

INDIGO: The “Blue” in Blue Jeans

By Jeffrey Deakin and Raymond Cooper

IN 2015, 1.24 BILLION PAIRS OF JEANS WERE SOLD AROUND THE WORLD, according to data compiled by Statistic Brain. On average, a pair of jeans requires 3 to 12 grams of indigo dye to turn them blue, and about 20 million kilograms of indigo are produced annually. That's a lot of dye for a lot of jeans! But why and how is indigo used to give jeans their blue color, and where does all of this dye come from?

The original blue jeans

The California Gold Rush in the mid-1800s attracted entrepreneurs from all over the world. One of those entrepreneurs was a Bavarian emigrant named Levi Strauss, who headed to San Francisco in 1853 to establish a wholesale dry-goods business. He immediately noticed that gold miners and other laborers required durable clothing, particularly pants.

Even though denim pants had been around as work wear for many years, the story of jeans really begins with one of Strauss's customers, a Nevada tailor named Jacob Davis. In 1870, Davis was asked by one of his customers to make a pair of work pants for her husband that wouldn't fall apart. Davis tried to think of a way to strengthen his trousers and came up with the idea of putting copper rivets at the points of strain, such as pocket corners and the base of the button fly. These riveted pants were an instant hit. Davis quickly decided to apply for a patent, but needed a business partner to help get the project rolling. He immediately thought of Levi Strauss, his fabric supplier, and the first patent for Levi's jeans was issued in 1873.

The reason blue denim was more popular has quite a bit to do with the indigo dye. Unlike most natural dyes that, when heated, penetrate cloth fibers directly, indigo binds externally to the cloth's threads. With each washing some of these dye molecules are stripped away. The washing process individualizes the color and also softens the rough fabric to individualize the fit, as well. So, not only were Levi's jeans durable, they were comfortable.



Natural indigo

Indigo dye can be produced naturally or synthetically. The most common natural source for indigo is from the woad plant, which is native to tropical climates. But woad flowers are yellow, and the leaves are green, so how is a blue-colored dye extracted from this plant?

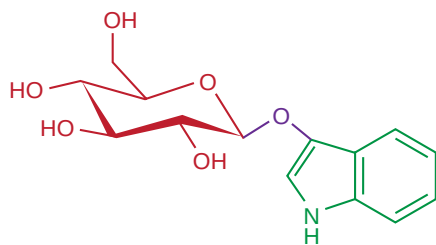


Figure 1. Chemical structure of indican, a glycoside composed of the sugar glucose bonded to indoxyl by a glycoside bond.



Woad flower and solid indigo

Woad plant with open flowers

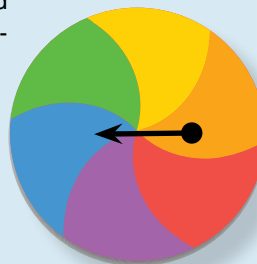
The indigo pigment itself is not found in the plant. But soaking the leaves of the plant in water in the presence of air releases a dark-blue precipitate. It starts with indican (Fig. 1), a colorless compound present in the tissues of the woad plant. Indican is a glycoside—a molecule with a sugar connected to a non-sugar with a glycoside bond.

In the presence of an enzyme already in the plant, indican reacts with water to result in glucose and a water-soluble compound called indoxyl.

The indoxyl-rich mixture is stirred to mix it with air. The air (O_2) oxidizes the indoxyl to indigo, which is dark blue in color. Indigo (also called indigotin) is insoluble in water and precipitates out of the solution. The precipitated indigo is dried and pressed into cakes for distribution.

Indigo Absorbs Orange Light. What?

DYES ARE ORGANIC MOLECULES THAT ARE COLORED because they absorb certain wavelengths of visible light and transmit or reflect others. A chromophore is a region in a molecule that usually contains alternating double and single bonds and produces the color. When visible light hits the chromophore, an electron in the molecule can jump from its ground state to an excited state. The indigo molecule absorbs light in the **orange** part of the visible spectrum (wavelength (λ) = 613 nanometers), but the compound appears to the human eye as the complementary color: **purplish-blue**. Need to remember the complementary color? Make a simple 6-piece color wheel without the indigo of ROYGBIV (an acronym that describes the colors of the rainbow: red, orange, yellow, green, blue, indigo and violet). If a compound is green, look across the wheel, chances are it absorbs light in the red range. Just be wary—prediction can get complicated in a hurry because mixtures and even pure compounds can absorb in more than one area of the visible spectrum.



Dyeing textiles with indigo

When indigo first became widely available in Europe in the 16th century, dyers found that indigo was difficult to control as a textile dye because it is not soluble in water.

To overcome this problem, indigo was subjected to chemical reduction involving carbon-to-oxygen double bonds. (Fig. 2) The reduction product is commonly known as indigo white, or leuco indigo.

A fabric made from cellulose (cotton, for example) would be submerged in a dye-bath that contains indigo white. The indigo white molecules would then bind to the cellulose molecules via hydrogen bonds. When this fabric is removed from the dye-bath, the white indigo is quickly oxidized by oxygen in the air and reverts to the insoluble, intense color of indigo. Because indigo is now lodged inside the cellulose material—through

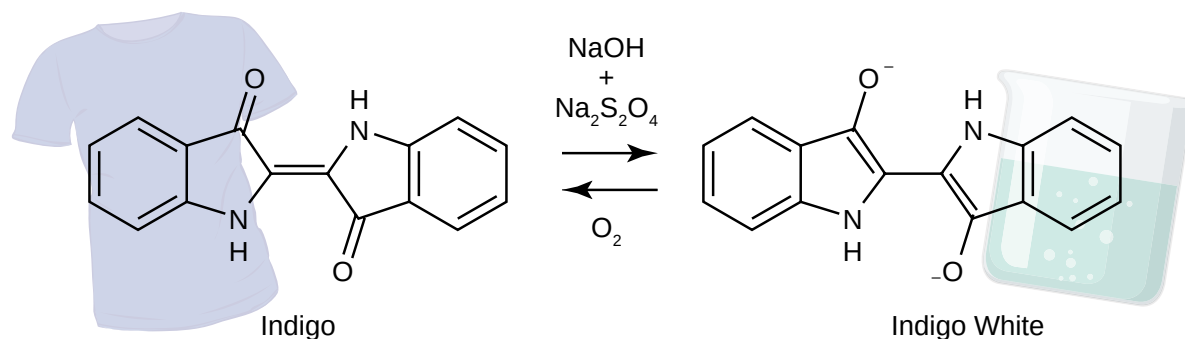


Figure 2. The reduction of indigo to water-soluble indigo white appears from left to right. Indigo White is light green in solution. Exposure to O_2 (air) oxidizes it back to Indigo.



**FADED DENIM APPAREL
IS CONSIDERED
FASHIONABLE TODAY,
AND SOME PEOPLE
PREFER JEANS WITH
A FADED BLUE COLOR
OVER DARK BLUE.**



This strip of cloth shows the saturation of indigo dye from 0–10.

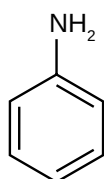
hydrogen bonding—it remains inside the fabric.

Over time, though, because hydrogen bonding is an intermolecular force, which is weaker than a chemical bond, some indigo molecules will separate from the cellulose molecules in the fabric, and the blue color will slowly fade. This is triggered by frequent washing of the fabric. Faded denim apparel is considered fashionable today, and some people prefer jeans with a faded blue color over dark blue.

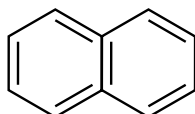
Synthetic indigo

During the 1800s, natural indigo production could no longer meet the demands of the clothing industry, and a search for synthetic indigo started.

Fascinated by the blue dye, the German chemist Adolf von Baeyer started work in 1865 that soon led to the discovery of indole



Aniline



Naphthalene

Figure 3. Molecular structures of (3a) aniline and (3b) naphthalene



Traditional boro (patchwork) denim kimono from Japan.

and to the partial synthesis of indigotin. In 1882, von Baeyer published the “Baeyer–Drewson indigo syntheses.” It turned out to be an easy route for producing indigo at laboratory scale. In 1905, Von Baeyer was awarded the Nobel Prize, recognizing his work in organic dyes and other advances in organic chemistry.

The synthesis of indigo remained impractical, so the search was on for alternative starting materials. In 1901, Johannes Pfleger and Karl Heumann came up with an industrial mass-production synthesis of indigo from aniline (Fig. 3a). Aniline was readily avail-

able in large quantities from coal, so it was an economically feasible route to synthesizing indigo. At the time synthetic indigo was launched, natural indigo production was 19,000 metric tons, and soon declined to 1,000 metric tons by 1914.

Variations using coal-based aniline are still in use today, but modern production of indigo starts with petroleum-based naphthalene (Fig. 3b) through a different synthetic route that is even more economically viable.

Aniline was first isolated in 1826 by Otto Unverdorben by destructive heating and distillation of indigo. Naphthalene was traditionally used in moth balls, which accounted for their characteristic smell. We have certainly come a long way from the ancient methods of extracting naturally occurring indigo from the woad plant to the modern mass-production techniques of synthetic indigo. If the synthesis of this dye weren't so successful, who knows what would be in fashion for casual wear these days! 

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