IN'DIGO (Sp. *índigo, índico*, from Lat. *indicum*, from Gk. *ἰνδικόν, indikon*, indigo, from *Ἰνδία, India*, India). A coloring matter first employed as a dyestuff in India, whence it was brought by traders to the Mediterranean countries. Europeans were not acquainted with its vegetable origin until the time when its importation assumed considerable dimensions, after the circumnavigation of Africa; and as the method of dyeing with woad did not present the

indigo in substance, the virtual identity of the two was not suspected. Of late years artificial indigo has been produced from coal-tar products and is seriously threatening the existence of the indigo plantations. For the history of artificial indigo, see COAL-TAR COLORS.

Most of the natural indigo of commerce is obtained from species of *Indigofera*, of the family Leguminosæ. The genus embraces about 400 species, widely distributed throughout tropical

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and subtropical regions. The best-known and most widely cultivated species, as well as the ones which supply nearly all the indigo found in the markets, are *Indigofera anil*, a native of tropical America, and *Indigofera tinctoria*, the original home of which is not positively known, although it is said to occur wild in the Bombay Presidency. *Indigofera argentea*, a native of Arabia and parts of Africa, is a source of much of this valuable dye. Indigo plants are extensively cultivated in the East and West Indies (especially in Bengal), in Central America, parts of Europe and Africa, etc. The plants are shrubby, attaining a height of about 6 feet, have pinnately compound leaves and usually pink or purple flowers. The pods of *Indigofera anil* are sickle-shaped, short, and compressed, while those of *Indigofera tinctoria* are straight, cylindrical, and many-seeded. When cultivated, the indigo plant requires a rich, friable soil, well watered, but not too wet. The seeds are sown in drills about a foot apart, and the plants are cut when beginning to flower. In the tropics this can be done at frequent intervals, and four or five crops a year obtained. After cutting, the crop is handled in various ways, fermented in tanks, as described below, and the indigo extracted. Although the plants are perennial, the greatest yields are obtained from annual plantings. In addition to the species mentioned above, at least half a dozen other species of *Indigofera* are known to produce indigo of good character. It is also produced by species of *Sophora*, *Baptisia*, *Amorpha*, *Tephrosia*, and *Galega*, all belonging to the order Leguminosæ. *Baptisia tinctoria* and *Amorpha fruticosa* are known as "false indigo" in the United States, where they are widely distributed. Plants of other families produce indigo, as *Isatis tinctoria*, a cruciferous plant which was cultivated in Europe during the Middle Ages and is still planted in southern France (see WOAD); *Wrightia* and *Nerium*, which belong to the family Apocynaceæ; *Marsdenia tinctoria* and *Gymnema tingens*, of the natural order Asclepiadaceæ; *Polygonum tinctorium*, of the order Polygonaceæ; *Strobilanthes flaccidifolius*, of the order Acanthaceæ; *Spilanthes tinctoria* (Compositæ), and *Scabiosa succisa* (Dipsacaceæ), as well as many others, representing widely separated orders of plants.

Neither the indigo plant nor *Isatis tinctoria* contains the dyestuff (indigotin) ready formed, but rather a colorless glucoside, indican (q.v.), which breaks up, by fermentative processes, into indigotin, and a glucose sugar called indiglucin. It is a curious fact that indican is a normal constituent of human urine and becomes very plentiful in certain diseases. Natural indigo is prepared for the market in the following fashion: The plants are cut down just before reaching the flowering stage and are thrown into vats, where they are steeped in water and allowed to ferment for 12 to 15 hours, practically out of contact with air. This produces the soluble *indigo white*, which is taken up by the water; the liquid is then drawn off into "beating vats," where it is violently agitated by machinery, in order to promote contact with the air, so that the indigo white is oxidized to the insoluble *indigo blue*, which forms a thick scum on the surface and then sinks to the bottom as a bluish mud. After settling, the clear liquid is drawn off, and the indigo blue is collected, squeezed between cloths, and dried in the air. It is sold in irregular lumps, which differ in tint, size, and texture according to the various localities in which they are produced. The amount of available dyestuff ranges from 20 to 90 per cent of the commercial product, some of the impurities being accidental, although intentional adulteration is common enough. This irregularity of composition in the natural product is one of the causes that have advanced the manufacture of artificial indigo, which is always chemically pure.

There are a large number of patented processes for the preparation of synthetic indigotin, chiefly held by the German color factories and largely based upon the researches of Adolf Baeyer, who showed, about 1880, what the exact chemical constitution of this substance is and indicated the general principles for its preparation from aniline derivatives. At present artificial indigo is manufactured by a process worked out by the Badische Anilin-und Sodafabrik at Ludwigshafen upon a basis furnished by Heumann. Naphthalene, an abundant ingredient of coal tar, is first oxidized by fuming sulphuric acid to phthalic acid, from this phthalimide is formed, and this converted into anthranilic acid. This latter reacts with monochloracetic acid to form a compound (phenylglycocoll-carboxylic acid) which fused into caustic soda is converted into indoxyl, which by atmospheric oxidation yields pure indigo blue. The working out of the artificial indigo manufacture brought in its wake the development of the new contact process for sulphuric acid and the production of electrolytic chlorine. In 1906 it was estimated that 80 per cent of the world's consumption of indigo was supplied by the artificial product, while the cultivation of the indigo plant has shrunken correspondingly. Natural indigo is still used, either with or without woad, in certain cases of cloth dyed for government consumption. Pure indigotin, whether extracted from natural indigo or prepared artificially, is crystalline, with a coppery

lustre and a very characteristic odor; when crushed, it forms a blue powder, and when fixed upon the fibre it constitutes a remarkably fast and brilliant "navy-blue" dye. Numerous compounds of indigo are now prepared as dyes, such as indigo red, indigo scarlet, and indigo yellow. In the first two indigo is combined with sulphur as Thio-Indigo Red B and Thio-Indigo Scarlet R; in the last the combination is with benzoyle chloride.

Dyeing with Indigo. As indigo blue is insoluble in water, it must first be converted into indigo white, which is soluble in alkaline liquids. This change is produced by the chemical addition of hydrogen, so that the blue, $C_{16}H_{10}N_2O_2$, goes over into the white, $C_{16}H_{12}N_2O_2$. This is effected in *cold* vats, which are employed for the dyeing of cotton and linen, by metallic reducing agents, such as sulphate of iron, zinc dust, and alkaline sulphites; while wool and silk are dyed in *warm* vats, where the reduction is caused by a fermentation of vegetable substances, preferably woad, in a manner analogous to that by which indican is converted into indigo white. These vats are always alkaline. When the reduction of the indigo is completed, the liquid is colorless, with a light bluish scum on top. The scoured materials are then drawn through the vats and exposed to the air while drying. The atmospheric oxygen immediately reconverts the white into the blue, by removing the extra hydrogen atoms. Indigo blue is also soluble in fuming sulphuric acid, forming "indigo-sulphonic acid," or Saxon blue, which was formerly known as a dyestuff, but has been replaced in modern practice by its sodium salt, *indigo carmine*. The solution of this carmine produces a blue precipitate upon the fibre with an alum mordant, but the color is neither as deep nor as fast as that of the unaltered indigotin from the reducing vats. With artificial indigo the final synthesis can be produced on the fibre itself, as when orthonitrophenylpropiolic acid and potassium xanthogenate are applied separately and the doubly impregnated cloth is then steamed.

Printing with Indigo. Indigotin is not suited to printing in pigment form, and figured goods are produced by dyeing processes. To procure a blue-and-white pattern, the whole fabric may first be dyed blue, and the white produced by printing on bleaching agents which will remove the color. Or the cloth may first be printed with a "reserve," or resist, a paste composed of gum, pipe clay, and copper salts, to prevent the deposit of indigo upon the spots which they protect, while the material passes through the vat. Artificial indigo can again be produced by printing one chemical upon the fibre and putting the other into the bath through which it is subsequently passed.

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