness caused by the high impact velocity imparted to the sprayed particles which results in high dislocation density and high ionic copper diffusivity. The cold spray process is a mature technology which is currently in use for a variety of applications requiring various metal coatings. The cold spray process can readily apply copper coatings onto touch surfaces.

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