



WorldLinks The Chemistry of Temporary and Permanent Tattoos

Tattoos are found in many cultures worldwide. Many of these tattoos have cultural, social, or religious significance. They may be given as a rite of passage into adulthood or as part of a religious ritual, or they may indicate social status or warrior class. Tattoos consist of pigments that are applied on or below the top layer of skin. Pigments that are absorbed in the top layer of the skin (the *epidermis*) are not permanent and gradually fade as the outer skin cells slough off. Pigments that are injected deeper into the skin (the *dermis*) become permanently embedded there.



The tattoo design is first transferred to the skin, and then it is traced over with needles covered in ink.

The earliest known tattoos date back to ~3250 BC, on a glacier mummy (called Ötzi) that was found in the Italian Alps. The mummified body of Ötzi revealed 61 tattoos. The lines that were tattooed on his lower legs, lower back, wrist, and torso may have been applied for therapeutic purposes. Tattoos have been found on female mummies in Egypt dating to ~1300 BC. These ancient tattoos were made with black lines and dots, and they included symbolic images, such as snakes. Tattoos may have been popularized in western Europe as a



Nanaia Mahuta served as New Zealand's Minister of Foreign Affairs from 2020–2023. The tattoos on her lips and chin (called *moko*) are a tradition of the indigenous Māori.

result of Captain Cook's voyage to Polynesia in 1776. Tattoos were very common in the Pacific islands and Captain Cook brought back the "tattoo man" from Tahiti, who went "on tour" as a curiosity in Great Britain. Dating back to the Civil War, tattoos have had a rich history among those who serve in the US military. Historically, tattoos were commonly associated with bikers, gang members or a criminal subculture, giving them a taboo vibe. Throughout much of the 1900s in the United States, tattoos were mostly given to men and largely symbolized strength. Over the past 50 years, however, tattoos have become much more mainstream. In the US, there is no longer widespread stigma associated with having "ink," although employers may insist that tattoos be covered up while working. Tattoos are now common among both men and women in Western society.



This flying dragon was designed by a tattoo artist.

It is estimated that about 40% of the US population between the ages of 18 and 35 have at least one tattoo. No longer reserved for certain populations, tattoos can be found on college students and soccer moms alike. Tattoos are often elaborate, colorful works of art that can range from deeply meaningful symbols to playful references to pop culture.



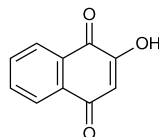
Two sailors aboard the American battleship USS New Jersey in 1944.

They can even be used as permanent make-up on the eyes and lips. Tattooing also serves an important function when it is used to restore features that were lost to surgery, injury or illness. After a reconstructive breast surgery, for example, the mental well-being of the patient can be improved when a tattoo artist adds a realistic-looking areola around the nipple. Likewise, for someone missing a belly button or a fingernail, getting a tattoo can restore a sense of wholeness.

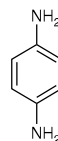
Let's take a look at some of the organic compounds used in tattoo art. Henna dye imparts a reddish-brown color when applied to hair or skin, and it has been used for thousands of years. The leaves and stems of the henna plant contain lawsone, an organic compound that undergoes a chemical reaction with keratin, a protein found in hair and skin. After a design is drawn on the skin using henna, the henna reacts with the skin's keratin. This reaction causes the skin to be stained, and the applied design becomes a *temporary* tattoo that lasts for up to 6 weeks. To make a black tattoo, other compounds are added to the henna, such as paraphenylenediamine (PPD). Such additives can cause significant allergic reactions and can sometimes lead to permanent scarring or a lifelong sensitivity to certain chemicals.



An Indian wedding tradition is to apply intricate Mehndi (henna) designs to the bride's hands, as a way to bestow good luck to the marriage.



lawsone – from the henna plant
(2-hydroxynaphthalene-1,4-dione)



PPD – an additive in "black henna"
(paraphenylenediamine)

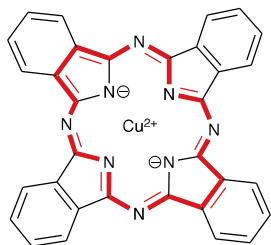
The ink in a *permanent* tattoo consists of colored pigments that are relatively insoluble in water. Tiny nanoparticles of pigment are dispersed in a solvent such as ethanol, isopropyl alcohol or glycerin and injected by a needle into the inner layer of skin cells (the *dermis*). The pigment molecules cause an inflammatory response which attracts immune cells called macrophages. The macrophages accumulate the pigment nanoparticles and (mostly) keep them from diffusing throughout the body.

Tattoos with a black color come from injection of elemental carbon called *carbon black*. Soot or charcoal was used in earlier cultures. Colored tattoos started becoming more common in the 1940s and 1950s. Earlier forms of tattoo pigments were

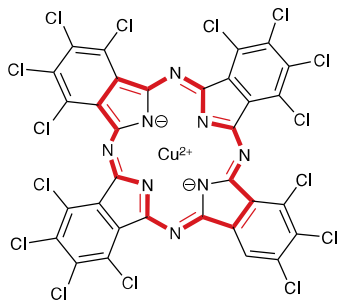
made from inorganic compounds such as red cinnabar (HgS), yellow-orange cadmium sulfide (CdS), and blue-green chromium oxides (Cr₂O₃), but these compounds have toxicity issues and have largely been replaced with organic pigments. Some tattoo pigments are organic compounds that are used as dyes in the textile industry, such as phthalocyanine dyes and azo dyes. Phthalocyanine dyes include Pigment Blue 15 (copper phthalocyanine) and Pigment Green 7 (chlorinated copper phthalocyanine). The structures of these two compounds (shown below) are very similar. When the aromatic protons are replaced with Cl atoms, the color shifts from blue to green.



Personal art, such as this whimsical clown cat, can be turned into a tattoo.



Pigment Blue 15
(copper phthalocyanine)



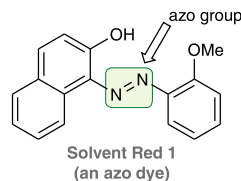
Pigment Green 7
(phthalocyanine green)



The highly conjugated π system gives rise to the observed colors (Section 16.12). These compounds also exhibit aromaticity. In addition to the four benzene rings in the outer corners of the molecule, note that there are alternating

double and single bonds in the large 18-membered ring that is highlighted in red. These conjugated double bonds can delocalize over the entire 18-membered ring. There are nine π bonds in the conjugated system, so there is a total of 18 π electrons in the continuous system of p orbitals. This satisfies Hückel's rule for aromaticity ($4n + 2 = 18$, if $n = 4$). As a result, these large aromatic systems are expected to be planar. Experimentally, it is found that the plane is slightly warped.

Azo dyes are compounds that contain two aromatic systems that are linked together by an azo group (a $\text{N}=\text{N}$ double bond). An example, called Solvent Red 1, is shown below.



Note that the $\text{N}=\text{N}$ double bond connects the aromatic ring systems (on either side of the $\text{N}=\text{N}$ bond) into a single, continuous, conjugated system. This extensive overlap of p orbitals requires that the rings are in the same plane, and that is experimentally found to be the case. The extensive conjugated π system of azo dyes results in absorption of visible light, so these compounds are usually colored. Azo dyes are frequently used for red colors in tattoos.

In addition to the risk of allergic reactions (such as those described with PPD in black henna), the use of contaminated ink can lead to infections. There are also some safety concerns over the various pigments used in tattoo art. For many of the pigments, there is very little toxicity testing available about their long-term safety when injected under the skin. For azo dyes in particular, there is concern that they could metabolize into compounds that can react with amine groups in DNA. Such compounds, called mutagens, have the potential to cause cancer. For that reason, the European Union has discontinued the use of many pigments, including Pigment Blue 15 and Pigment Green 7.



Circus performer Maud Wagner is credited as the first female tattoo artist. (Circa 1907 photo)

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Nanaia Mahuta photo by New Zealand Labour Party, Wikimedia/CC-BY-SA 4.0; Black and white image of two US Navy sailors, by Fenno Jacobs/Department of Defense/Wikimedia (cropped), is in the public domain; Image of flying dragon tattoo worn by Cal Poly Pomona faculty member Sarah Wallin Huff, by artist Nikola Ivana, is printed with permission; Bride with red henna palm photo by Noranina, Wikimedia/CC-BY-SA 4.0; Henna powder and pigment powders, from Wikimedia, are in the public domain; Black henna on two hands photo by Ishan Mittal, Wikimedia/CC-BY-SA 4.0 • **Page 914** Image of clown cat tattoo worn by Jo Forschner, designed by Elizabeth Starkey, is printed with permission; First female tattoo artist Maud Wagner photo, from The Plaza Gallery in Los Angeles, is in the public domain

