



# COPPER AS AN ANTI-VIRUS SKIN PROTECTOR

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## INTRODUCTION

We humans need and live with enormous numbers of microorganisms. These include viruses, called bacteriophages, which infect and destroy specific nasty bacteria in our digestive, respiratory and reproductive tracts. We also contain in our blood and bone, and need, many metals, like iron and copper.

But there are bacteria and viruses which are lethal, and too much copper or lead can kill us.

Late 2019 saw the entry of a new coronavirus (SARS-Cov-2), commonly called Covid-19, into humanity with devastating effects. As of the time of writing this note on 21 May 2020, there were over 5 million documented cases world-wide, with over 330,000 deaths. On that day the World Health Organisation (WHO) recorded the highest number of daily infections since the start of the epidemic (106,000). In many countries the epidemic was still out of control, other countries fear a second wave.

The world-wide societal defences have been disinfecting surfaces and skin, face masks and various forms of lockdown and isolation. Economic impacts have been massive. A vaccine is a long way off, and a safe one may not be found.

Many of us have discovered that viruses and bacteria are very different, and so-called anti-bacterial sprays and hand treatments may not kill viruses, and that what kills one kind of virus may not kill another. So the development and production of sprays, sanitisers and wipes to protect us humans from Covid-19 has seen exponential growth over a few months.

This note collects information germane to skin protection against coronaviruses. The objective is to provide the basis for developing better virus-killing and skin protective products. Whilst much of this document deals with potentially toxic materials entering through skin, and or damaging skin, the ultimate focus is what can we place on our skin to kill virus and, importantly, what could remain on our skin to provide ongoing protection?

## ANALYSIS AND DISCUSSION

### Copper

Copper commonly exists in three atomic forms.

The first is metallic copper as we know from pipes and coins and the roofs of old churches. In shorthand this is written as Cu.

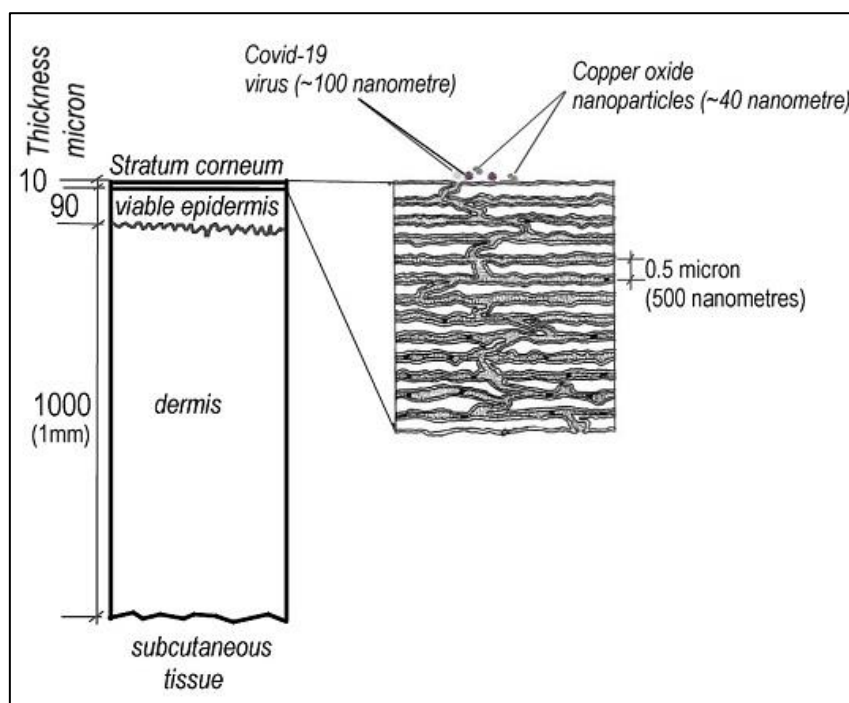
The second is an atomic form which has lost one electron so is called an ion with one positive charge, written  $\text{Cu}^+$ . The third form has lost two negative electrons, and is an ion written  $\text{Cu}^{++}$ . These ions attach to other elements to form materials like Copper Sulphate ( $\text{CuSO}_4$ ) and Copper Oxide ( $\text{CuO}$ ). Compounds like Copper Sulphate dissolve in water and



the  $\text{Cu}^{++}$  ions float around separated from the Sulphate ( $\text{SO}_4^-$ ). The water solution is a beautiful blue, being a property of copper ions. Copper Oxide is insoluble in water.

A fascinating fact is that Copper, particularly Copper ions, are lethal to coronaviruses. This was discovered before the 2020 Covid-19 epidemic. Copper is also lethal to many bacteria. In this regard it must be noted that bacteria are alive; they can reproduce themselves. Viruses are not alive; they are proteins which cannot reproduce without manipulating a host cell.

It is important to put a scale to these beasts. The Covid-19 virus is about 100 nanometres in diameter, which means you could put about 1000 side by side across a human hair. Bacteria are roughly ten times the size of the Covid-19 virus. If we place Covid-19 viruses on the human skin it looks roughly as in the following picture.



The complex human skin is explained in more detail in the next section; for now we remain focussed on copper.

For thousands of years humans have used copper for medical purposes (as a biocide), so this matter is a little like Solomon observed some 2500 years ago: "*What has been will be again, what has been done will be done again; there is nothing new under the sun.*"<sup>1</sup> But in truth much has been learned in the last two decades and key points in respect to copper and viruses are set out below.

1. The major chemical text book *Chemistry & Chemical Reactivity (10th Ed)* records how fitting 282 objects in 32 rooms in a hospital at the Medical University South

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<sup>1</sup> Ecclesiastes 1:9



Carolina with copper alloys (bed rails, tray tables, chair arms, call buttons and IV poles etc.) reduced the microbial burden of pathogens by between 40% and 99%. The text book notes *"The underlying mechanism by which bacteria are destroyed by copper ions is not yet well understood, but there is research activity on this question in laboratories around the world."*

Similar results were obtained in other hospitals in Birmingham, UK and in Clinics in South Africa and Germany (Grass and co-workers, *Metallic Copper as an Antimicrobial Surface, 2011*).

2. Professor Bill Keevil at Southampton University has been demonstrating the antimicrobial effectiveness of copper for about 20 years (*Smithsonian Magazine 14 April 2020*)
3. In 2008 The Environmental Protection Agency (USA) registered about 300 different copper surfaces as antimicrobial.
4. A 2018 paper by Betts and others titled *Novel Antibacterials: Alternatives to Traditional Antibiotic*, summarises the 'vast array of research' showing the effectiveness of copper ions, in particular copper sulphate, in killing *E.coli*, *Staph* and *Streptococcus*. The article notes that in recent years, copper nanoparticles have been shown to be more effective than other forms of copper.
5. Research work in Israel by Borkow (2012 & 2015) has shown the substantial efficacy of copper ions in killing bacterial spores, fungi and viruses. He describes how very fine copper oxide particles embedded in textiles provide potent biocidal protection in face masks, socks, pillow cases and wound dressings.
6. A 2015 paper by Sarah Warnes and co-workers, in the American Society of Microbiology, includes the statement; *"We have shown previously that noroviruses are destroyed on copper alloy surfaces. In this new study, human coronavirus 229E was rapidly inactivated on a range of copper alloys (within minutes for simulated fingertip contamination)"*.  
Coronavirus 229E was used as surrogate for the SARS and MERS viruses which were at that time sources of great concern.  
The paper includes the following statement *"Inactivation of coronavirus on copper and copper alloy surfaces results in fragmentation of the viral genome ensuring that inactivation is irreversible"*.
7. An article in *Engineers Australia* dated 27 April 2020 reports a clinical trial at the NATA 360Biolabs which showed that copper touch surfaces contact-killed 96% SARs-CoV-2, the virus that causes Covid-19, in 2 hours.



8. Professor Keevil of Southampton University has shown that copper contact killed the MERS virus and Swine Flu virus (H1N1) in minutes. He is quoted as saying "*It just blew it apart*".
9. It has been shown in several studies (see Grigore and co-workers, 2016) that if non-soluble copper is used, such as native copper or copper oxide, then the finer the particles the more effective the biocidal properties (faster and greater kill). The extreme is to use nanoparticles which are in the size range of 10 to 100 nanometres (.00001 to .0001 millimetres). These are about the same size as the Covid-19 virus.

The obvious question following from the above information is: if copper is so lethal to bacteria, fungi and viruses, how toxic is it to humans? The answer is not straightforward.

Copper is essential for humans, playing a role in many physiological processes. A normal healthy adult has about 120mg of copper in bones, muscles, skin, liver and the brain. But much more than this amount and copper becomes toxic; in particular if ingested or taken into the lungs as fine powder, whether native copper or copper compounds. For example copper sulphate solution is toxic to humans when ingested in amounts greater than about 12 milligram per kilogram body weight. So an 80kg person swallowing more than about a gram of copper sulphate powder will be very sick. But this article is part of work related to copper on human skin, so detailed discussion of the effects of copper taken directly through the mouth or into the lungs humans (systemic copper) is not directly relevant.

What is very relevant is what, if any, forms of copper can be absorbed through the skin, and could that absorption be toxic. This requires some detailed discussion because of the different impacts of different forms of copper, such as copper sulphate in solution in water, fine native copper powder, or copper oxide ranging from fine to nanoparticle size. Before dealing with this key issue some consideration must be given to human skin.

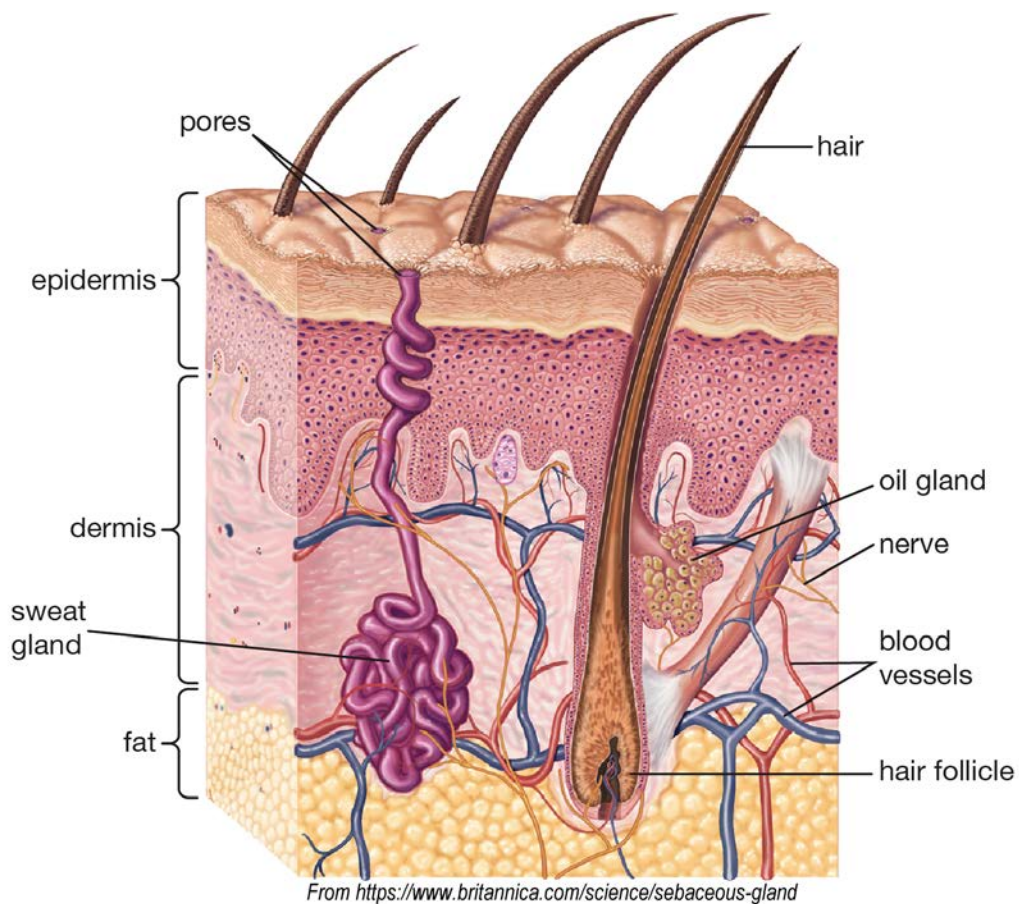


## Human Skin

The skin is the body's largest organ and is very complex. In very simple terms it comprises:

- epidermis, with a top cornified layer (*stratum corneum*) of flattened cells, and
- dermis, a thick layer of fibrous connective tissue which supports and nourishes the epidermis.

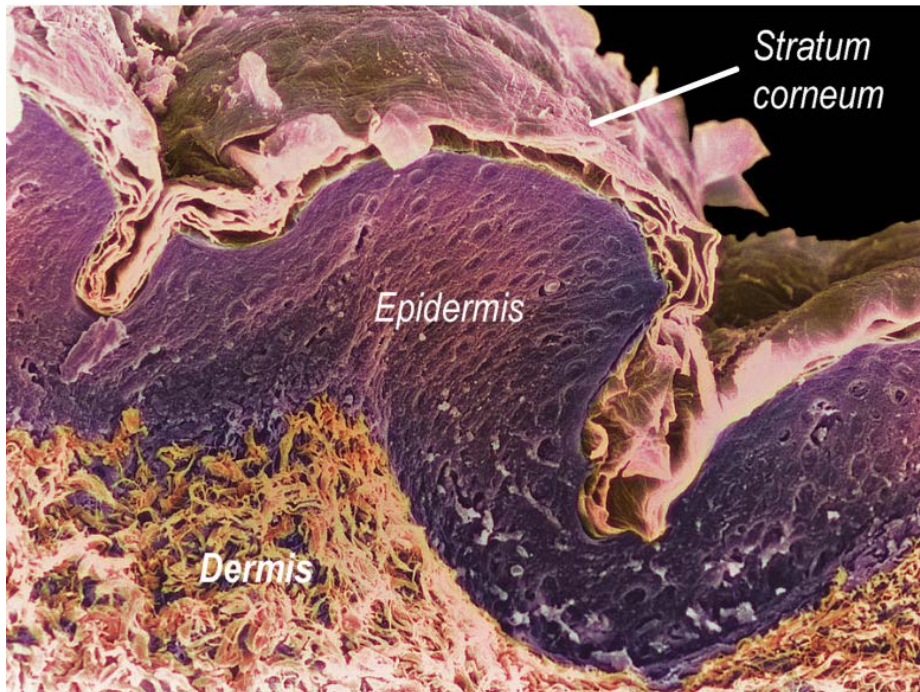
Also there are hair follicles penetrating the layers, with their associated sebaceous (oil) glands, and then also sweat glands. Scalp and face may have approximately 900 sebaceous glands per square centimetre. Palms have none - but have the equivalent number of sweat glands.







The following figure is real skin under a scanning electron microscope.



The epidermis is the primary protective layer and is waterproof. The stratum corneum consists of a series of layers of specialized skin cells that are continuously shedding. "If everything is working properly in the stratum corneum, it will help defend you against: dehydration toxins and bacteria" (<https://www.healthline.com/health/stratum-corneum>)

Sebaceous glands secrete and release sebum, which eventually coats the surface of the skin. Sebum is a complex mixture of fatty acids and waxes (lipids), sugars and other natural chemicals, which form a protective barrier. The unusual lipids found on skin's surface make the skin unfriendly to fungi and bacteria. Sebum is acidic, with pH between 4.5 and 6, which is why man-made moisturisers mimic such a low pH.

As cells move from the dermis to the epidermis, changes to the lipids occur so as to ensure that, amongst other factors, the stratum corneum is water repellent. This requires changes to cell structure because ordinary cells are relatively water permeable. It is important to note that depletion of the lipid barrier is caused by lipid-dissolving alcohols in sanitisers. In this regard ethanol is less severe than isopropanol and n-propanol (WHO Guidelines on Hand Hygiene, 2009). These WHO Guidelines state "frequent use of alcohol-base formulations for hand sanitisers causes drying of the skin unless skin conditioning agents are added to the formulations".

However, the issue is more serious than simple 'drying' because the free fatty acids in sebum, which have antibacterial activity against a range of Gram-positive bacteria, are removed by alcohol, particularly isopropanol. And it gets worse; quoting again the WHO document "hand hygiene products cause denaturation of *stratum corneum* proteins and



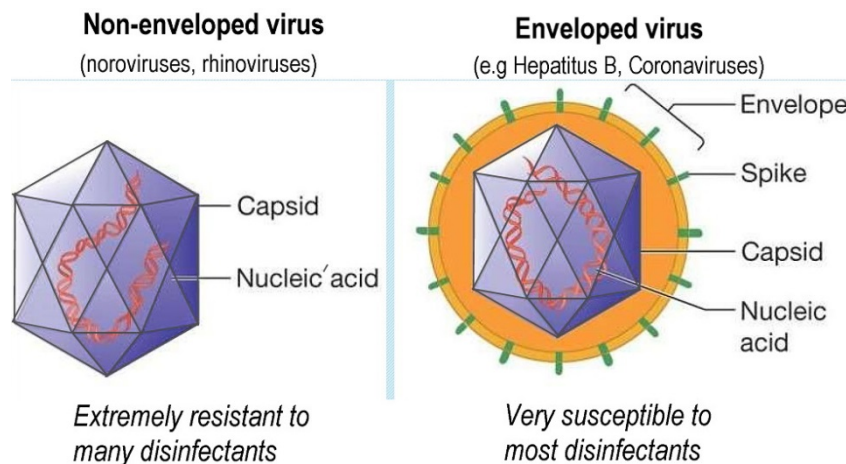
change skin flora, resulting in more frequent colonization by staphylococci and Gram-negative bacilli".

Gram-positive bacteria are bacteria which give a positive colour result to a Gram stain test. They have thicker cell walls compared with the thinner layered walls of Gram-negative bacteria

Damage by alcohol-based formulations can be substantially mitigated by appropriate moisturisers, and to this end several natural oils have protective and restorative properties. Macadamia oil with its substantial proportion of unsaturated fats is readily absorbed into the epidermis. Coconut oil, with high saturated fat content, penetrates less than macadamia but is reported as having anti-bacterial and anti-inflammatory effects (Int. Journal Molecular Sciences, Dec. 2017), as too do grapeseed and soybean oils.

### Alcohol for Killing Viruses on Skin

Obviously protection against viruses is only part of sanitising skin; bacteria and fungi are as significant. However, this note is focussed on viruses, in particular coronaviruses because of the Covid-19 epidemic. Viruses come in two basic forms; enveloped and non-enveloped; the Covid-19 virus is an enveloped virus.



There is no doubt (WHO Guidelines on Hand Hygiene, 2009) that ethyl alcohol water solutions at concentrations between 60% and 75% are very effective biocides because of the ability to denature proteins. Concentrations greater than 75% are progressively less effective because proteins are not denatured easily in the absence of water. Both isopropanol and ethyl alcohol are effective against coronaviruses; isopropanol alcohol is not effective against non-enveloped viruses. The WHO notes that "alcohols are rapidly germicidal when applied to the skin, but have no appreciable residual activity". Also "small volumes (0.2 to 0.5ml) applied to hands are no more effective than washing hands with plain



soap and water. It is probable that more than 3ml is required (more than half a teaspoon) to be effective.

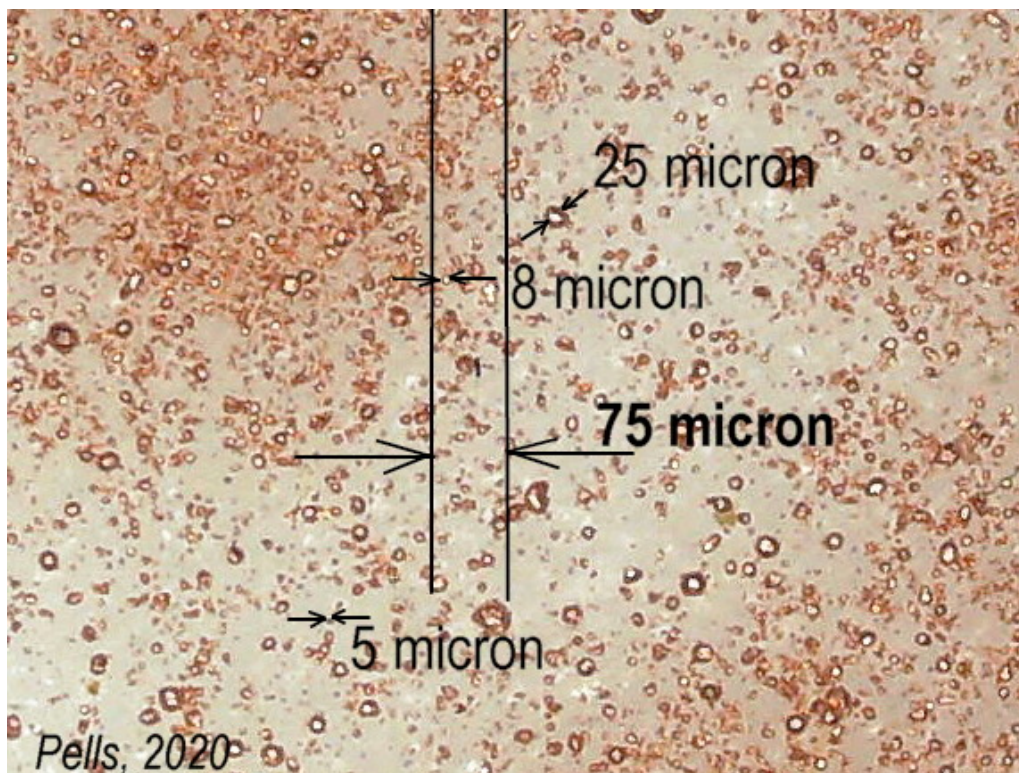
### **Copper and the Skin**

The first part of this note sets out the antimicrobial powers of copper, but also flags the toxicity of systemic copper (copper taken into the body). That copper can be toxic if ingested, or taken into the lungs, or injected, is well established. Therefore, from the viewpoint of this note, a key question is; "can copper be absorbed through the skin to be systemically toxic?"

Fortunately, there have been many studies of this issue, and in 2006 a book was published by workers at the University of California titled *Copper and the Skin*. The easiest way to summarise relevant findings is by considering the different forms of copper.

#### Native copper powder (Cu)

Copper powder of high purity is readily available. Under an optical microscope it is seen that the Cu particles typically range between about 5 micron and 25 micron (.025mm). The finest particles are about 1 micron (1000nanometres).



An article in Nanotechnology Reviews (Vol 4 Issue 5, 2015) states:

"The greater the size of the nanoparticles (>30 nanometres) the safer they are for human health, as they will not enter the bloodstream through skin when applied with a lotion or cream based product. The biggest concern with nanoparticles in cosmetics is a threat of inhalation when they are used in powders and sprays; this is not a matter of concern with Cu) nanoparticles dispersed in lotion."





Nanoparticles of Copper Oxide (CuO) are discussed in more detail below because the truth is a little more complicated than the above bold statement. The point of the above quote is that with microparticles of copper powder (in the range 1000 to 25000 nanometres) there is insignificant systemic risk arising from particulate skin penetration.

However, the real issue is not the particles, it is that fact that copper reacts with sweat, sebum and other chemicals on the skin to form compounds which release copper ions (Cu<sup>+</sup> and Cu<sup>++</sup>). These ions and compounds can penetrate the skin, and to an extent can penetrate through the skin. This is shown unequivocally by test data in the book *Copper and the Skin*. But that treatise shows equally clearly that the quantity of copper ions or copper compounds passing through the skin is substantially less than the amount causing systemic toxicity.

To quote;

"Data available indicate that copper may have noxious effects only following chronic (or parenteral) exposure in high amounts of the metallo-element, particularly upon chronic oral ingestion with food (e.g. Water) that exposes the human organism to more than 5mg/kg of copper per day"

A study involving applying elemental copper, and separately copper oxide, in an ointment form at 20% concentration over a four week period, presented no risk "*of systemic toxicity nor any untoward effects on the skin exposed*" (Gorter & co-workers, *American Journal of Therapeutics*, Vol 11, No 6, 2004)

#### Copper Oxide (CuO) nanoparticles

Copper oxide is black and a stable compound. It is insoluble in water. It has been shown to provide effective biocidal action through the release of copper ions and is used in copper oxide impregnated fabrics used for face masks, pillows, bed sheets, socks and robes (Borkow, *Using Copper to Fight Microorganisms*, *Current Chemical Biology*, Vol 6, 2012).

It has been shown that the finer the CuO particles, the more effective they are as a biocide (Betts & co-workers, *Novel Antibacterials: Alternatives to Traditional Antibiotics*, 2018). The extreme is to consider nanoparticles which are of the same size, or smaller than a Covid-19 virus. Such nanoparticles are commercially available, although substantially more expensive than copper powder.

There are two indications of caution in the use of CuO nanoparticles:

1. They are systemically very toxic and dangerous if inhaled as part of a manufacturing process, although safe within a cream or lotion, and
2. Although they are insoluble in distilled water, a detailed publication by 18 Russian scientists (*Int. Journal Molecular Sciences*, Vol 15, 2014) shows that "nanoparticles would completely vanish (presumably dissolving) within 20min after the addition of normal saline" and "their solubilization in biological fluids presumably playing a role as a prerequisite for their toxicity"



On the positive side, a 2019 paper in the *New Journal of Chemistry* titled *CuO nanoparticle penetration through intact and damaged human skin* (Zanoni and co-workers) concludes:

"To the best of our knowledge, this paper presents one of the first-time results on human skin penetration of CuO NPs. We demonstrated how Cu generated by CuO NPs is able to penetrate an intact skin but with very limited risk through a cutaneous route for workers and also for consumers. The intact epidermis acts as a good barrier against both the Cu<sup>++</sup> ions and Cu NPs dispersion, presenting negligible copper passage through the skin"

### Copper Sulphate (CuSO<sub>4</sub>)

Copper sulphate (technically copper sulphate pentahydrate, CuSO<sub>4</sub>.5H<sub>2</sub>O) has had pharmacological use for thousands of years. Such use is documented in the ancient Chinese book *The Canon of Medicine* as representing practice from pre-BC times. The Aztec and Inca people of South America used gauze soaked in copper sulphate for wound sterilization and healing.

Copper sulphate is cheap, can be bought at a local garden centre and is safe to handle. It dissolves in water liberating 'squillions' of Cu<sup>++</sup> ions. It is safe on skin (Grade I allergen), although can be a skin irritant for some people at concentrations of 1% to 2% in aqueous solution. It is reported that most skin sensitization is caused by cross-reactivity with other metals like nickel.

As already stated it is toxic when ingested in quantities greater than about 12mg per kg body weight.

### **CONCLUDING COMMENT**

Most alcohol based products currently in use as hand disinfectants are effective in killing SARS-Cov-2 coronaviruses on contact if used in sufficient quantity. However, they have no persistence; no residual effect. So recontamination can be very rapid.

In addition the needed high alcohol content for contact killing (60% to 75%) is very damaging to skin, destroying the protective system we naturally have.

Clearly there would be value in developing a single product that destroys the virus, provides some on-going protection against that virus, and rejuvenates our natural skin protection against invaders.

### **CONFLICT OF INTEREST**

The writer has no association with any organisation of any kind related to the copper industry or to the manufacture of skin sanitising products