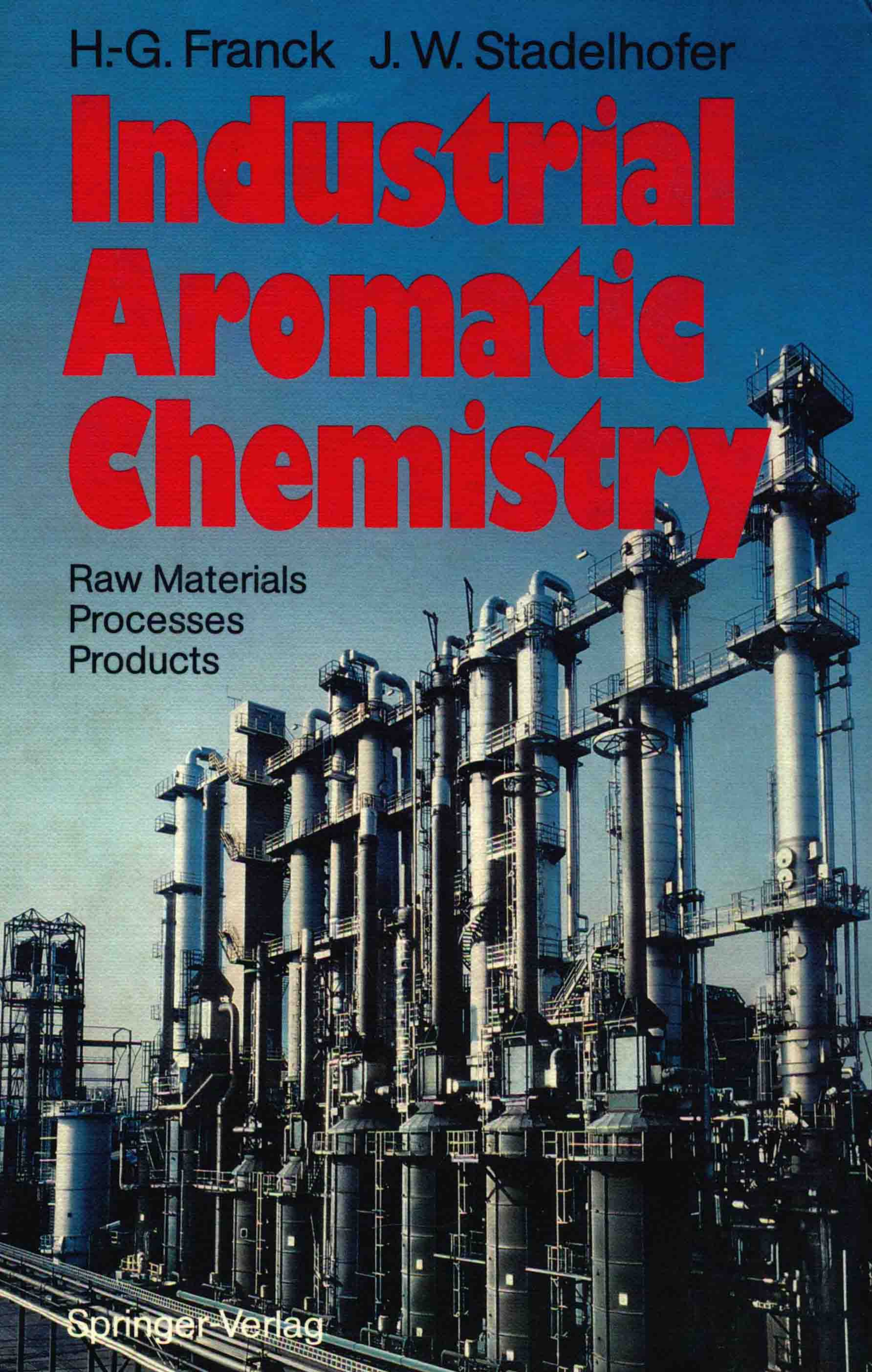
H.-G. Franck J. W. Stadelhofer

Industrial Aromatic Chemistry

Raw Materials
Processes
Products



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Industrial Aromatic Chemistry

Raw Materials · Processes · Products

With 206 Figures and 88 Tables
and 720 Structural Formulas

Springer-Verlag
Berlin Heidelberg New York
London Paris Tokyo

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Title of the original German edition: Industrielle Aromatenchemie.
© Springer-Verlag Berlin Heidelberg 1987. ISBN 3-540-18146-6

The cover shows the tar refinery of *Rütgerswerke*
in Castrop-Rauxel, West Germany

ISBN 3-540-18940-8 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-18940-8 Springer-Verlag New York Berlin Heidelberg

Library of Congress Cataloging-in-Publication Data
Franck, H.-G. (Heinz-Gerhard) Industrial aromatic chemistry.
Translation of: Industrielle Aromatenchemie. Bibliography: p. Includes index.
1. Aromatic compounds. I. Stadelhofer, J. W. (Jürgen Walter), 1949- . II. Title.
TP248.A7F7313 1988 661'.816 88-4365

Printed in Germany

Flow sheets: Wolfgang Lücke
Graphic layout: Klaus Langhoff
Media conversion, printing, and bookbinding: G. Appl, Wemding

2152/3140-543210

Preface

Aromatic chemicals represent about 30% of the total of some 8 million known organic compounds; the percentage of aromatic chemicals produced by the entire organic chemical industry is of the same order.

The importance of aromatics in hydrocarbon technology is, however, greater than the percentage figures indicate. Quantitatively, the most important processes in hydrocarbon technology are catalytic reforming to produce gasoline, which has a worldwide capacity of around 350 Mtpa, and the carbonization of hard coal to produce metallurgical coke, on roughly the same scale. A characteristic of both processes is the formation of aromatics. The third most important process in hydrocarbon technology in terms of quantity is catalytic cracking, which is also accompanied by an aromatization, as is the most important petrochemical process, steam cracking of hydrocarbon fractions.

The recovery and further refining of aromatics was the basis of the industrial organic chemistry in the middle of the last century. In the early 1920's, aromatic chemistry was complemented by the chemistry of aliphatics and olefins, which today, in terms of quantity, has surpassed the industrial chemistry of aromatics.

From the beginning of industrial aromatic chemistry there have been fundamental new developments in the production of aromatics. Until the 1920's, coal tar and coke-oven benzole were virtually the sole sources of aromatics available on an industrial scale. Coal tar contains a host of widely used aromatic compounds, such as benzene, toluene, naphthalene, anthracene and pyrene, as well as styrene and indene. In addition coal tar contains some important recoverable aromatic compounds with hetero atoms, such as phenols, anilines, pyridines and quinoline.

As the growing demand for some coal-tar constituents for the development of mass-produced plastics, such as phenolic resins and polystyrene, and the increasing production of explosives could not be met by coal tar alone, new sources of aromatics were developed, starting from petroleum. The development of the production of reformate-gasoline and steam cracking of petroleum fractions has made two further feedstock sources for the production of aromatics available today; renewable raw materials are also used for the manufacture of aromatics, albeit on a much smaller scale.

Processes for the refining of crude aromatics, in common with methods for their further processing, are complicated by the occurrence of by-products; individual aromatics are usually accompanied by associated products, and must be isolated by subsequent separation processes. Aromatic chemistry is characterized by the high reactivity of the π-electron system, which enables substitutions to take place not only at one position in the aromatic ring, but also, especially for polynuclear aromatics, at several different sites, thus leading to isomers as well as multiple substitution. Refining processes have, therefore, to be optimized to produce the desired compounds in pure form from the crude products. Thus, industrial aromatic chemistry involves close collaboration between chemists and process engineers.

The present applications and future developments of aromatic chemicals are characterized by a number of inherent properties. These are in particular:

1. the facile substitution and high reactivity, which can be further increased by the introduction of suitable substituents,
2. the relatively easily activated π-electron system which, coupled with auxochromic groups, is capable of absorbing part of the spectrum of light and is used in the production of dyes and pigments,
3. the high solvent power, especially of alkylated derivatives,
4. the high C/H ratio, which renders polycyclic aromatics particularly suited to the production of high-value industrial carbon products, such as premium coke, graphite and carbon black, and
5. the affinity and tendency for association, which make aromatic molecules suitable mesogens for the formation of liquid-crystalline phases.

Approximately 800,000 tpa of organic dyestuffs (dyes, pigments and optical brighteners) are produced worldwide. Since the beginning of the industrial production of organic dyestuffs, aromatics have been the dominant raw materials for this group of products.

In addition, their versatility regarding substitution and resistance to premature biological degradation have made aromatics essential for the manufacture of plant protection agents. Of the ca. 300 registered plant protection agents in Japan, over one-half are aromatic in nature. A considerable proportion of the 160,000 t of pesticides (also ca. 300) produced in West Germany in 1985 is based on aromatics. In the USA likewise, the most important organic plant protection agents in terms of quantity, such as atrazine, alachlor, trifluralin and metolachlor, are aromatic in nature.

The traditional applications of aromatic chemistry, such as the production of dyestuffs and the manufacture of plant protection agents have constantly expanded since their early days. The latest advances in the production of aromatics have led to new catalytic processes from simple compounds such as methanol and propane/butane. The manufacture of aromatic monomer building blocks for the production of polymers for high-performance engineering plastics is in rapid development. The liquid-crystalline nature of a number of aromatic-based polymers is the key to obtaining high-performance properties in diverse applications such as high-value aramid fibers and carbon artifacts.

Against the background of these developments, the authors of this monograph have put together a review of aromatic chemistry from benzene through the polynuclear aromatics such as naphthalene, anthracene and pyrene, up to industrial graphite products, concentrating on the industrially important raw materials and intermediates as well as the quantitively most important final products. Some particularly interesting compounds of less importance in terms of quantity have been included to illustrate the broad range of aromatic chemistry.

The concentrated survey, complemented by detailed, standardized process flow sheets, provides chemists and process engineers engaged in the production and research, scientists in neighbouring disciplines, and advanced students of chemistry and chemical engineering with a brief insight into industrial aromatic chemistry, thus making possible a comprehensive review.

Thanks are due to numerous colleagues, both at home and abroad, for their valuable suggestions.

Frankfurt/Main (West Germany), *H.-G. Franck*
March 1988 *J. W. Stadelhofer*

Contents

1 History

Aromatic compounds are currently defined as cyclic hydrocarbons in which the carbon skeleton is linked by a specified number of conjugated π-bonds in addition to σ-bonds (Hückel's rule). During the early days of industrial aromatic chemistry in the mid-19th century, the structure of aromatic compounds had not yet been elucidated. The name of this class of compounds is historically-based since the first members were obtained from aromatic, i.e. pleasant-smelling resins, balsams and oils; examples of this are benzoic acid, which was obtained from gum benzoin, toluene from tolu balsam and benzaldehyde from oil of bitter almonds.

The history of aromatic chemistry was, at the outset, closely linked to the development of coal carbonization to produce coke, gas and tar.

Coke was mainly used as a substitute for charcoal in the production of pig iron, coal gas was used for lighting, and coal tar initially replaced wood tar for impregnating timber used in ship-building.

As early as 1584, the Duke of Brunswick recommended the application of 'desulfurized' coal as an alternative to charcoal for the production of salt. The first patent for the production of coke for use in blast furnaces for iron smelting was granted to Dud Dudley in England in 1622.

The first large-scale attempts to manufacture lighting gas were initiated by the French engineer Philippe Lebon in 1790. He degasified wood chippings in an iron retort on the grate of a kitchen stove and fed the resultant gas by pipe to other rooms, where it was burned in lamps. His discovery, which he called 'Thermolamp', aroused great interest but never found practical application.

The real founder of gas engineering was the Scotsman William Murdoch, who carried out experiments in Redruth, Cornwall, in 1792 on the degasification of hard coal. He lit his house with gas which he brought daily from the factory in containers. (This portable gas was one of the major products of the company *Engelhorn & Comp.*, founded in 1848 by Friedrich Engelhorn, later to be one of the co-founders of *BASF.*)

The German philosopher and chemist, Johann Becher, is considered to be the discoverer of coal tar. In 1691, together with the Englishman Henry Serle, he obtained the English patent no. 214 for the production of pitch and tar from coal.

The German privy councilor Winzler, known in England as Windsor, was particularly successful in marketing the idea of using coal gas for lighting and founded a number of gas companies. In London in 1813, Westminster Bridge was lit by gas from the *London & Westminster Chartered Light & Coke Co.*, established by Windsor; in 1819 he introduced gas lighting to Paris. Lighting with coal gas began in Germany in 1824 in Hanover, and 1826 in Berlin, when gas works were set up by the *London Imperial Continental Association*. The first gas works in the USA was already operating in Baltimore in 1802; gas lighting was introduced into New York in 1824.

The first distillation of gas-works tar from coal carbonization was carried out at Leith in Scotland in 1822. The tar oil was used in timber impregnation, while the distillation residue, namely pitch, was employed in coal briquetting.

The key factor in the development of the tar industry was the accelerated growth of the railroad system. Tracks were laid on wooden sleepers, which were impregnated with coal tar oil to preserve them from rapid decay. The first railway lines started operation in England between Stockton and Darlington in 1825, and in Germany between Nuremberg and Fürth in 1835.

In spite of the demand for impregnation oil, by the mid-19th century, owing to the rapid growth in the production of gas for lighting and the tremendous development of the iron and steel industry, there was a considerable over-supply of coal tar. Although some of the tar could be used in the production of roofing tar felts and in carbon black manufacture, these applications were not sufficient to absorb all the tar being produced.

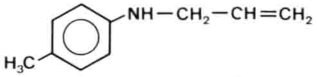
The first estimates of annual tar production from gas works in Europe date from 1884. Great Britain led the way with a production of 450,000 t, followed by Germany (85,000 t), France (75,000 t), Belgium (50,000 t) and the Netherlands (15,000 t).

The parent compound of the aromatics is benzene; it was first discovered by Michael Faraday in 1825 in the condensed part of a lighting gas derived from whale oil and obtained some years later by Eilhard Mitscherlich by decarboxylation of benzoic acid (as calcium benzoate). The occurrence of benzene in coal tar was first described by August Wilhelm v. Hofmann in 1845. John Leigh had already demonstrated to the British Natural Research Conference in 1842, that benzene is present in coal tar; this claim was not immediately published, however. Even before the discovery of benzene, Ferdinand Runge had found aniline and phenol in coal tar in 1834.

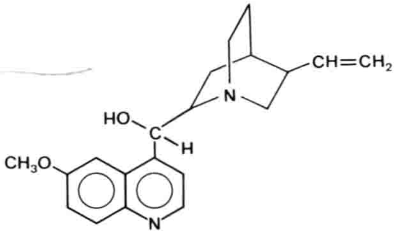
The composition of the aromatic mixture, coal tar, was still largely unknown up to the middle of the 19th century. As tar production grew, so analytical investigations increased; August Wilhelm v. Hofmann, a disciple of Justus v. Liebig, was particularly active in this field.

In 1845, Hofmann went to London as Principal of the newly-founded Royal College of Chemistry, to continue his investigations at the original source of coal tar. Hofmann gathered a number of young chemists around him, who concentrated on investigating the reactions of tar components. London thus became the Mecca of aromatic chemistry.

One of the principal objectives of Hofmann's work was to synthesize quinine, at that time the only known agent effective against malaria. William Henry Perkin, one of Hofmann's youngest students, devoted a great deal of imagination to the synthesis of quinine. In 1856, Perkin tried to synthesize quinine by oxidation of N-allyltoluidine, but instead obtained only a red-brown precipitate. As a model reaction Perkin chose to investigate the treatment of aniline sulfate with potassium dichromate.



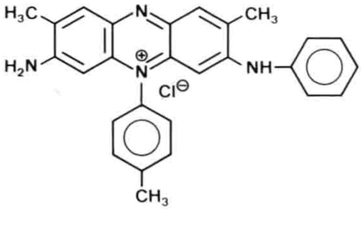
N-Allyltoluidine



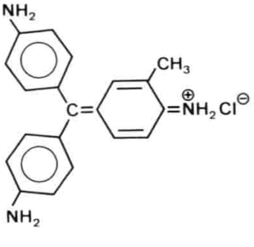
Quinine

On working-up the reaction mixture he produced a violet dyestuff; Perkin had synthesized the first tar-derived dyestuff, mauveine. Within barely 18 months, together with his father and brother, he set up a factory in Greenford Green to manufacture aniline dyes, the first time that coal-tar dyestuffs had been produced on an industrial scale. By 1860, there were already five companies in England engaged in the production of synthetic dyes. Apart from Perkin, *Read & Holliday* should be mentioned among the founders of English companies; they established the first subsidiary in the USA in 1861. Synthetic dyestuffs found a ready market, since to satisfy growing demand from the textile industry, 75,000 t of natural dyes were imported annually into Great Britain alone.

Production of coal-tar dyes developed dramatically on the European continent too, following Perkin's discovery. In Lyons in 1859, Francois Emanuel Verguin produced the red-violet fuchsin (Basic Violet 14) by oxidation of technical aniline, a mixture of aniline and toluidines. This dyestuff provided the basis for the production of coal-tar dyestuffs in France; it is still important today. At the World Exhibition in London in 1862, the coal-tar dyestuffs industry celebrated great triumphs. The thirteen prize winners were almost exclusively English and French dye manufacturers.



Mauveine (Main component)



Fuchsin

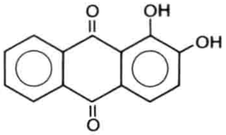
Following the pattern of England and France, new manufacturing facilities were set up in Germany for production of synthetic dyes. The first were established by existing natural-dye traders such as Rudolf *Knosp* and Gustav *Siegle* in

Stuttgart; these companies later became part of the *Badische Anilin- und Sodafabrik* (*BASF*). In 1860, the dyestuff merchant Friedrich Bayer set up a fuchsin factory in Elberfeld. In 1863, Meister, Lucius and Brüning also began the production of fuchsin in Höchst (*Hoechst*).

In the same year, Paul Wilhelm *Kalle* founded a dyeworks in Biebrich (Wiesbaden). In 1865, the *Badische Anilin- und Sodafabrik* was established in Mannheim; its founder company, *Sonntag, Engelhorn & Clemm* had already begun production of coal-tar dyes in 1861. In 1865, Carl Alexander Martius, a disciple of Hofmann, returned from England to Germany and became a co-founder of the *Aktiengesellschaft für Anilinfarben* (*Agfa*). In 1870, the dyestuffs company *Leopold Cassella & Companie* was founded in Mainkur (Frankfurt).

The growing demand from the dyestuffs industry for aromatics was met by the rapidly developing tar industry. In Germany, the companies *Rütgerswerke,* founded initially for timber impregnation by Julius Rütgers in 1849, and the *Gesellschaft für Teerverwertung* (*GfT*), founded by August Thyssen, are worth mentioning. The basis of tar refining was fractional distillation, first used by Charles Blachford Mansfield in 1847 for the production of benzene from coal tar on a large scale.

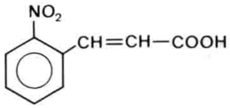
Lively competition developed among the European dyestuff producers. The race to produce alizarin was particularly dramatic. In 1867, Adolphe Wurtz and August Kekulé had discovered that the sulfonic acid group in aromatics could be replaced by a hydroxyl group by alkali fusion. Perkin used this process to manufacture alizarin from anthraquinone, which up to this time was produced from madder. When he applied for a patent on his process, he learned that Carl Graebe and Carl Liebermann had already submitted an application for this product on 25th June 1859, just one day earlier than himself. However, Perkin did not give up, but developed a new process, which subsequently led to an exchange of licenses. In 1873, he produced 435 t of alizarin, while German alizarin production had already reached 1,000 t.



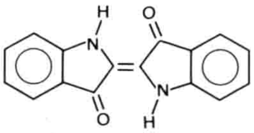
Alizarin

Just as madder extracts were used for red coloring, so indigo had been used since olden times as a blue coloring agent, especially in India. The source of indigo was woad, which was cultivated in Germany, mainly in Thuringia. In the 16th and 17th centuries, there were large woad plantations found in the area around Gotha, Erfurt and Weimar, which were largely abandoned when imports of indigo from India took over. Production of natural indigo was around 8,200 tpa in 1885, with over half this dyestuff being produced in Bengal by biochemical decomposition from Indigofera tinctoria.

Synthesis of indigo was a particular challenge for dyestuff chemists in the second half on the 19th century. Adolf von Baeyer first successfully synthesized indigo in 1869, starting from o-nitrocinnamic acid.

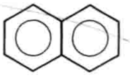


o-Nitrocinnamic acid

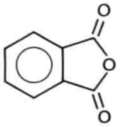


Indigo

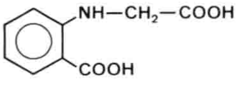
Since Baeyer's work was more directed to the elucidation of the structure of indigo, the synthesis he had discovered could not be applied economically on a large scale. Karl Heumann, at the Federal Polytechnic in Zurich, discovered a method of synthesis which was based on phenylglycine, which can be produced from aniline and chloroacetic acid. The yield from this process, however, was still unsatisfactory. Heumann's second proposal used phenylglycine-o-carboxylic acid, obtained by first oxidizing naphthalene to phthalic anhydride.



Naphthalene



Phthalic anhydride



Phenylglycine-o-carboxylic acid

The oxidation of naphthalene was carried out with chromic acid and chromates, regenerated by electrochemical reoxidation. This method was first used by the *Farbwerke Hoechst*. In 1891, it was accidentally discovered at *BASF* that naphthalene could be oxidized by concentrated sulfuric acid in the presence of mercury. In 1897, *BASF* introduced the first synthetic indigo to the market, followed shortly thereafter by *Farbwerke Hoechst*. Synthetic indigo rapidly replaced the natural product in the market in spite of harsh competition of the producers of natural indigo, especially of the Provence/France.

As a result of intensive research in the dyestuff sector by the turn of the century, around 15,000 dyes had already been patented in Germany. The largest portion were azo-dyes, obtained by coupling diazotized amines with suitable organic compounds.