16 - 18 YEARS

Copper Reactivity: Patination

Reactivity

Metals can be listed according to their reactivity. Some, like sodium, are so reactive that they explode on contact with water. Some, like gold, are so unreactive that they appear to be unchanged after being buried for thousands of years. Copper is low on this scale. It will react, but slowly. This low reactivity, combined with its malleability makes it ideal for use in architecture. It can be cut and hammered into ornate shapes and it will protect itself with a pale green coating of copper salts called a patina. Note this is not to be confused with verdigris, the name given to the green finish obtained by treatment with acetic acid to form copper acetate. Verdigris is soluble and not as durable as natural patinas.



These are the two telescope domes of the Royal Observatory Edinburgh. The picture was taken before the restoration in 2010. The copper cladding has a layer of green "patina", that has built up since the domes were built in 1894. The patina is



The restored domes show new copper that will take many decades to develop the patina of the original copper. (Courtesy of Royal Observatory Edinburgh.)



This view inside the dome shows how thin the structure is. (Courtesy of Eric Begbie.)

a combination of copper salts that are unreactive and protect the copper from further corrosion.

The domes are quite lightweight structures that rotate on a circular rail to allow the telescopes to point in any direction through a panel that slides open. They are also exposed to high winds.

It was not corrosion of the copper that was the problem. The thin dome structures had been shaken and buffeted for over a century and were simply falling apart. (Courtesy of Royal Observatory Edinburgh.)

The Chemistry of Patination

The first step in the development of a patina is oxidation to form copper (I) oxide (Cu₂O), which has a red or pink colour (Equation 1), when copper atoms initially react with oxygen molecules in the air. Copper (I) oxide is further oxidized to copper (II) oxide (CuO), which is black in color (Equation 2). If air is polluted with sulfur, for example from the burning of fossil fuels, then black copper (II) sulfide (CuS) also forms Equation 3.

Equation 1 4Cu + $0_2 \rightarrow 2Cu_20$

Equation 2 $2Cu_20 + 0_2 \rightarrow 4Cu0$

Equation 3 Cu + S \rightarrow CuS

Over the years, CuO and CuS slowly reacts with carbon dioxide (CO_2) and hydroxide ions (OH^-) in water from the air to eventually form $Cu_2CO_3(OH)_2$ (Equation 4), $Cu_3(CO_3)_2(OH)_2$ (Equation 5) and $Cu_4SO_4(OH)_6$ (Equation 6), which constitute the patina. The extent of humidity and the level of sulfur-related air pollution have a significant impact on how fast the patina develops, as well as the relative ratio of the three components.

Equation 4 2Cu0 + CO₂ + H₂O \rightarrow Cu₂CO₃(OH)₂ Equation 5 3Cu0 + 2CO₂ + H₂O \rightarrow Cu₃(CO₃)₂(OH)₂ Equation 6 4CuO + SO₃ + 3H₂O \rightarrow Cu₄SO₄(OH)₆



This famous statue has hardly corroded at all. It is almost exactly the same age as the observatory. The copper sheets visible in the picture are only 2.5 mm thick and since 1886 they have only lost 0.1 mm in thickness. (Courtesy of National Parks.)



The 3000 m² of copper sheet on the Copper Box in London's Olympic Park is pre-oxidised in the copper factory. The chocolate brown film of copper oxide advances the patination process and provides architects with a different colour option to the bright new copper. Eventually a film of green copper salts will appear on top of the oxide layer. This will take up to twenty years or more. (Courtesy of Make Architects.)



The reactivity series lists metals in order of their reactivity. The top five are extremely dangerous. The wedge shapes indicate how reactive they are. Copper is the only metal apart from precious metals that will not react with dilute acids. It will react very slowly with oxygen.

Questions and Activities

- 1. Which metals will not react with oxygen or water to form patinas?
- 2. Is gold ever used on the outside of buildings?
- 3. Find out which is the most reactive metal that can be used for roofing material.
- 4. On buildings close to the sea, the patina contains copper chloride as well as copper carbonate and copper sulfate. What causes this?



The top of the July Column in the Place de la Bastille in Paris. The monument is made from bronze (copper and tin), but the bronze figure at the top (Spirit of Freedom) is gilded with gold foil. (Wikimedia Commons.)

Click here for answers

Copper Development Association is a non-profit organisation that provides information on copper's properties and applications, its essentiality for health, quality of life and its role in technology. It supports education through a collection of resources spanning biology, chemistry and physics. These materials have been developed in conjunction with the Association for Science Education, and reviewed by teachers.

For more resources, visit www.copperalliance.org.uk/education.





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