INDIGO (Sp. índigo, índico, from Lat. indiguum, from Gk. ἰνδῖκον, indikon, indigo, from Ἰνδία, Indía, 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 Leguminosae. The genus embraces about 400 species, widely distributed throughout tropical 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, having 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 of right, 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 Leguminosae. *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 *Inia tinctoria*, a cruciferous plant which was cultivated in Europe during the Middle Ages and is still planted in southern France (see WOOF); *Wrightia* and *Nerium*, which belong to the family Apocynaceae; *Marica tinctoria* and *Gymnema tinctoria*, of the natural order Asclepiadaceae; *Polygnum tinctorium*, of the order Polygonaceae; *Strobilanthes faevidifolius*, of the order Acanthaceae; *Spinthes tinctoria* (Composite), and *Saccharum succa* (Dipsacaceae), as well as many others, representing widely separated orders of plants and plants.

Neither the indigo plant nor *Inia 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 indigucin. 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 "heating 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, 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 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 Soda-Fabrik at Ludwigshafen upon a basis furnished by Hennemann. 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 (phenylglycine-carboxylic acid) which fused into caustic soda is converted into indoxyl, which is 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 shrunk considerably. Natural indigo is still used, either with or without woad, in certain cases of cloth dyed for government consumption. Pure indigo, 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 com-
ounds 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 benzoyl
carbonate.

Dyeing with Indigo. As indigo blue is in-
soluble 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, \( C_6H_4N_2O_2 \),
goes over into the white, \( C_6H_9N_3O_2 \). This is ef-
cected 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 fer-
mentation of vegetable substances, preferably
wool, 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 atmos-
pheric 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 prac-
tice by its sodium salt, indigo carmine. The
solution of this carmine produces a blue precip-
itate 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
orthonitrophenylpropiolie acid and potassium
xanthogenate are applied separately and the
doubly impregnated cloth is then seammed.

Printing with Indigo. Indigotin is not
suited to printing in pigment form, and figured
goods are produced by dyeing processes. To pro-
cure a blue-and-white pattern, the whole fabric
may first be dyed blue, and the white produced
by printing on bleaching agents which will re-
move the color. Or the cloth may first be printed with a "reserve," or resist, a paste com-
pared of gum, pipe clay, and copper salts, to pre-
vent 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 put-
ting the other into the bath through which it is
subsequently passed.

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