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HISTORY OF INDIGO AND OBTAINING CHEMICAL INDIGO DYE FROM INDIGOFERA AUSTRALIS.

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Abstract

This article describes history of indigo, the methods of adaptation of Indigofera australis to our climatic conditions, the agrotechnical measures taken and methods of obtaining chemical dyes from it.

Keywords

Indigofera, indigo, indumum, indicum, indikon, izatin, indoxyl, Indigofera tinctoria, Indigofera australis, dye.

Indigo dye is an organic compound with a distinctive blue color. Historically, indigo was a natural dye extracted from the leaves of some plants of the *Indigofera* genus, in particular *Indigofera tinctoria* and *Indigofera australis* dye-bearing *Indigofera* plants were commonly grown and used throughout the world, in Asia in particular, as an important crop, with the production of indigo dyestuff economically important due to the previous rarity of some blue dyestuffs historically.[1]

Most indigo dye produced today is synthetic, constituting several thousand tons each year. It is most commonly associated with the production of denim cloth and blue jeans, where its properties allow for effects such as stone washing and acid washing to be applied quickly.

History of indigo

Indigo, historical dye collection of the Technical University of Dresden, Germany The oldest known fabric dyed indigo, dated to 6,000 years ago, was discovered in Huaca Prieta, Peru.[7] Many Asian countries, such as India, Japan, and Southeast Asian nations have used indigo as a dye (particularly silk dye) for centuries. The dye was also known to ancient civilizations in Mesopotamia, Egypt, Britain, Mesoamerica, Peru, Iran, and West Africa. Indigo was also cultivated in India, which was also the earliest major center for its production and processing.[8] The *I. tinctoria* species was domesticated in

India.[8] Indigo, used as a dye, made its way to the Greeks and the Romans, where it was valued as a luxury product.[8]

India 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, *indikon* (Ἰνδικόν, Indian).[9] The Romans latinized the term to *indicum*, which passed into Italian dialect and eventually into English as the word indigo.

Cake of indigo

In Mesopotamia, a neo-Babylonian cuneiform tablet of the seventh 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.[9] 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. A chemically identical dye derived from the woad plant *(Isatis tinctoria)* was used instead. In the late 15th 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. Many indigo plantations were established by European powers in tropical climates. Spain imported the dye from its colonies in Central and South America, and it was a major crop in Haiti and Jamaica, with much or all of the labor performed by enslaved Africans and African Americans. In the Spanish colonial era, intensive production of indigo for the world market in the region of modern El Salvador entailed such unhealthy conditions that the local indigenous population, forced to labor in pestilential conditions, was decimated.[10] Indigo plantations also thrived in the Virgin Islands. However, France and Germany outlawed imported indigo in the 16th century to protect the local woad dye industry.

Sources

A variety of plants have provided indigo throughout history, but most natural indigo was obtained from those in the genus *Indigofera*, which are native to the tropics, notably the Indian Subcontinent. The primary commercial indigo species in Asia was true indigo (*Indigofera australis*). A common alternative used in the relatively colder subtropical locations such as Japan's Ryukyu Islands and Taiwan is *Strobilanthes cusia*.

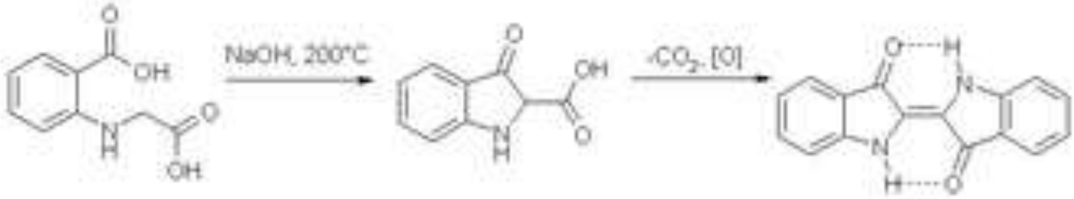
Until the introduction of *Indigofera* species from the south, *Polygonum tinctorum* (*Dyer's knotweed*) was the most important blue dyestuff in East Asia; however, the crop produced less dyestuff than the average crop of indigo, and was quickly surpassed in terms of favour for the more economical *Indigofera tinctoria and Indigofera australis* plants. In Central and South America, the species grown is *Indigofera suffruticosa*, also known as *anil*, and in India, an important species was *Indigofera arrecta*, Natal indigo. In Europe, *Isatis tinctoria*, commonly known as *woad*, was used for dyeing fabrics blue, containing the same dyeing compounds as indigo, also referred to as indigo.

Several plants contain indigo, which, when exposed to an oxidising source such as atmospheric oxygen, reacts to produce indigo dye; however, the relatively low concentrations of indigo in these plants make them difficult to work with, with the color more easily tainted by other dye substances also present in these plants, typically leading to a greenish tinge.

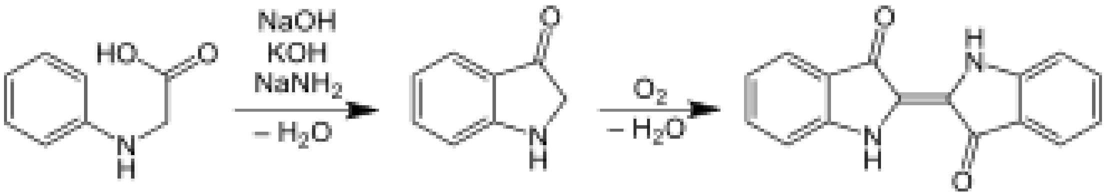
The precursor to indigo is indican, a colorless, water-soluble derivative of the amino acid tryptophan. Indican readily hydrolyzes to release β-D-glucose and indoxyl. Oxidation by exposure to air converts indoxyl to indigotin, the insoluble blue chemical that is the endpoint of indigo dye. Indican was obtained from the processing of the plant's leaves, which contain as much as 0.2–0.8% of this compound. The leaves were soaked in water and fermented to convert the glycoside indican present in the plant to the blue dye **indigotin**.[2] They precipitate from the fermented leaf solution when mixed with a strong base[3] such as lye, pressed into cakes, dried, and powdered. The powder was then mixed with various other substances to produce different shades of blue and purple.

Natural sources of indigo also include mollusks; the Murex sea snail produces a mixture of indigo and 6,6'-dibromoindigo (red), which together produce a range of purple hues known as Tyrian purple. Light exposure during part of the dyeing process can convert the dibromoindigo into indigo, resulting in blue hues known as royal blue, hyacinth purple, or tekhelet.

Chemical synthesis



Heumann's synthesis of indigo



Pfleger's synthesis of indigo

Given its economic importance, indigo has been prepared by many methods. The Baeyer-Drewson indigo synthesis dates back to 1882. It involves an aldol condensation of o-nitrobenzaldehyde with acetone, followed by cyclization and oxidative dimerization to indigo. This route is highly useful for obtaining indigo and many of its derivatives on the laboratory scale, but proved impractical for industrial-scale synthesis. Johannes Pfleger[4] and Karl Heumann (de) eventually came up with industrial mass production synthesis.[5]

The first commercially practical route of producing indigo is credited to Pfleger in 1901. In this process, *N*-phenylglycine is treated with a molten mixture of sodium hydroxide, potassium hydroxide, and sodamide. This highly sensitive melt produces indoxyl, which is subsequently oxidized in air to form indigo. Variations of this method are still in use today. An alternative and also viable route to indigo is credited to Heumann in 1897. It involves heating *N*-(2-carboxyphenyl)glycine to 200 °C (392 °F) in an inert atmosphere with sodium hydroxide. The process is easier than the Pfleger method, but the precursors are more expensive. Indoxyl-2-carboxylic acid is generated. This material readily decarboxylates to give indoxyl, which oxidizes in air to form indigo.[1] The preparation of indigo dye is practised in college laboratory classes according to the original Baeyer-Drewsen route.[6]

Uses

Indigo dye

The primary use for indigo is as a dye for cotton yarn, mainly used in the production of denim cloth suitable for blue jeans; on average, a pair of blue jeans requires just 3 grams (0.11 oz) to 12 grams (0.42 oz) of dye. Smaller quantities are used in the dyeing of wool and silk.

Indigo carmine, also known as indigo, is an indigo derivative which is also used as a colorant. About 20 thousand tons are produced annually, again mainly for the production of blue jeans.[1] It is also used as a food colorant, and is listed in the United States as FD&C Blue No. 2.

Direct printing

Two different methods for the direct application of indigo were developed in England in the 18th century and remained in use well into the 19th 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.

Pot of freeze-dried indigo dye

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.

Since 2004, freeze-dried indigo, or instant indigo, has become available. In this method, the indigo has already been reduced, and then freeze-dried into a crystal. The crystals are added to warm water to create the dye pot. As in a standard indigo dye pot, care has to be taken to avoid mixing in oxygen. Freeze-dried indigo is simple to use, and the crystals can be stored indefinitely as long as they are not exposed to moisture.

REFERENCES:

1. Jump up to:a b c d e *Steingruber, Elmar (2004). "Indigo and Indigo Colorants". Ullmann's Encyclopedia of Industrial Chemistry. Weinheim: Wiley-VCH. doi:10.1002/14356007.a14_149.pub2.*
2. *Schorlemmer, Carl (1874). A Manual of the Chemistry of the Carbon compounds; or, Organic Chemistry. London.*Quoted in the Oxford English Dictionary, second edition, 1989
3. *"Indigo Dyeing". Coyuchi Inc. Retrieved 2019-05-24.*
4. Jump up to:a b *"Johannes Pfleger - Das Evonik Geschichtsportal - Die Geschichte von Evonik Industries". history.evonik.com. Retrieved Jun 7, 2020.*
5. Jump up to:a b *"The Synthesis of Indigo". Archived from the originalon 2016-03-04. Retrieved 2015-01-05.*
6. *McKee, James R.; Zanger, Murray (1991). "A microscale synthesis of indigo: Vat dyeing". Journal of Chemical Education.* **68** *(10): A242. Bibcode:1991JChEd..68..242M. doi:10.1021/ed068pA242.*
7. *Splitstoser JC, Dillehay TD, Wouters J, Claro A (2016-09-14). "Early pre-Hispanic use of indigo blue in Peru". Science Advances.* **2** *(9): e1501623. Bibcode:2016SciA....2E1623S. doi:10.1126/sciadv.1501623. PMC 5023320. PMID 27652337.*
8. Jump up to:a b c Kriger & Connah, page 120
9. Jump up to:a b *St. Clair, Kassia (2016). The Secret Lives of Colour. London: John Murray. p. 189. ISBN 9781473630819. OCLC 936144129.*
10. Fowler, Walter (6 August 1991). *The Formation of Complex Society in Southeastern Mesoamerica*. CRC Press.
11. Kriger, Colleen E. & Connah, Graham (2006). *Cloth in West African History*. Rowman Altamira. ISBN 0-7591-0422-0.

12. *Eiko Ikegami (28 February 2005). Bonds of Civility: Aesthetic Networks and the Political Origins of Japanese Culture. Cambridge University Press. p. 284. ISBN 978-0-521-60115-3.*