Helmut Schmidt

100 years of industrial synthesis

BASF

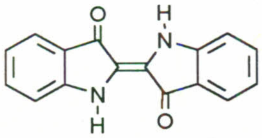
Indigo – 100 years of industrial synthesis

Helmut Schmidt

The "king of dyes" was a challenge for scientists and entrepreneurs alike. The first synthetic indigo was brought on to the market in July 1897, after long years of development at huge financial expense.

Historic 1903 label for indigo shipments to China, one of the main export markets for the BASF product.

The name "blue jeans" is derived from "Bleu de Gênes" , a blue-dyed cotton fabric that came to America chiefly from Genoa. But what gives jeans their characteristic blue colour and causes them to fade a bit more with every wash as true jeans are supposed to? Their typical appearance is due to indigo, the "king of dyes". Initially, indigo was derived exclusively from plants. Only once it was prepared synthetically did it become available for a broad range of applications. But it was a long, hard road before the blue dye could be synthesized on an industrial scale, a venture in which BASF played a decisive role. This year BASF is celebrating synthetic indigo's 100th "birthday", for it was in July 1897 that it first appeared on the market.



indigo

At that time more than 700,000 hectares of land in Bengal, in the Indian subcontinent, was cultivated with the indigo plant (*Indigofera tinctoria*). This corresponded to an annual production, in terms of pure dye, of around 8,000 tonnes, worth 100 million marks [1].

Indigofera tinctoria had little competition to fear. Another plant, woad (*Isatis tinctoria*), was grown in Britain, France and Germany (especially in Thuringia) until the end of the Middle Ages. But the much lower yields obtained from woad (only approximately 1/30 that of the indigo plant) meant that it was unable to compete with the imported Asian product, despite import duties and other protectionist measures.

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A third plant cultivated for indigo, *Polygonium tinctorium*, is still grown in Japan on the island of Shikoku and is used for blue dyeing.

However, natural indigo was of variable composition. Depending on its origin and the harvest, it contained different concentrations of both dye and impurities. This had to be compensated for with high levels of skill and experience on the part of the dyer.

Replacement of the natural product by synthetic indigo therefore represented a significant advance for indigo dyeing and gave it enormous impetus. Synthetic indigo was available in guaranteed high purity.

Exact, universally applicable recipes could be prepared for industrial use, resulting in dyeings that were consistently uniform and clean. Instead of the unsuitable lumps in which natural indigo was supplied, synthetic indigo was available as a homogeneous powder or paste.

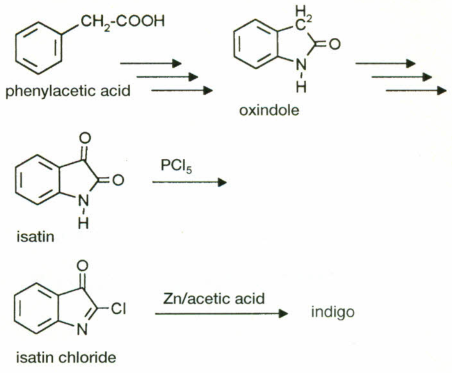
Very early on, processors sought to remedy the shortcomings of natural indigo by refining it industrially. Natural indigo was vatted in a purification step with glucose, impurities were separated out of the solution, and on aeration the indigo was isolated in approx. 95 % purity. It was sold in either moist or dried form. Since BASF also operated this process, sales logistics, customer contacts and technical service were already established at the time synthetic indigo was launched.

The mechanism of indigo dyeing

Only in the last 300 years have indigo dyers had the benefit of products from the chemical industry. Arsenic sulfide (arsenic vat), iron(II) sulfate (vitriol vat) and zinc dust (zinc vat) have all been used as vatting agents. In 1906 BASF brought sodium dithionite, as "Hydrosulfite Conc. BASF", on to the market. Because of its effectiveness as a reducing agent and its solid, stable, easily handled form, this product has become standard in indigo dyeing.

Grappling with formula and synthesis

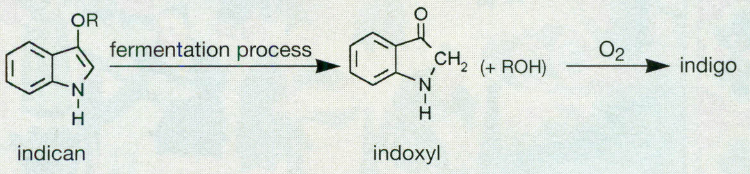
From about 1870 onwards, spurred on by the successful synthesis of alizarin*, numerous laboratories in universities and the chemical industry competed to find the structure of the indigo molecule. It was already known from earlier experiments that indigo decomposed to form aniline and anthranilic acid. Adolf von Baeyer identified the additional decomposition products indole and isatin. It was von Baeyer, later winner of the Nobel prize for chemistry, who succeeded in 1878 in the first laboratory synthesis of indigo. The last step, conversion of isatin to indigo by chlorination to isatin chloride with PCl_5 and subsequent reduction with zinc/acetic acid, he had already accomplished in 1870 [2]:



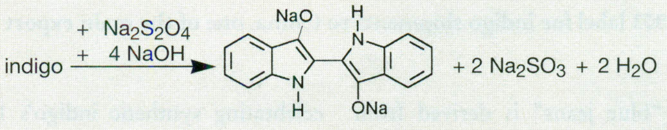
Five years later, von Baeyer was finally sure of his ground. In the famous letter of 3 August 1883 (today in the Deutsche Museum in Munich, letter no. 207, signature 1779), he casually interrupts an account of private and family matters to mention the indigo formula

Extraction and application as a dye

The leaves and stems of the three plants Indigofera, woad and Polygonium contain 0.2–0.8 % of the glucocide indican (R = β-D-glucosyl), which is split by fermentation into glucose and indoxyl. Intensive aeration of the fermenting mass oxidizes the indoxyl to indigo.



For thousands of years, textiles were dyed with indigo in fermentation vats. In these vats the insoluble blue indigo was converted to a yellow solution of leuco indigo (indigo white disodium salt), i.e. it was reduced.



leuco indigo (indigo white disodium salt)

The vats contained a fermentable, carbohydrate-based material, such as bran, molasses or gelatin. They were made alkaline by adding lime, potash, soda or ammonia (urine was also used). Immersion of the textile material impregnated it with leuco indigo. Subsequent air-drying restored the blue shade, which could no longer be washed out.

$$\text{leuco indigo} + 1/2\ O_2 + H_2O \xrightarrow{\text{textile material}} \text{indigo} + 2\ NaOH$$

Overall reaction:

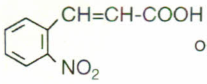
$$\text{indigo} + Na_2S_2O_4 + 2\ NaOH + 1/2\ O_2 \longrightarrow \text{indigo} + 2\ Na_2SO_3 + H_2O$$

---

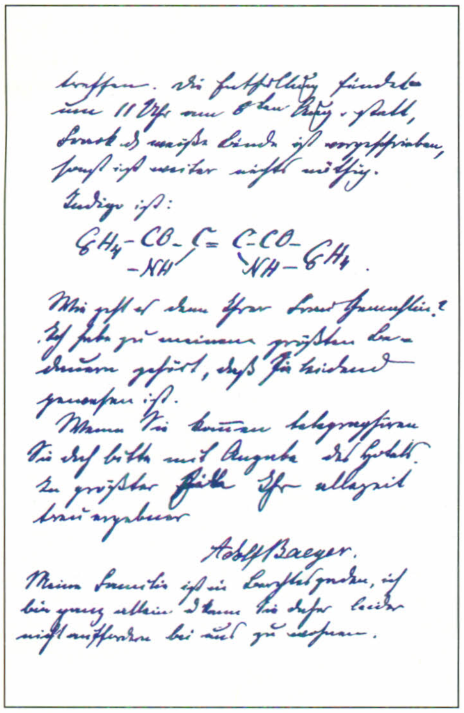
* Alizarin, synthesized by a process discovered by Carl Graebe and Carl Liebermann, was first brought on to the market by Hoechst in 1869, followed one year later by BASF.

to his friend Heinrich Caro [3]. Caro, at that time head of BASF's research laboratories, was particularly interested in finding a synthesis route that could be applied on an industrial scale. Two further syntheses discovered in the years 1880-1882, also by Adolf von Baeyer, appeared to Caro to have potential. They were based on cinnamic acid [4] and o-nitrobenzaldehyde respectively [5].

Caro discovered that o-nitrophenylpropiolic acid, arising as an isolable intermediate in the synthesis based on cinnamic acid, could be reacted with mild reducing agents under alkaline conditions to yield indigo directly on the textile fibre. The two men were hopeful that this process could be used industrially. The process was patented and the patent assigned by contract to BASF for 100,000 marks, a contract that was later extended to include Hoechst. Both companies began intensive research. In April 1881, BASF brought its o-nitrophenylpropiolic acid as "propiolic acid" or "little indigo" on to the market.



o-nitrophenylpropiolic acid



treffen. Die Festlichkeit findet um 11 Uhr am 6ten Aug. statt, Frack u. weiße Binde ist vorgeschrieben, sonst ist weiter nichts nöthig.

Indigo ist:

$$C_6H_4{-}CO{-}C{=}C{-}CO{-}C_6H_4$$
$$-NH \qquad NH-$$

Wie geht es denn Ihrer Frau Gemahlin? Ich habe zu meinem größten Bedauern gehört, daß Sie leidend gewesen ist.

Wenn Sie kommen telegraphiren Sie doch bitte mit Angabe der Ankunft. In größter Eile Ihr allezeit treu ergebener

Adolf Baeyer.

Meine Familie ist in Berchtesgaden, ich bin ganz allein. Ich kann Sie daher leider nicht auffordern bei mir zu wohnen.

Page of a letter from Adolf von Baeyer to Heinrich Caro, with the indigo formula.

PATENT-URKUNDE

№ 54626

AUF GRUND DER ANGEHEFTETEN BESCHREIBUNG IST DURCH BESCHLUSS DES KAISERLICHEN PATENTAMTES

an die Badische Anilin- und Soda-fabrik in Ludwigshafen a. Rh.

EIN PATENT ERTHEILT WORDEN.

GEGENSTAND DES PATENTES IST:

Verfahren zur Darstellung künstlichen Indigos.

GESETZ v. 25. MAI 1877

ANFANG DES PATENTES: 6. Mai 1890.

DIE RECHTE UND PFLICHTEN DES PATENT-INHABERS SIND DURCH DAS PATENT-GESETZ VOM 25. MAI 1877 [illegible] BESTIMMT.

ZU URKUND DER ERTHEILUNG DES PATENTES IST DIESE AUSFERTIGUNG ERFOLGT.

Berlin, den 19. November 1890.

KAISERLICHES PATENTAMT.

Beglaubigt durch Frank,

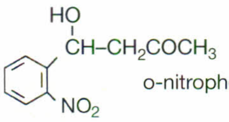
Bureau-Vorsteher des Kaiserlichen Patentamtes.

Wegen der Patentgebühr ist die zweite und letzte Seite dieser Urkunde zu beachten!

Patent document for a "Process to prepare synthetic indigo" issued to BASF by the Imperial Patent Office, Germany, on 6 May 1890.

The product was used by a few calico printers but failed to catch on generally and become an economic success. Three years later production was discontinued. Baeyer's second process began with o-nitrobenzaldehyde and appears fascinatingly simple and elegant.

o-Nitrobenzaldehyde is condensed with acetone in an alkaline solution. The product is an aldol, "o-nitrophenyllactic acid ketone" (1-(2'-nitrophenyl)-1-hydroxy-3-oxobutane). This splits off acetic acid and water to form indolone, which is unstable and dimerizes to produce indigo [5].



o-nitrophenyllactic acid ketone

The patent for this process, too, went to Hoechst and BASF. As early as 1880, the two firms agreed to develop the Baeyer processes industrially, using all the means at their disposal.

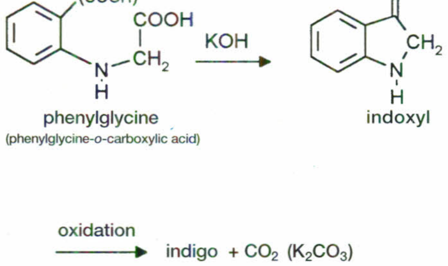
But while the industrial preparation of cinnamic acid from benzaldehyde and sodium acetate soon became feasible, preparation of o-nitrobenzaldehyde remained an insurmountable obstacle. All the routes attempted, starting with toluene and applying various chlorination and nitration methods, were unsatisfactory. The nitration step was expensive and inevitably produced undesirable para and meta derivatives.

A sole attempt at commercial exploitation of the second process was made by the Kalle company in Wiesbaden in 1898, when the bisulfite adduct of o-nitrophenyllactic acid ketone, a water-soluble product that is readily split into its components, was brought on to the market as "indigo salt" for application in calico printing. But neither "propiolic acid" nor "indigo salt" could compete with natural indigo in meeting world demand. It was too difficult to obtain the necessary quantities of raw materials for either process. For example, only 5000 – 6000 tonnes of toluene from coal tar was available annually, but 4 tonnes of toluene was required to make 1 tonne of indigo.

The Hoechst/BASF cooperative venture was no nearer to its objective of producing "big indigo". Again and again, the firms' technical managers had to persuade and convince their commercial departments to finance the expensive projects so that the work could be continued. A mood of discouragement and resignation became prevalent. "For technology, methods are not sufficient; it needs processes, feasible processes", remarked a BASF manager on those unsuccessful years. But Heinrich von Brunck, since 1884 director of BASF, never missed an opportunity to inspire confidence and optimism: "The word 'impossible' doesn't exist in my vocabulary. If it doesn't work one way, it'll work another. But it will work!". The possibility of losing millions in what for the chemical industry of that day were unheard-of research costs prompted him to say: "You mustn't always think of profits when you are fighting for progress!" [6].

The Heumann syntheses

Suddenly, in 1890, fresh impetus came in the form of the publications of the Zurich professor K. Heumann. He had discovered that when phenylglycine or phenylglycine-o-carboxylic acid – prepared by reacting aniline and anthranilic acid respectively with chloroacetic acid – is fused with solid caustic potash indigo is produced („first" and "second" Heumann syntheses) [7, 8]:



The indigo research laboratory around the turn of the century.

The corresponding patents were acquired by Hoechst and BASF. Having been shown this new direction, both firms resumed intensive research activity. The chemists soon realized that the indigo yields obtainable from phenylglycine were extremely low – a maximum of 10 %. BASF therefore abandoned its experimental work in 1893. Phenylglycine-o-carboxylic acid, on the other hand, gave much higher yields. There were good prospects of developing and improving this process.

The starting material anthranilic acid could be made from naphthalene, available in unlimited quantities from tar manufacture, via the synthesis steps phthalic acid, phthalic anhydride and phthalimide. The oxidation of naphthalene was at that time carried out with dichromate. This process was expensive – too expensive to compete with natural indigo – because the resulting chromium(III) liquors could not be reconverted to dichromate. Finding a cheaper way to oxidize naphthalene was therefore crucial for an economically efficient indigo synthesis.

Hoechst and BASF go separate ways

To solve this major problem, the two firms adopted different methods:

Hoechst had already developed a process for the electrochemical regeneration of chromium(III) liquors. Once the company had secured a supply of cheap power from a hydroelectric station on the Lech river, a decision was made to build a new plant in Gersthofen for the production of indigo and its precursors. The cost of the project was estimated at around 3.5 million marks.

BASF resumed earlier, less-than-successful attempts to oxidize naphthalene with oleum. Then, in 1891, the all-important lucky break (literally!) occurred. A mercury thermometer was accidentally broken by a laboratory assistant, and it was precisely this experiment that produced the best results. The chemist E. Sapper could only explain this by presuming that the mercury had catalyzed the oxidation. A simple means of producing phthalic acid had been found. This gave BASF, which also had the know-how for manufacturing oleum and sulfuric acid from sulfur dioxide and air, a considerable advantage over Hoechst in the competition to synthesize indigo.

Development of BASF indigo production

At last H. von Brunck saw his lifelong goal, synthetic indigo, within grasp. With great daring and entrepreneurial courage he tackled the task of adapting the laboratory results. He was assisted in this by R. Knietsch, a successful BASF chemist. The first step was to ensure a supply of the starting materials anthranilic acid, chloroacetic acid and their precursors [9]. This required a series of measures:

- Construction of an industrial-scale plant for synthesizing phthalic acid by oxidizing naphthalene with oleum and a mercury catalyst
- Expansion of the sulfuric acid factory for regenerating the sulfur dioxide produced to a capacity of 80,000 tonnes per annum
- Erection of a new phthalimide and anthranilic acid plant. To be able to produce anthranilic acid, BASF purchased a patent from the Amsterdam Quinine Factory (Hofmann decomposition of phthalimide with sodium hypochlorite solution) [10]
- Construction of a new chlorine-alkali electrolytic plant to produce the necessary quantities of chlorine and caustic soda, since the existing chlorine factory was too small
- Expansion of the chlorine liquefaction plant to allow preparation of chlorine in the required purity for the production of anthranilic and chloroacetic acids
- Installation of a chloroacetic acid plant, supplying approx. 2,000 tonnes annually and consuming about 100,000 m^3 of beech wood*

Even so, it was not all plain sailing. For example, the neutral dipotassium salt of phenylglycine-o-carboxylic acid prepared from anthranilic and chloroacetic acids had to be free of any acid monosalt. Another big challenge for

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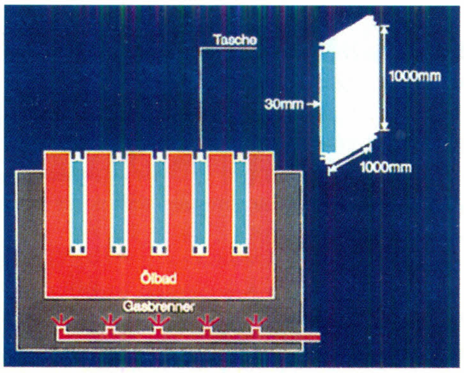
* The beech wood served to manufacture wood vinegar, an aqueous mixture of methanol and acetic acid from which glacial acetic acid was obtained by distillation.

the chemists, engineers and technicians was the fusion step that led to the indigo itself. A salt-caustic soda mixture was preferred over the salt-caustic potash mixture originally used by Heumann because, although it was even more difficult to stir, it could be dehydrated at 180 °C instead of at 260 °C. In any case, a sintering or baking process had to be developed. The chemist Paul Seidel designed what was known as a "Taschenofen", a gas-fired muffle furnace whose basic element was a cell consisting of steel sheets bolted together and containing 25 kg of a finely ground and homogenized salt-caustic soda mixture. The furnace, which held ten such cells, was heated to 260 °C. At the end of the process the cells had to be cooled in the open air, the smoke released being very unpleasant.

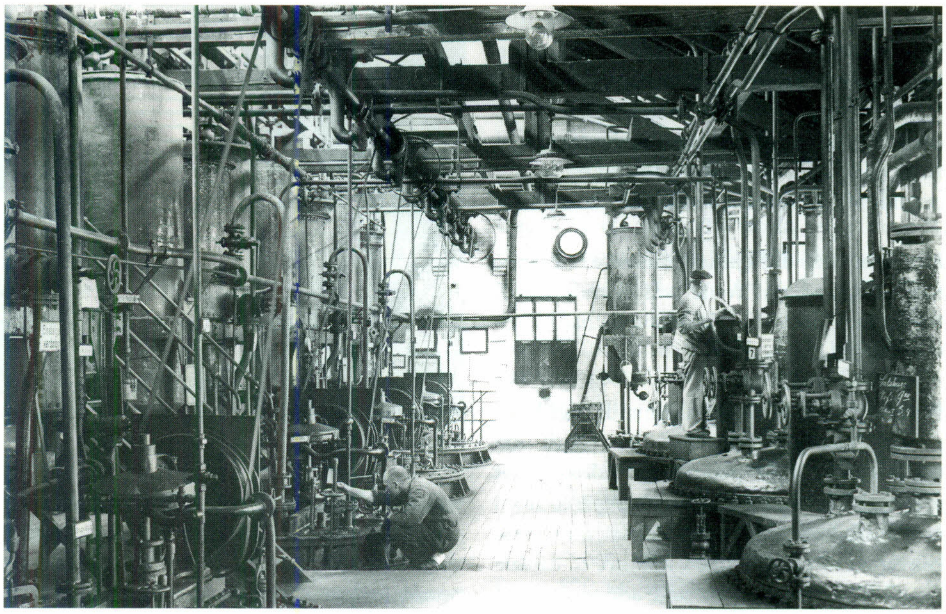
The sintered material was then broken out of the cells and transferred in drums to the oxidation vessel, where it was oxidized by air to indigo. Each cell yielded three kilograms. In March 1894, a pilot plant was put into operation with three furnaces and a daily production of 500 kg of indigo a day. It included a vacuum evaporation plant for recovering the caustic soda from the spent liquors.

BASF indigo manufacture from 1897 to 1904

At the beginning of 1897, the new indigo production complex was complete. It covered an area of 5.4 hectares and comprised 34 furnaces with a total capacity of 2,000 tonnes a year. The newly formed indigo department under R. Knietsch began large-scale production in February. Shortly afterwards, on 10 July 1897, came the long-awaited event: the first "Indigo Pure BASF" was brought on to the market.



Schematic diagram of a "Taschenofen".



Interior of indigo plant (1921) with view of fusion tanks (right).

It caused quite a sensation. Scepticism, disbelief and displeasure on the part of competitors faced with the threat of business losses culminated in accusations that BASF was engaged in fraud and that the product was purified plant indigo or a surrogate. Customers received strange circulars, like this one, written by the Elberfelder Dye Factories:

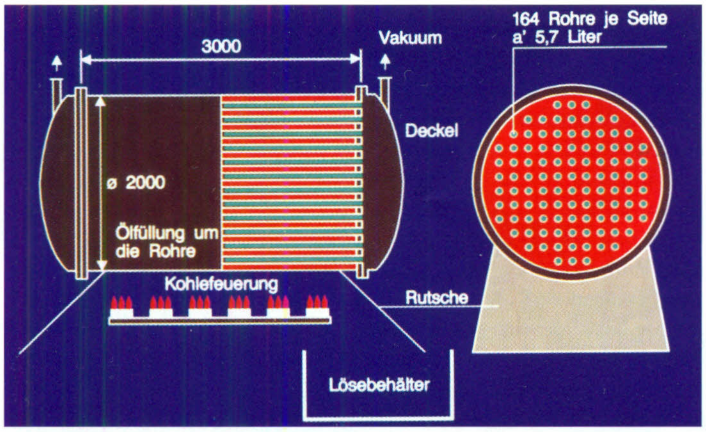
> "Badische Anilin- und Sodafabrik has recently brought on to the market a new product: Indigo Pure B.A.S.F., the same having attracted not a little attention, because a great number of the public have apparently thus been led to believe that the object of endeavours pursued by various parties, in particular B.A.S.F., to prepare indigo by artificial means for industrial purposes has been attained, and that the aforementioned commodity is the result of these endeavours.
>
> Numerous enquiries that have been addressed to us, and that we are still receiving daily, by reason of the associated publication, occasion us hereby to bring to general notice that the above product is none other than natural indigo in a certain prepared form, and has absolutely nothing in common with artificial indigo. The brochures and circulars of B.A.S.F. do not mention a word about the commodity being artificial indigo, whereas the company would undoubtedly proclaim it from the rooftops, were this the case." [11]

BASF countered with an intensive public relations campaign. It provided information to customers throughout the world and set up an indigo dyehouse at the Ludwigshafen works to advise customers on the application of indigo. In addition, it had a comprehensive, independent report made by the respected chemist Prof. Otto N. Witt of Berlin [12]. But ultimately, the quality and application advantages of synthetic indigo spoke for themselves.

In the years that followed production figures rose steadily, not least because of constant improvements to the processes used. A competition was run within the company to find process alternatives. In 1903, before the Taschenofen plant had expanded to its final capacity, a "vacuum melt process" offering considerable advantages was ready to begin operation. In this process caustic soda and sodium phenylglycine-o-carboxylate solution were mixed in cast-iron vacuum pans with agitators and boiled down to a paste.

Extruders pressed the paste into iron tubes (1.5 m long, 75 mm diam.), which were pushed into a vacuum-melt furnace. The furnace held around 350 tubes and produced 500 kg of indigo in 24 hours. On completion of the reaction the tubes were thrown down chutes into water-filled dissolving boxes, where the contents were dissolved and subsequently air-oxidized to indigo.

The vacuum-melt process began operation in 1905 and within three years it had replaced Taschenofen production entirely. Its advantages were that it eliminated the heavy physical work involved in handling cells and dusty solids mixtures, halved the amount of caustic soda required, and increased indigo yields by up to 25 %.



Schematic diagram of a vacuum-melt furnace.

But the BASF scientists were also on the lookout for chemical process alternatives. An attempt was made to produce the needed disodium phenylglycine-o-carboxylate more cheaply than with chloroacetic acid, from anthranilic acid, formaldehyde and hydrogen cyanide via cyanmethylanthranilic acid [13].

However, the difficulties encountered were too great, and this route was abandoned in 1902 after approx. 120 tonnes had been synthesized.

Because the company's anthranilic acid capacities had not yet been fully built up, another means of producing indoxyl was sought. *N*-ethylphenylglycine, prepared from *N*-ethylaniline and chloroacetic acid, was converted to indigo with a mixture of caustic potash and caustic soda and added calcium oxide in Taschenofen furnaces at 280 °C (imidoglycine process).

This process yielded a very pure indigo but in yields of only 60 %. It was discontinued in 1904.

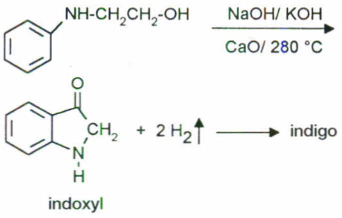
Pfleger's discovery – Hoechst indigo manufacture from 1902

As early as 1901, J. Pfleger at Degussa had succeeded in obtaining high yields of indigo from phenylglycine by adding the new product sodamide to the alkaline melt in the Heumann synthesis [14]. The corresponding patent was acquired by Hoechst. Immediately, Hoechst and Degussa established the "Indigo Company" to exploit the Pfleger process. Trial production lots at Hoechst led to a rapid decision: completion of the indigo plant in Gersthofen, virtually ready to go into operation, was stopped, and the existing plant at Hoechst was converted, at a cost of 11 million marks, to accommodate the sodamide indigo process. Gersthofen was designated for the production of the necessary intermediates and auxiliaries chloroacetic acid and sodium. By 1902, Hoechst was producing 300 tonnes, and one year later 800 tonnes of indigo [15], making it – five years after BASF – the world's second-ever indigo manufacturer.

BASF indigo manufacture from 1905 to 1914

Pfleger's discovery pointed to the necessity for completely anhydrous melts to successfully convert phenylglycine to indigo. This was the starting point for a new BASF process. When dry phenylglycine salt was fused with a eutectic mixture of anhydrous caustic potash and caustic soda, to which was added finely ground calcium oxide, the indigo yields were almost as high as those obtained with added sodamide, at that time still very expensive. Production by this technique began in 1906.

The new know-how was then applied to another process, which had been developed in 1904. The alkaline fusion of 2-anilinoethanol – synthesized from aniline and ethylene chlorohydrin – produced indigo in excellent yields:



By this means BASF produced its "ethylene indigo", with interruptions, from 1909 to 1924.

The company's 1913 production of indigo, from three simultaneously operated processes (starting with anthranilic acid, aniline and 2-anilinoethanol respectively), was the highest ever: 4,900 tonnes. In the same year, Hoechst produced 4,500 tonnes by the sodamide process.

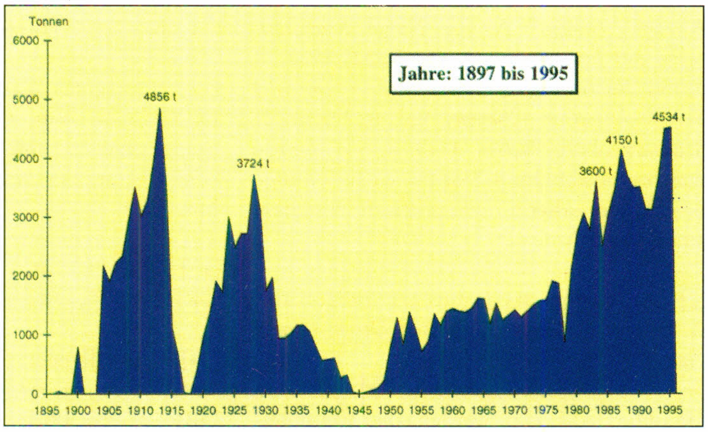
World War I and the years to 1939

Even before the outbreak of World War I, synthetic indigo had virtually forced the natural product from the market. India's crop area had fallen from approx. 700,000 hectares in 1897 to 121,000 hectares in 1914. Whereas Germany had imported natural indigo worth 12.7 million marks in 1897, in 1913 the two German manufacturers BASF and Hoechst exported 10,000 tonnes of synthetic indigo worth 53.3 million marks. In 1897, refined natural indigo cost 20 marks/kg. Within a few years, its price sank to half that amount and then remained stable. Synthetic indigo came on to the market at 16 marks/kg. The rivalry between Hoechst and BASF caused the price to tumble to 7 marks/kg in 1904. Only after the two firms had concluded an "indigo convention" could the price be stabilized at about 8 marks/kg, keeping it below that of the natural product.

Indigo production fell during the war years, dropping to zero in 1918, because the naval blockade imposed on Germany by the Allies prevented all exports. This revived the demand for natural indigo, so that by 1916 the crop area had risen to 300,000 hectares. But the renaissance was short-lived. After the war, numerous dyestuff companies in Switzerland, the USA, Japan and Britain began their own indigo production, spelling the ultimate finish of natural indigo.

Under such competitive pressure, BASF had to rationalize its own indigo processes. In 1925, it successfully introduced the manufacture of phenylglycine from aniline, formaldehyde and hydrogen cyanide via phenylglycinonitrile. The anthranilic acid route was abandoned.

In the mean time, a new process had allowed Degussa to greatly reduce the price of its sodium. BASF, following Hoechst, took advantage of this in 1926, securing a contract for a low-cost supply. This made it possible



BASF indigo production over the years

to discontinue the practice of fusing phenylglycine and finely ground calcium oxide with its considerable dust problems. From that time on, indigo was manufactured only by the Heumann-Pfleger process – the process still used by BASF today. The same standard process was adopted by the two rival companies BASF and Hoechst, since 1925 under a common holding company, I. G. Farben. At the same time, BASF had become – with the exception of sodium – self-sufficient in all the necessary raw materials.

BASF's indigo production grew steadily in the period between the wars, peaking in 1928 at 3,724 tonnes in 1928. Its world sales to 1930 totalled nearly 70,000 tonnes. But output dropped significantly in the 1930s. The appearance of numerous competitors and the increasing popularity of blue dyes with better fastness properties (Indanthren Blue, Hydron Blue, Naphthol AS Variamine Blue) caused production to fall to an average of only 1,000 tonnes per annum. BASF responded with restructuring, divesting itself of superfluous buildings and plants and merging its indigo and dye departments. A series of technical advances helped bring about the necessary reduction in costs:

- Continuous solvent extraction replaced steam distillation for removing the excess aniline in the phenylglycinonitrile step.
- A high-speed Hoesch stirrer in the air-oxidation step resulted in shorter oxidation times, higher indigo yields and greater purity.
- Continuous rotary presses replaced the labour-intensive filter presses for filtering the indigo.

The improvements and rationalizations benefited I. G. Farben's indigo plants in both Hoechst and Ludwigshafen.

World War II and a new start to competitive indigo production at BASF

I.G. Farben's Hoechst works stopped producing indigo in 1939, the main reason being a shortage of chloroacetic acid. The Ludwigshafen plant continued operating at the rate of a few hundred tonnes per annum until 1944, when air attacks in the autumn and winter caused considerable damage to buildings and plant, and production had to be abandoned.

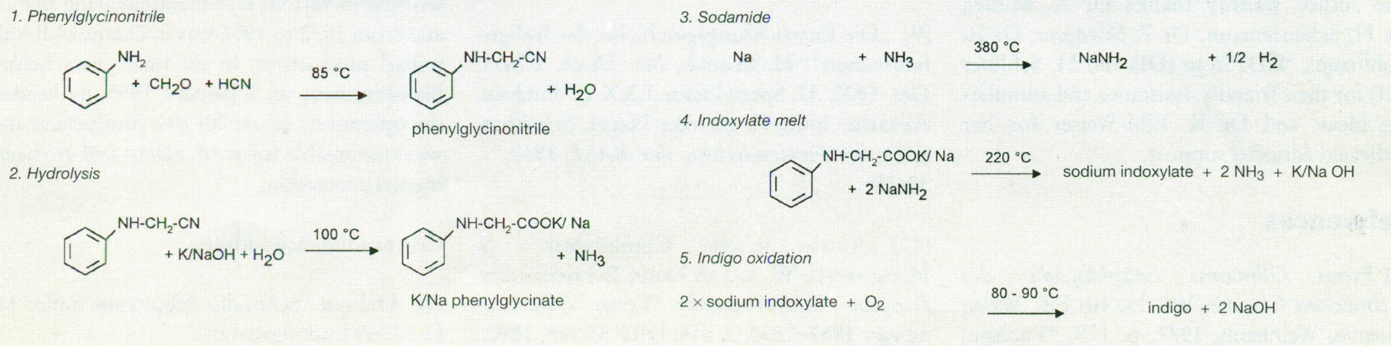
On 23 March 1945, the works were occupied by American troops. Undamaged equipment was dismantled for reparation purposes. Nevertheless, indigo production recommenced in October 1946, albeit on a makeshift, irregular basis. For the next four years, raw materials were frequently in short supply and it was not until 1951 that prewar production levels could again be achieved. In that year, BASF produced more than 1,000 tonnes, much of which was sold to China. Figures until the end of the 1970s ranged from 800 to 1,600 tonnes per annum. At Hoechst, however, indigo production was not resumed.

To continue manufacturing indigo in the long term, BASF's plant, heavily marked by war damage and age, had to be completely renewed. The ongoing repair and maintenance costs were simply too high. A number of concepts discussed from 1960 to 1966 ranged from designing a completely new indigo plant to abandoning production after 1968.

At the end of 1967, a concept for long-term redevelopment finally won through. The concept was successfully implemented and led to a significant increase in productivity.

Today, BASF is still the world's largest single indigo producer, and last year increased its market share to more than 40 % when it acquired the textile dye business of the British company Zeneca. This year, the 100th anniversary of indigo, its production capacity is about 7,000 tonnes p.a.

Synthesis of indigo by the Heumann-Pfleger process



Indigo owes its continuing popularity to the fashion for jeans and denim. This market absorbs 99 % of all the indigo produced. At the end of the 1970s, the world's population of 4 billion people was estimated to purchase 500 million pairs of blue jeans a year, one pair for every eight people. Since about 10 g of indigo is required to dye a pair of jeans, this represents 5,000 tonnes of indigo, a figure that falls far short of the actual world consumption of 14,000 tonnes in 1995. A more recent, 1989 estimate of world jeans sales, giving a figure of one billion pairs a year [16], results in a closer approximation to this amount. The 1995 Yearbook of the United States Population Institute in Washington states the world population to be 5.75 billion. Thus indigo's prospects for the future are bright.

Summary

Up until 100 years ago, indigo was derived mainly from the indigo plant, cultivated in huge plantations in the Indian subcontinent. Developing an industrial synthesis for the king of dyes was a challenge for both scientists and entrepreneurs. BASF, as well as Hoechst, played a decisive role in this venture. It took 17 years of development and enormous financial investment – around 18 million gold marks, an amount exceeding the company's share capital of the day – before the first Indigo Pure BASF was manufactured and brought on to the market in July 1897. Of the various alternative synthesis routes that became available initially, only the Heumann-Pfleger process proved successful in the long term, and it is still the standard method of industrial indigo manufacture. In this process, phenylglycine, produced from aniline, formaldehyde and hydrogen cyanide, is fused with sodamide under anhydrous, alkaline conditions.

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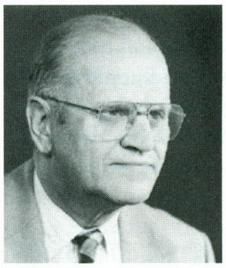

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