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Copper - More Than Just a Metal We Electroplate

by
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Editor's Note: Over many years, well-regarded AESF/NASF contributor Jack Dini contributed a series of fascinating columns to *Plating & Surface Finishing*, under the title *Fact or Fiction?*. After his new offering in July, we are happy to offer a second welcome contribution to his output for the NASF. A printable version of this article can be accessed **HERE**.



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Not many people know that without copper the human body cannot survive.

Copper has many uses in our lives, even for our health. Copper is in our blood, and without it the body dies. Too much of it and we also die. For most of us, balancing the correct amount of copper happens without ever thinking about it in a lifetime. We don't have to put much effort to get the correct amount of copper, since it is found as a natural substance in common foods such as sunflower seeds, walnuts, almonds, mushrooms, shrimp and most types of beans.

To avoid copper on any given day would take nothing short of a monastic effort. No one living in an urban setting would pass this test. Even a person camping in the wilderness is likely to be using copper. Do they have a GPS device? That has copper. Do they have a small cooking stove? That has copper inside the elements. Do they have a cell phone for emergencies? Loaded with copper. Did they drive to their remote location to get away from everything? Their car has forty pounds of copper in it.

Every coin has copper in it. Every house has, on average, four hundred pounds of copper pipe and wiring. Since 1963, it is estimated that more than 35 billion feet of copper plumbing have been installed in the United States. Every 747 jet airliner has 1.35 miles of copper wire weighing nine thousand pounds.

Copper has natural antimicrobial properties. The metal releases ions that penetrate the cell walls of microbes, which in turn disrupts their ability to reproduce; in other words, spread as an infection.



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Electroplating

Copper is the most common metal plated, exclusive of continuous strip plating and nickel. The major uses of electroplated copper are on plastics, printed wiring boards, zinc die castings, rotogravure rolls, electrorefining and electroforming. Copper is electrodeposited for numerous engineering and decorative applications requiring a wide range of mechanical and physical properties. This range extends from properties superior to full-hard wrought copper to properties equivalent to annealed pure copper.

Copper is an excellent choice for an underplate, since it often covers minor imperfections in the base metal. Copper deposits act as thermal expansion barriers by absorbing the stress produced when metals with different thermal expansion coefficients undergo temperature changes.

Copper in our bodies

Copper is an essential trace mineral necessary for survival. It is found in all body tissues and plays a role in making red blood cells and maintaining nerve cells and the immune system. It also helps the body form collagen and absorb iron and plays a role in energy production. At least twenty enzymes contain copper, and at least ten of those depend on copper to function.

Copper combines with certain proteins to produce the enzymes that act as catalysts to help a number of body functions. Some help provide energy required by biochemical reactions. Others are involved in the transformation of melanin for pigmentation of the skin and still others help to form cross-links in collagen and elastin and thereby maintain and repair connective tissues. This is especially important for the heart and arteries.¹

Table 1 - Copper in the Human Body*

Blood	1 ppm
Bone	1-25 ppm
Tissue	2-10 ppm (highest in liver)
<u>Total amount in body</u>	<u>70 milligrams</u>

*John Emsley, *Nature's Building Blocks*, Oxford University Press, 2001.

An adult needs to ingest around 1.2 milligrams of copper per day, and breast feeding women need around 1.5 milligrams, although it has been suggested that 2 milligrams per day would be more beneficial for everyone. Volunteers on low-copper diets have increased levels of cholesterol, high blood pressure and an impaired ability to digest glucose.

While drinking water is the most obvious source of copper in our diet, because of copper pipes, the substance is also quite common in red meat, nuts, shellfish and many fruits and vegetables. Other sources include mushrooms, trail mix, barley and canned tomato puree.

My favorite choices: a beer or a chunk of chocolate are rich in copper.²

Medical Issues

Copper is essential to all species, but it can be toxic and as little as 30 grams (one ounce) of copper sulfate has been known to kill. However, we are not likely to be poisoned by copper sulfate because a large dose will act as an emetic and we would quickly vomit it back.³

Menkes syndrome is a disorder that affects copper levels in the body. It is characterized by sparse, kinky hair, failure to gain weight and grow at the expected rate and deterioration of the nervous system. As a result of a mutation of a certain gene (ATP7A), copper is poorly distributed to cells in the body. The decreased supply of copper can reduce the activity of numerous copper-containing enzymes that are necessary for the structure and function of bone, skin, hair, blood vessels and the nervous system. It begins in early childhood and at present there is no complete cure for Menkes disease.⁴



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Then there is Wilson's disease, which is essentially chronic copper poisoning. In it the natural balance between copper is disturbed and the copper thus retained is stored in certain organs. The liver is the first and chief repository. In time, as the storage capacity of the liver is exhausted, the continuing accumulation passes from the liver into the blood stream and is carried to the other organs for which copper has a grim affinity. These are most conspicuously the brain and the cornea of the eye. The relentless retention of copper begins at birth, but so efficient is the liver in its protective role that 10 to 20 years may elapse before the first indications of morbidity are felt. The gravitation of copper to the eye has a curious impact. It produces a phenomenon known to medicine as the Kayser-Fleisher ring. It consists of a more-or-less complete ring of rusty brown pigmentation - a literal implantation of copper - around the rim of the cornea, or to put it another way, a deposit of copper.

The treatment of Wilson's disease is basically very simple and straightforward. The idea is to remove the toxic concentration of copper in the body and prevent its re-accumulation. Penicillamine, a derivative of penicillin, is used. Penicillamine is a chelator and mobilizes copper from the tissue and excretes it in the urine. It is truly a life-saving drug and the results can be dramatic. Little-by-little, the liver returns to normal, the Kayser-Fleisher rings fade away, and the neurological manifestations disappear. The standard regimen combines penicillamine and potassium sulfide which act to prevent the absorptions of copper by forming an unabsorbable copper sulfide in the gut.⁵

This leads to an interesting tie-in with electroplating. Copper is removed as a sulfide in nickel plating solutions. It has been shown that pure nickel can passivate readily when it is made anodic in either solutions of dilute acids or in typical electroplating solutions. However, the incorporation of sulfur in the nickel effectively prevents passivation and allows dissolution to proceed at more active potentials. The sulfur in the active anode material remains behind in the anode bags as a sulfide residue. Copper sulfide is less soluble than nickel sulfide; thus, copper can displace nickel from the sulfide anode residue. This is important in nickel plating because copper, an undesirable contaminant, is thereby removed from the solution.

Antimicrobial copper

Copper kills MRSA and a number of other microorganisms. Independent laboratory testing has demonstrated that, when cleaned regularly, antimicrobial copper products kill greater than 99% of microorganisms. So, the next time you're in a hospital, if you see a lot of copper, rest assured your chances of getting an infection have been minimized.⁶ Recent research has shown copper to be effective against COVID-19 within 4 hours whereas it can survive for days on glass, plastic and stainless steel surfaces.

Copper sulfate

Copper sulfate is useful to people who own swimming pools, French vineyard operators, and organic farmers.

Copper sulfate controls downy mildew fungus, which can devastate grapevines. Downy mildew flourishes in wet weather, showing up initially as a downy patch on the bottom of the leaf. If rain persists, the fungus establishes itself, eventually destroying the crop. It can even carry over into the next season. Here's a bit of trivia for wine drinkers: it has been speculated that the reason that the heart attack rate in France is lower than in the rest of Europe is because of the French practice of drinking wine. Red wine has a higher copper content than white wine because it's prepared with the skin of the grape intact. The copper originates in the wine from the copper fungicides used on the grapes in the field.

Algae often invade swimming pools, turning the water greenish and cloudy. By adding a very small amount of copper sulfate to pool water, it clarifies the water and makes the pool more inviting. There is another benefit: by using copper sulfate, one can reduce the amount of chlorine or bromine needed to disinfect the pool. Unlike earlier when high amounts of copper sulfate were discussed, in this case the copper sulfate is so dilute that is safe.

A few words about pesticides. Alex Avery reports that the biggest myth of all about the term *organic* is that it means pesticide-free. Why? Because it isn't pesticide-free. Organic farmers are allowed to use numerous natural poisons as pesticides. These include:

- Sulfur, which Cornell University concluded was the most environmentally harmful substance widely used in farming.



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- Pyrethrum, a mixture of nerve toxins squeezed from African-chrysanthemums deemed by the EPA to be a "likely human carcinogen."
- Rotenone, a neurotoxin that causes symptoms similar to Parkinson's disease when administered to rats.

Copper sulfate is still used in some places but was banned by European regulators because of environmental concerns. Electroplaters can relate to these words from Alex Avery, "We all know darn well that if the shoe were on the other foot, and non-organic farmers were using copper sulfate, proponents of organic agriculture would be screaming to high-heaven about the eco-sins of copper sulfate and would be demanding that it be banned and that only safer, biodegradable synthetic fungicides be allowed."⁷

Architecture and industry

Copper is waterproof, so it has been used as the roofing material on many buildings since ancient times. The green color on these buildings is due to a long-term chemical reaction: copper is first oxidized to copper(II) oxide, then to cuprous and cupric sulfide and finally to copper (II) carbonate, also called verdigris, which is slightly corrosion-resistant. The copper used in this application is phosphorus-deoxidized copper (Cu-DHP); also used as anode material in acid copper plating solutions.

A good example of copper verdigris that we are all familiar with is the Statue of Liberty, weighing in at one hundred tons of copper.

Old Works Golf Course

This is a good one to conclude with since it could be of interest to a specialized group of electroplaters.

The Old Works Golf Course in Anaconda, Montana is the state's only Jack Nicklaus signature golf course open to the public. Rich in history, the site was the original location for Anaconda's first copper smelter. After laying idle for nearly a century, it became a Super Fund clean-up site in 1983. In the late 1980s, the idea of reviving the Old Works site with a world class golf course became a dream of the Anaconda community and Arco. Now through exhaustive efforts to make the site safe, the Old Works Golf Course is a reality.

Measuring from 5,300 to 7,700 yards, the course is situated along Warm Springs Creek and the mining remnants against the hill sides. Among the mining relics that are predominant around the course none is more dramatic than the huge piles of black slag, a by-product of the copper smelting process. The slag is also utilized in the bunkers of the Old Works, making for a dramatic contrast to the lush green of the course.⁸

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About the author



Jack Dini earned a Bachelor of Metallurgical Engineering degree from Cleveland State University and began his career in the 1950s with Cleveland Supply Co. (now Pavco). He spent a few years at Republic Steel's research center and Battelle Columbus Laboratories. In 1962, he joined Sandia Laboratories, Livermore, CA, where he was involved with electrodeposition projects for 18 years before moving to Lawrence Livermore (LLNL) in 1980. He was section leader, fabrication processes. Responsibilities included direction of activities in five groups: electroplating and metal finishing, vacuum processes, metal fabrication, plastics and optics.

Mr. Dini is a prolific scientist. He is the author or coauthor of some 125 technical papers and, while many researchers are content to specialize in one or two fields, he made significant contributions to more than half a dozen disciplines in surface finishing. The scientific community is fortunate that he carefully documented his work, sharing it with others around the world. It includes plating uncommon metals, alloy plating, printed circuits, chemical milling, electrojoining and gathering electrochemical/property data.