Indigo dye

Lump of Indian indigo dye

Indigo dye is dye with a distinctive blue color (see indigo). The chemical compound that constitutes the indigo dye is called indigotin. The ancients extracted the natural dye from several species of plant as well as one of the two famous Phoenician sea snails, but nearly all indigo produced today is synthetic.

- Among other uses, it is used in the production of denim cloth for blue jeans. The form of indigo used in food is called "indigotine", and is listed in the USA as FD&C Blue No. 2, and in the European Union as E Number: E132.

Sources and uses

Indigo dye

A variety of plants, including woad, have provided indigo throughout history, but most natural indigo is obtained from those in the genus *Indigofera*, which are native to the tropics. In temperate climates indigo can also be obtained from woad (*Isatis tinctoria*) and dyer's knotweed (*Polygonum tinctorum*), although the *Indigofera* species yield more dye. The primary commercial indigo species in Asia was true indigo (*Indigofera tinctoria*, also known as *Indigofera sumatrana*). In Central and South America the two species *Indigofera suffruticosa* (Anil) and *Indigofera arrecta* (Natal indigo) were the most important.

Natural indigo was the only source of the dye until about 1900. Within a short time, however, synthetic indigo had almost completely superseded natural indigo, and today nearly all indigo produced is synthetic.

In the United States, the primary use for indigo is as a dye for cotton work clothes and blue jeans. Over one billion pairs of jeans around the world are dyed blue with indigo. For many years indigo was used to produce deep navy blue colors on wool.

Indigo does not bond strongly to the fiber, and wear and repeated washing may slowly remove the dye

Indigo is also used as a food coloring, and is listed in the USA as FD&C Blue No. 2. The specification for FD&C Blue No. 2 includes three substances, of which the major one is the sodium salt of Indigotindisulfonate.

Indigotinesulfonate is also used as a dye in renal function testing, as a reagent for the detection of nitrates and chlorates and in the testing of milk.

History

Indigo is among the oldest dyes to be used for textile dyeing and printing. Many Asian countries, such as India, China, Japan and South East Asian nations have used indigo as a dye (particularly silk dye) for centuries. The dye was also known to ancient civilizations in Mesopotamia, Egypt, Greece, Rome, Britain, Mesoamerica, Peru, Iran, and Africa.

India is believed to be the oldest center of indigo dyeing in the Old World. It was a primary supplier of indigo to Europe as early as the Greco-Roman era. The association of India with indigo is reflected in the Greek word for the dye, which was *indikon*. The Romans used the term *indicum*, which passed into Italian dialect and eventually into English as the word *indigo*.

In Mesopotamia, a Neo-Babylonian cuneiform tablet of the 7th century BC gives a recipe for the dyeing of wool, where lapis-colored wool (uqnatu) is produced by repeated immersion and airing of the cloth. Indigo was most probably imported from India.

The Romans used indigo as a pigment for painting and for medicinal and cosmetic purposes. It was a luxury item imported to the Mediterranean from India by Arab merchants.

Indigo remained a rare commodity in Europe throughout the Middle Ages. Woad, a chemically identical dye derived from the plant *Isatis tinctoria* (Brassicaceae), was used instead.

In the late fifteenth century, the Portuguese explorer Vasco da Gama discovered a sea route to India. This led to the establishment of direct trade with India, the Spice Islands, China, and Japan. Importers could now avoid the heavy duties imposed by Persian, Levantine, and Greek middlemen and the lengthy and dangerous land routes which had previously been used. Consequently, the importation and use of indigo in Europe rose significantly. Much European indigo from Asia arrived through ports in Portugal, the Netherlands, and England. Spain imported the dye from its colonies in South America. Many indigo plantations were established by European powers in tropical climates; it was a major crop in Jamaica and South Carolina, with much or all of the labor performed by enslaved Africans and African-Americans. Indigo plantations also thrived in the Virgin Islands. However, France and Germany outlawed imported indigo in the 1500s to protect the local woad dye industry.

Tuareg wearing an indigo-dyed tagelmust.

Indigo was the foundation of centuries-old textile traditions throughout West Africa. From the Tuareg nomads of the Sahara to Cameroon, clothes dyed with indigo signified wealth. Women dyed the cloth in most areas, with the Yoruba of Nigeria and the Manding of Mali particularly well known for their expertise. Among the Hausa male dyers working at communal dye pits were the basis of the wealth of the ancient city of Kano, and can still be seen plying their trade today at the same pits.

In Japan, indigo became especially important in the Edo period when it was forbidden to use silk, so the Japanese began to import and plant cotton. It was difficult to dye the cotton fiber except with indigo. Even today indigo is very much appreciated as a color for the summer Kimono Yukata, as this traditional clothing recalls Nature and the blue sea.

In 1865 the German chemist Johann Friedrich Wilhelm Adolf von Baeyer began working with indigo. His work culminated in the first synthesis of indigo in 1880 from o-nitrobenzaldehyde and acetone upon addition of dilute sodium hydroxide, barium hydroxide, or ammonia and the announcement of its chemical structure three years later. BASF developed a commercially feasible manufacturing process that was in use by 1897, and by 1913 natural indigo had been almost entirely replaced by synthetic indigo. In 2002, 17,000 tons of synthetic indigo were produced worldwide.

In the nineteenth century, the British obtained much indigo from India. With the coming of the synthetic substitute, the demand for natural indigo dropped and indigo farming became unprofitable.

In literature, the play Nildarpan by Dinabandhu Mitra is based on the indigo slavery and forceful cultivation of indigo in India. It played an essential part in the Bengali indigo revolt of 1858 called Nilbidraha.

Developments in dyeing technology

Indigo is a challenging dye to use because it is not soluble in water; to be dissolved, it must undergo a chemical change. When a submerged fabric is removed from the dyebath, the indigo quickly combines with oxygen in the air and reverts to its insoluble form. When it first became widely available in Europe in the sixteenth century, European dyers and printers struggled with indigo because of this distinctive property. It was also a toxic substance that, by requiring several chemical manipulations, had many opportunities to injure workers. In fact, during the 19th century, English poet William Wordsworth referred to the plight of indigo dye workers of his hometown of Cockermouth in his autobiographical poem "The Prelude". Speaking of their dire working conditions and the empathy that he feels for them, he writes, "Doubtless, I should have then made common cause/ With some who perished; haply perished too,/ A poor mistaken and bewildered offering - / Unknown to those bare souls of miller blue."

A preindustrial process for dyeing with indigo, used in Europe, was to dissolve the indigo in stale urine. Urine reduces the water-insoluble indigo to a soluble substance known as *indigo white* or *leucoindigo*, which produces a yellow-green solution. Fabric dyed in the solution turns blue after the indigo white oxidizes and returns to indigo. Synthetic urea to replace urine became available in the 1800s.

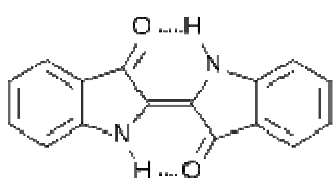
Another preindustrial method, used in Japan, was to dissolve the indigo in a heated vat in which a culture of thermophilic, anaerobic bacteria was maintained. Some species of such bacteria generate hydrogen as a metabolic product, which can convert insoluble indigo into soluble indigo white. Cloth dyed in such a vat was decorated with the techniques of shibori (tie-dye), kasuri, katazome, and tsutsugaki. Examples of clothing and banners dyed with these techniques can be seen in the works of Hokusai and other artists.

Two different methods for the direct application of indigo were developed in England in the eighteenth century and remained in use well into the nineteenth century. The first method, known as *pencil blue* because it was most often applied by pencil or brush, could be used to achieve dark hues. Arsenic trisulfide and a thickener were added to the indigo vat. The arsenic compound delayed the oxidation of the indigo long enough to paint the dye onto fabrics.

The second method was known as *china blue* due to its resemblance to Chinese blue-and-white porcelain. Instead of using an indigo solution directly, the process involved printing the insoluble form of indigo onto the fabric. The indigo was then reduced in a sequence of baths of iron(II) sulfate, with air-oxidation between each immersion. The china blue process could make sharp designs, but it could not produce the dark hues possible with the pencil blue method.

Around 1880 the *glucose process* was developed. It finally enabled the direct printing of indigo onto fabric and could produce inexpensive dark indigo prints unattainable with the china blue method.

Chemical properties

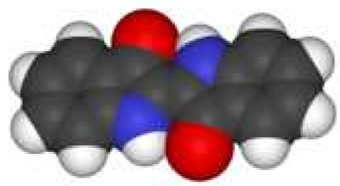


Indigo molecule

Indigo is a dark blue crystalline powder that melts at 390°–392°C. It is insoluble in water, alcohol, or ether but soluble in chloroform, nitrobenzene, or concentrated sulfuric acid. The chemical structure of indigo corresponds to the formula $C_{16}H_{10}N_2O_2$.

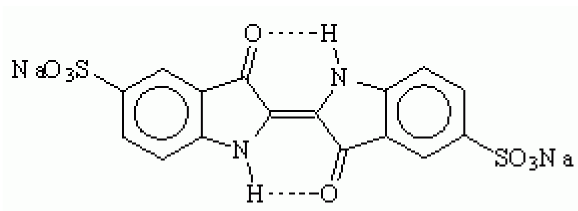
The naturally occurring substance is indican, which is colorless and soluble in water. Indican can easily be hydrolyzed to glucose and indoxyl. Mild oxidation, such as by exposure to air, converts indoxyl to indigo.

The manufacturing process developed in the late 1800s is still in use throughout the world. In this process, indoxyl is synthesized by the fusion of sodium phenylglycinate in a mixture of sodium hydroxide and sodamide.



Indigo

Several simpler compounds can be produced by decomposing indigo; these compounds include aniline and picric acid. The only chemical reaction of practical importance is its reduction by urea to indigo white. The indigo white is reoxidized to indigo after it has been applied to the fabric.



indigo carmine

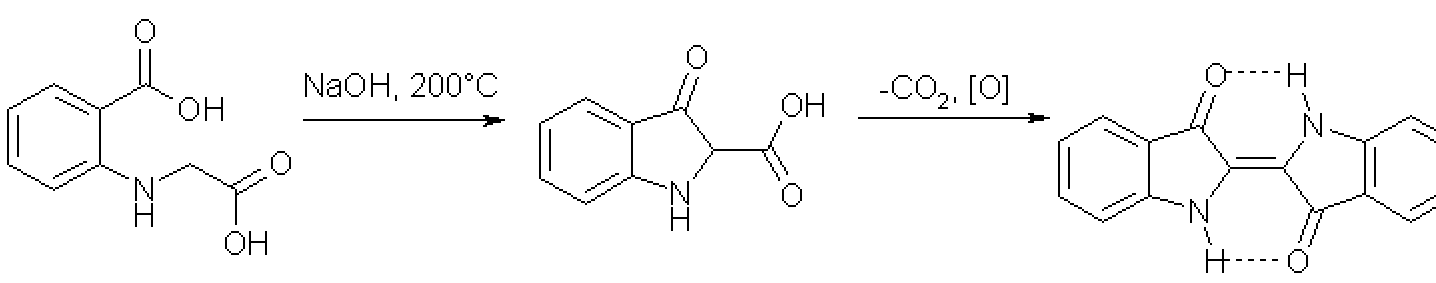
Indigo treated with sulfuric acid produces a blue-green color. It became available in the mid-1700s. Sulfonated indigo is also referred to as *Saxon blue* or *indigo carmine*.

Tyrian purple was a valuable purple dye in antiquity. It was made from excretions of a common Mediterranean Sea snail. In 1909 its structure was shown to be 6,6'-dibromoindigo. It has never been produced synthetically on a commercial basis.

The SMILES structure of indigo is O=c3c(=c2[nH]c1ccccc1c2=O)[nH]c4ccccc34 and its CAS number is [12626-73-2].

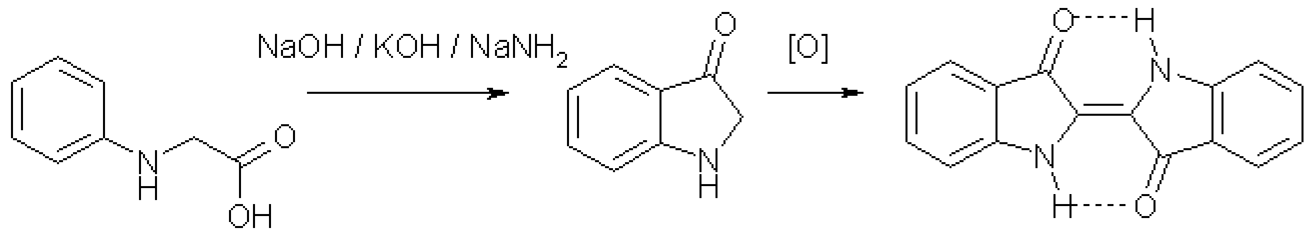
Chemical synthesis

Indigo may be synthetically manufactured in a number of different ways. The original method, first used to synthesise indigo by Heumann in 1897, involves heating N-(2-Carboxyphenyl)glycine acid to 200°C in an inert atmosphere with sodium hydroxide. This produces indoxyl-2-carboxylic acid, a material that readily decarboxylates and oxidises in air to form indigo.



Heumann's original synthesis of Indigo

The modern synthesis of indigo is slightly different from that route originally used and its discovery is credited to Pfleger in 1901. In this process, N-phenylglycine is treated with an alkaline melt of sodium and potassium hydroxides containing sodamide. This produces indoxyl, which is subsequently oxidised in air to form indigo.



Pfleger's modern synthesis of Indigo