

## **The Development and Functions of Silver in Water Purification and Disease Control.**

By Richard L. Davies and Samuel F. Etris. [The Silver Institute](#), Washington DC.

### **1. Silver, The Oxidation Catalyst.**

Among all the metals, silver is unique in its behavior with oxygen. For example, when pure silver is melted in ambient air it absorbs about ten times its volume, or 0.3% of its weight of oxygen. On cooling to a few degrees above solidification, it abruptly releases most of its oxygen in a dramatic phenomenon which the industry calls a "spit."

The catalytic power of silver to bring about oxidation has been known at least since 1908 when the gaseous conversion of methanol to produce formaldehyde was disclosed in the German Patent No. 228,687 (1908). Today some 23,000,000 troy ounces of silver are in the operating inventory in the chemical process industry worldwide for the conversion of methanol to formaldehyde and ethylene to ethylene oxide, which reaction has been thoroughly elucidated (1).

It has long been known that oxygen is adsorbed on the surface of silver in its atomic state. Also that oxygen diffuses more freely within silver than within any other metal (2). Ronald Outlaw, working at NASA/Langley, undertook a fundamental study of oxygen diffusion with the objective of producing atomic oxygen for the evaluation of the degradation of organic materials in space. He discovered the most prolific source of nascent oxygen to be metallic silver. Atomic oxygen fits very well in the octahedral holes of gold, silver, and copper. In gold, the electron cloud of oxygen tends to be repelled by the lattice electrons of the gold atoms stopping movement through the holes. With copper, the oxide is formed resulting in a barrier. Silver, with an almost a perfect fit, offers so little repulsion that a little thermal energy will readily move it from hole to hole (3).

Outlaw constructed a silver membrane (heated to 350 to 450 C) into which oxygen is pumped in and from which the pure atomic oxygen atoms emerge into a vacuum with their bond energies at the ready (4).

In 1971 The Silver Institute began to report worldwide developments for the uses of silver in its publication, *New Silver Technology*, and encouraged the development of silver systems to purify water and control bacteria.

In 1986 a patent covering the aqueous, catalytic action of silver for the oxidation of bacteria, was issued to Charles Heinig (5), assigned to Fountainhead Technologies, Providence, RI, USA. The fluid to be treated passes through a bed with a large surface area of metallic silver, on a benign substrate. Molecular oxygen is present and silver readily adsorbs it converting it to nascent oxygen which is available to oxidize bacterial enzymes and other organics.

Their reaction with the atomic oxygen is instantaneous.

### **2. Epidemiological Background of Silver**

The use of silver vessels to keep liquids pure longer has been known throughout history. Cyrus the Great King of Persia (550 - 529 B.C.), who established a board of health and a medical dispensary for his citizens, had water drawn from a favorite stream then "...boiled,

and very many four wheeled wagons drawn by mules carry it in silver vessels, following the king whithersoever he goes at any time" (6). Since ancient times silver vessels have been used in Mexico, the world's major producer of silver, to keep water and milk sweet.

Pliny, the Elder, in his great work, Natural History, (78 A.D.) reports in Book II, Section XXXV, that the slag of silver "... has healing properties as an ingredient in plasters, being extremely effective in causing wounds to close up..." (7 ).

In 1884 the German obstetrician, F. Crede, observing a relationship between the 20% to 79% of children in various institutions of the blind and the presence of maternal venereal disease, began the use of a 1 % silver nitrate solution dropped into the eyes of newborns. Following the introduction of this treatment, the incidence of gonococcal ophthalmia neonatorum dropped to about 0.2% . This prophylaxis became a state regulation in countries in Europe, North America, and elsewhere (8).

Hundreds of millions of children and adults have been exposed to silver either in clinical treatment or for drinking water sanitation since ancient times with no reports of toxic reactions. During World War H, however, it was discovered that when severe injuries to the skull were repaired by the use of a silver plate, a toxic reaction resulted. The fact that toxicity to nerve cells in the brain and the spinal column had never been previously observed was due to the blood brain barrier, a cellular membrane which blocks the entry of heavy metals into this domain. This mechanical barrier effectively blocks silver from the one area of the body where it would be toxic.

Thus the epidemiological history of silver has an established non-toxicity in normal use. Nor has silver evidenced carcinogenic activity (9).

A word must be said about the activity of the body in combating the presence of heavy metals such as silver. In addition to the blood-brain barrier, a membrane which prevents silver from entering the brain and spinal cord, there is an additional safety system in the body, the metallothioneins. These ubiquitous proteins found in all life were first characterized in 1957. They have the property of binding metals in metal thiolate cluster structures to transport, store, and detoxify essential and nonessential trace metals that may enter the body (10). The coordination chemistry which binds metals into these thiolate cluster complexes is remarkable, but all we need say here is that the metallothioneins remove heavy metals such as silver from the body, making internal therapy with exposed silver ions or atoms not feasible.

### **3. Mechanisms of Silver Sanitation:**

Three mechanisms of silver sanitation are reported in the literature: catalytic oxidation of cell surface radicals to inhibit transfer of oxygen, reaction with surface radicals on the surface of bacteria and viruses to interfere with electron transport, and binding with DNA in disease organisms to prevent unwinding.

Catalytic Oxidation -- Atomic (nascent) oxygen adsorbed onto a bed of silver atoms or ions in solution readily reacts with the sulfhydryl (H) groups surrounding the surface of bacteria or viruses to remove the hydrogen atoms (removed as water) causing the sulfur atoms to form an R-S-S-R bond; respiration is blocked and the bacteria expire.

Albert T. McManus, MD, Chief of Microbiology, Institute of Surgical Research, Fort Sam Houston Army Burn Center, Houston, Texas, observes, "Silver kills bacteria by simple catalytic reduction/oxidation by reacting with any available negative charge. There are all kinds of transport proteins and membrane proteins that have charges on them. For pure protein enzymology, silver is a very potent inhibitor; the reactions it catalyses inactivate the proteins. When it binds to nucleic acid, it is simple oxidation at a phosphate radical. Silver will bond to any organic acid that is ionized. Any organism that is available to powerful catalytic activity of silver for oxidation is inactivated" (11).

Reaction with Bacterial Cell Membranes -- There is evidence that silver ions may attach to surface radicals of bacteria, impairing cell respiration by blocking its energy transfer system. An unpublished study of bacteria treated with radiated silver showed that silver was present on the surface, but did not penetrate the cell. It should be noted that mammalian cells are not affected by silver because the protective cell walls block entry of large ions such as silver.

Some bacteria appear to develop a resistance to silver. This was noted within a few years of the introduction in 1968 of silver sulfadiazine by Fox. Among the early cases of bacterial resistance to silver was that reported by McHugh, et al., in *Lancet* (1975) wherein three patients died of a resistant strain of *Salmonella typhimurium*. He and his coworkers subsequently studied 13 strains of *S. typhimurium* not all of which were resistant to silver nor did the resistant strain transfer its resistance to the other strains (12). Those studying this problem have found resistance to be unstable and difficult to transfer from one strain to another. A list of bacteria evidencing some resistance to silver is shown by Clement and Jarrett in Table 11 (13).

The research at Columbia University, Department of Microbiology, continuing under Shanta Modak, is studying the development of a new family of quinolone silver compounds (14). These, when mixed with silver sulfadiazine, are expected to inhibit the generation of resistant bacteria.

According to McManus, resistance in the real world to silver metal's antimicrobial activity is still very, very rare. Silver is used extensively at the Sam Houston Bum Center, primarily as its solfonimide salt which has a low solubility, but it does its work (11).

Viruses-- There is no comprehensive study of viruses inactivated by silver. Viruses are basically pure DNA or RNA with a protein like coating and no cell membrane. Because many have sulphydral terminuses, their reaction to silver would be similar to that of bacteria. In one study, Fox showed that silver sulfadiazine causes direct inactivation of herpes simplex and vesicular stomatitis, viruses that affect the eyes (15).

Binding with DNA -- Studies by Fox of *Pseudomonas aeruginosa* with sublethal concentrations of silver sulfadiazine revealed that up to 12% of the silver was in the DNA fraction, 3% of silver was in the RNA fraction, less than 0.5% in the lipid fraction and the remainder in its proteins and polysaccharides (16). F.A. Cotton examined possible ways in which the large silver atom might fit into DNA, but believed that a N-N bonding with a separation of ca. 3.8 Å would increase the nearby N-H ... O separations and abolish the hydrogen bonds on which the DNA structure depends (17). More research is required.

When silver does bond with DNA, the resulting complex is not unwound (1 g). However, in treating the complex with chlorides, bromides, cyanides, etc, which remove the silver, regeneration of the native DNA takes place and its function is restored.

#### **4. Silver Agents.**

Catalytic Oxidation:

The Fountainhead System: The catalytic cartridge supplied by Fountainhead Technologies, Inc., contains a layer of silver microcrystals deposited on 14 to 18 mesh alpha-alumina having a surface area of about 250 square inch per grain. The bed of alumina is about five inches deep and is surrounded by a copper sheath. During operation, some silver and copper are made soluble by galvanic action and circulated in the swimming pool providing the pool with the bactericidal properties of silver and the algicidal properties of copper. In the Fountainhead system, no electric current is applied (19).

Studies by Charles Heinig showed that lightly bound nascent oxygen on the microcrystals of silver (about 40 kilocalories per mole) readily oxidizes bacteria or viruses, resulting in complete disintegration. It also oxidizes other organic and inorganic material, forming relatively stable peroxides that continue to sanitize the water downstream. His experiments with ozone gas additions showed that bacteria and viruses were being tom apart, the silver acting purely as an extremely efficient oxidative catalyst.

Laboratory tests by Fountainhead and their third-party commercial laboratories have demonstrated an instantaneous 99% kill rate, with complete removal of E. coli in 2.0 to 2.5 seconds in the catalytic cartridge. Heinig conducted one experiment in which he intentionally depleted oxygen from the water to less than 1 ppm; the result was a substantial increase in the survival rate of the test bacteria.

The Fountainhead cartridge is now being used primarily for circulation systems in swimming pools or spas coupled with a standard filtration system. Fountainheads patent attorneys are busily exploring all possible applications of the cartridge from pharmaceutical grade water production to municipal water purification systems.

The Katadyn System

This system, marketed by Katadyn Products, Inc., Switzerland, for some 50 years, uses metallic silver mixed with a ceramic which is fired to form a filter with a pore diameter of 0.2 micrometers (20). This pore size mechanically filters out living organisms. Bacteria that might squeeze into the pores meet pure silver with its adsorbed oxygen atoms and are destroyed. Because viruses can be smaller, and their destruction by silver cannot be certain, Katadyn does not guarantee elimination of viruses.

The Katadyn filter with its 0.28% by weight of silver has found wide acceptance throughout the world, especially in third world countries where reliable municipal water treatment systems are lacking. In the United States, Katadyn's sales in households depending on well drawn water is noteworthy; the company enjoys about 50% of this market in the U.S.A.

The Ionics System

Developed at the Johns Hopkins University some 50 years ago, the product of Ionics, Inc., Bridgeville, Pennsylvania, contains somewhat over 1% metallic silver deposited on activated carbon. Because carbon and silver form a mild galvanic couple, the catalytic activity of silver is supplemented by some dissolution that provides silver sanitation throughout the carbon filter, preventing buildup of bacteria.

Ionics is the major supplier of silver impregnated activated carbon in the United States and it is almost universally used by independent manufacturers of under-sink water purifying equipment. One of the several benefits of activated carbon is that it adsorbs organic compounds, including cancer inducing trihalomethanes which may be generated by chlorine treatment in municipal water treatment systems (21).

### **5: Tetrasilver Tetroxide.**

It was only a few years ago that x-ray and neutron diffraction analysis revealed the unit cell of silver peroxide, a black oxide marketed as AgO, which actually consisted of: 2 Ag(I), 2 Ag(III) and 4 oxygen atoms (Ag<sub>4</sub>O<sub>4</sub>). In acid, the interaction between the silver ions results in silver (I) being oxidized to silver (II) and the silver (III) being reduced to silver (I). Thus the actual valence of the silver atoms in silver peroxide was not apparent. The compound supplied by Jonas & Company, Bensalem, Pennsylvania (patents cover its use as a water purifier) is in the form of a black powder suspended in water. In water, it dissolves slowly remaining inactive until touched by bacteria or other organics.

Research by Marvin Antelman, Antelman Technologies, Rehovot, Israel, indicates that if the reproductive rates of a pathogen are slow, the ionic crystals of the compound are not attracted to them, but if their reproductive rates are high as in the case of bacteria with their exposed sulfhydryl and amino sites, these will attract oxidation by the silver ions (III) and these will oxidize the bacteria or pathogen. His research indicates that in an aqueous medium the peroxide (Ag<sub>2</sub>O<sub>2</sub>) works about 240 times as fast as Ag(I), and is up to 200 times more effective a disinfectant than Ag (I) compounds or metallic silver (22).

Tetrasilver tetroxide was selected as one of the 100 most technologically significant products of 1993 by R&D Magazine. It is now in testing for approval by the EPA for water purification. N. Jonas & Co., Bensalem, PA, USA, has obtained seven U.S. patents on the use of this compound for sanitation and clinical purposes. One of the benefits in its use in swimming pools is that close attention to the pH of the water is not required for the peroxide will not incur a black deposit of silver on the walls of the pool as could be the case with silver-copper ionization systems.

Marvin Antelman is pursuing the pharmaceutical potential of the compound. He has just been granted a U.S. Patent for the use of the compound for intravenous injection to combat *Candida albicans* (a yeast affliction of women) and amoebic dysentery. The compound has been successful in Central America, curing patients with otherwise terminal cases of amoebic dysentery. He is developing patents on other Ag<sub>4</sub>O<sub>4</sub> pharmaceuticals.

### **6: Silver Inorganic Compounds.**

Silver nitrate has been used as an antiseptic since ancient times. It is, however, very corrosive to human tissue and rapidly reacts with chlorides in wound fluids, precipitating silver chloride.

An example of a compound that releases silver slowly to provide a continuing presence of silver without being immediately precipitated is the silver thiosulfate complex developed by Professor Shigeharu Ueda, Osaka Research Institute for Medical Diseases. Marketed under the name Amenitop T1,1 for the Matsushita Electric Industrial Co., Ltd, it consists of silica gel microspheres containing a silver thiosulfate complex.

The silica gel coating allows gradual release of silver to provide long lasting bactericidal action (23).

It is planned to apply Amenitop to the surface of Matsushita plastic products to prevent harboring viruses (such as AIDS) left by infected users. Ueda has shown that Amenitop has positive bactericidal action against a variety of disease causing bacteria such as E. coli and S. aureus, as well as HIVA 103 (23).

### **7: Silver Organic Compounds.**

The usefulness of combining the bactericidal properties of silver with the antibacterial properties of an organic drug was explored by Charles L. Fox at Columbia University, New York. In a paper published in 1969 (24), he describes a combination of a sulfonamide drug with silver. This avoids the corrosive effects of silver nitrate and its tendency to be rapidly neutralized by chlorine and other organics in the wound, diminishing its effectiveness. The result, silver sulfadiazine, has proved to be the outstanding topical compound for reducing the development of early burn wound sepsis.

Previously, infection set in immediately, destroying the structures required for normal regrowth. With silver sulfadiazine, dermal structures could grow unimpeded by bacteria, spread out, and heal the burn spontaneously (and painlessly) without the need for a skin graft. Silver sulfadiazine has become the treatment of choice for burn wound therapy.

Silver sulfadiazine, unlike silver nitrate, is active against both gram positive and gram negative organisms, fungi, and protozoa, including mouse malaria. It is also topically effective against viruses such as herpes, and sexually transmitted diseases such as genital herpes, gonorrhea, trichomonas, and treponema pallidum. It also inhibits the colony formation of Staphylococcus, Streptococcus, Pseudomonas, etc.

### **8: Delivery Of Silver.**

Dissolution, from solid silver.

Metallic silver dissolves in water in about 10.5 g/l. (25) which accounts for the ancient as well as modern reliance on silver vessels to keep water and other fluids pure longer. At this minimal concentration, silver has been shown to be toxic to E. coli and Bacillus typhosus, virulent human diseases.

Electrically driven stream of silver ions:

Robert O. Becker, MD, orthopedic surgeon, Upstate Medical Center, Syracuse, New York, began experimentation in the mid-1970s, before his retirement, with electrically driven silver ions to treat serious bone infections (26). It is the lack of an adequate circulatory system in bone that makes treatment of bone infections with conventional blood-carried antibiotics

ineffective. The use of a silver impregnated nylon fabric soaked in saline solution placed over the depths of the wound and charged with a potential of about 0.9 volt was used to provide complete healing of the bone and surrounding tissues.

He reported on positive healing experience with some 75 patients, proving the efficacy of the bone therapy technique. Further, his experience in healing severe wounds in the skin showed the general efficacy of the technique and the lack of any side effects.

During the treatment of many patients, Dr. Becker noted that a copious exudate appeared in the wound area accompanied by a constant decline in bacterial count. Microscopic examination showed the exudate to be composed of a large number of primitive cells resembling a variety of primitive bone marrow type cells. With the appearance of the exudate, a dramatic increase in healing rate by a factor of at least two was observed. Further examination revealed that a process of de-differentiation had occurred; the mammalian fibroblast cells had reverted to the primitive stem cells. With the silver-ion technique it was now possible to do open bone grafts. In the case of skin, grafts are not necessary because the silver ions eliminate the bacteria that would otherwise impede the cell-by-cell reconstruction of the original (26).

Becker's procedure has now benefited hundreds of patients at Mountain Medical Specialties, Demorest, Georgia. With the silver ion treatment, the physician need only clean the wound, place a silver dressing on it and start an electric current flowing with a small battery. Then, show the patient how to take care of the wound and send the patient home. Once a week the patient comes in for check up and new dressings if necessary. Within a month the wound has healed and silver treatment may no longer be necessary. Within 3 to 6 months the darker skin begins to disappear, and when the darkness disappears, the location of the wound cannot be found (27).

A. Bart Flick, MD, practicing medicine at Mountain Medical Specialties, Demorest, Georgia, USA, uses silver ion therapy on cases of severe trauma. Loss of skin from hands and fingers presents a most difficult problem because the skin is thick and has a different sensory response from skin from other parts of the body. Thus skin grafted on hands and fingers from other parts of the body results in unsatisfactory function and is without normal sensation because nerves are not regenerated in grafted skin. However, the use of the silver technique results in the rapid regeneration of normal, full thickness, flexible skin of the type removed by the injury. The skin is regenerated in all of its complex tissue morphology even including a fingerprint. In process now is a scientific report on the spectacular regenerations resulting from this technique (28).

De-differentiation:

The de-differentiation Becker observed is the reversion of mature mammalian fibroblast cells to cells of an embryonic or primitive state. In this state, the cell is capable of normal cell division as well as subsequent re-differentiation into a mature cell of another type than its original. It was these primitive cells generated by the action of silver that were being rapidly absorbed into the regeneration of new tissue, doubling the rate of restoration.

If the palm of a hand or the tip of a finger should be severely burned or injured and just left to heal, it just scars down and the result is a limitation of motion and limited sensation. Should a skin graft be used from some place on the body such as the sole of a foot the result will be a

scarification around the edges of the graft and it will never-ennervate (will not develop sensation essential to react to heat, cold, etc) and the edges will have abnormal sensation.

However, if the wound is treated with electrically driven silver ions to eliminate any action by bacteria, the wound will heal in a period of a few weeks to full thickness and fully innervated skin consistent with the previous structure (26).

Wounds requiring this procedure are typical of the cases treated by the Mountain Medical Center (27).

#### Electrically Driven Silver-Copper Ion Swimming Pool Systems:

The search for a swimming pool sanitation system that could be used by those allergic to chlorine was the driving force behind what became the system produced by Caribbean Clear, Inc., Columbia, South Carolina. The system, electrically driven silver and copper ions with minimal or no chlorine, provides satisfactory sanitation without chlorine's assault on the sinuses, eyes, and lungs, as well as its corrosive effects. Olympic training pools using it find that swimmers can spend far more hours training with no eye, ear, or nose afflictions normally associated with long exposure to chlorine sanitation systems (29).

Tens of thousands of swimming pools in Europe and the United States use electrically driven silver-copper ion purification systems. Tarn Pure USA, Burr Ridge, Illinois, (a supplier of silver-copper ion systems) underwrote a study of the efficacy of these systems to provide the backup data for a protocol by which the NSF International (formerly National Sanitation Foundation), Ann Arbor, Michigan could certify the efficacy of silver-copper swimming pools systems which use a minimum of chlorine.

The data on the systems bacteria and virus effectiveness was developed by Professor Charles P. Gerba, Department of Microbiology, University of Arizona. His studies showed that silver ions at 75 ppb, copper ions at 460 ppb, and free chlorine at 200 ppb will reduce the number of *E. coli* by half in 30 seconds. He observed a synergistic effect by the silver, copper, and chlorine such that the combination was more powerful than individually (30).

Gerba showed that silver-copper systems are capable of inactivating enteric virus such as polio virus in the presence or absence of free chlorine, which should be useful in the control of these agents in swimming pools.

His study of *N. fowleri* showed significant enhancement of the reduction rates of these amoebas which cause a fatal disease to the human nervous system (Primary Amoebic Meningoencephalitis) (31). And it was shown that the addition of silver and copper to free chlorine significantly increased inactivation rates of *Legionella pneumophila*, which tend to populate cooling-tower water. Also silver and copper ions remain active in the water after shut-down, continuing the sanitation in a cooling tower during periods of inactivity when chlorine would evaporate (32).

Of the more than 50,000 large and small pools in the United States which use silver-copper ion systems for sanitation, two types of installations are of particular interest, both of which use the Caribbean Clear silver-copper ion treatment with greatly reduced concentrations of chlorine. The one installation in San Antonio, Texas, uses the system for fresh water aquatic

animal exhibition pools, and the other in the Gulfarium at Fort Walton Beach, Florida, uses the same system for treating sea water exhibition pools.

Judy Tuttle, Supervisor of the San Antonio Children's Zoo, says that the silver copper ion treatment has resulted in far healthier animals with healthier skin, and small scratches and abrasions that under chlorine did not heal well now heal more rapidly; most important, eye problems are markedly reduced (33).

Greg Siebenaler, Curator of Animals, The Gulfarium, uses fresh sea water from the Mexican Gulf. His sea lions, harbor seals, gray seals, and other mammals have experienced far fewer problems and avoided developing eye problems formerly seen in the heavily chlorine-only pools. And fecal coliform bacteria counts have been kept far below the maximum limits prescribed by the federal government. He thoroughly endorses the use of the silver-copper ion systems (34). Both of them report that the water needs replacement far less often and the amount of algae fouling the pools is significantly reduced.

#### Summary:

We have attempted to cover the significant developments in the use of silver for water purification and disease control. It is apparent that the predominant effect of silver in sanitation depends on its unique activity with oxygen. The clinical research efforts have so far revealed remarkable potential, but have been small, because, it is claimed, the large pharmaceutical houses are not interested in underwriting the high costs of research in a field where the opportunity for patent protection is marginal. After all, the observations of Pliny, the Elder, makes it clear that at least some of the values of silver therapy so useful to us now were practiced in ancient Roman times. However, today, in view of the increasing resistance of bacteria and viruses to organic compounds that have been our mainstay against major diseases, the availability of a viable alternative clearly needs serious exploration.

Profitable research could be conducted to answer such questions as:

1. Why do silver ions cause the de-differentiation of cells?
2. Can a compendium of diseases successfully treated by silver systems be made?
3. What viruses can and cannot be inactivated by silver?
4. Can a way be found to use silver to treat internal trauma?

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