

Heinrich Zollinger

# Color Chemistry

Syntheses, Properties and Applications  
of Organic Dyes and Pigments

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Prof. Dr. Drs. h.c. Heinrich Zollinger  
Technisch-Chemisches Laboratorium  
Eidgenössische Technische Hochschule  
CH-8092 Zürich  
Switzerland

Editorial Director: Dr. Hans F. Ebel and Dr. Christina Dyllick-Brenzinger  
Production Manager: Heidi Lenz

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# Preface

The origin of this book can be traced back in part to impressions formed during my early years as a research chemist in the area of industrial color chemistry. I realized then the extent of the knowledge and experience accumulated by generations of chemists who had been involved in the synthesis of thousands of dyes and pigments since 1856, when William H. Perkin by chance obtained Mauve, the first commercially successful synthetic dye. However, I was also struck by the fact that color chemists were in possession of a wealth of observations which would also be of interest to other branches of chemistry. Therefore, I have devoted practically all my own research activities since that time to the strengthening of the crosslinks between color chemistry and other areas of the chemical sciences; first, mainly to physical organic chemistry and reaction engineering, later also to physical chemistry. Finally, links have been traced to some – admittedly small – sections of the engineering and bio sciences (electrophotography, biodegradation and color vision).

This field of experience is reflected in the present book. I intend to demonstrate *how* the domain of organic colorants is connected with principles of modern inorganic, organic and physical chemistry and also various branches of engineering and of biology. Examples are to be found in the through-space interactions of molecules and in the field of surface chemistry: In the former, chemists and biologists have recently become interested, while in the latter case there has been a renaissance of the once unfashionable area 'surface science'. Color chemistry, on the other hand, has been involved in both areas for decades.

The book was written for three potential groups of readers:

*Firstly*, for organic chemists who regard color chemistry as closed, conservative and not readily amenable to new discoveries and methods. I hope that they will see in Chapters 3 to 10 that color chemistry must not be an enumeration of thousands of structures, but that dyes and pigments show a series of characteristic and fundamentally interesting structural features, and that they allow an understanding of a number of reactions of general relevance for organic chemistry. Natural dyes are included in the appropriate chapters.

*Secondly*, for color chemists who are either starting their career in that field or have worked in it for years. I hope that they will discover modern aspects of color chemistry related to their field of experience. Coverage is given to dye synthesis, emphasizing mechanisms, catalytic processes, *etc.*, as well as to the scientific basis of traditional col-

oration. New applications of dyes, e. g. for information storage devices, for liquid crystal displays, optical data disks or for solar energy conversion, are also of interest to the color chemist. Last but not least, a discussion of color *per se*, from principles of molecular orbital theory to color vision, will be found not only stimulating but useful.

Thirdly, for physical chemists, as well as engineering and biological scientists, who use dyes or pigments as a tool. I hope that they will gain insights from the purely chemical and physicochemical chapters, e. g. in rationalizing their observations when staining biological tissues by understanding the structure and reactivity of the dyes they use, or by investigating other colored compounds for the many new imaging, information and light energy storage systems which are in development at present. The sections originating from their own area of specialization offer little new information *per se*. For example, electronic spectra are not described for physical chemists, nor are lasers or liquid crystals and fluorescent staining described for physicists, engineers and biologists, respectively, but rather for the previously mentioned two groups of chemists.

It needs to be emphasized that this book is not intended to be a mere compilation of more topics than former books on color chemistry. In particular, it should not be regarded as a collection of unrelated chapters, each written by and for specialists in the respective subject area. It is not a reference book, but a book for reading.

This general aim of the book coincides with recent ideas about the future development of chemical science and technology, as discussed in a short article by Kline (1984) and in the voluminous report "Opportunities in Chemistry" written on behalf of the National Academy of Sciences (USA) by a committee under the chairmanship of Pimentel (1985). These publications emphasize the fact that the last twenty years have seen the near-extinction of the old subdisciplines in chemistry and the need for cooperation with neighboring disciplines. I fully support this as well as Kline's conclusion: "They will ... have to overcome the formidable obstacles to innovation created by minds set in old patterns by the parochialism of university departments and by the conservatism of industrial executives."

I hope this book will contribute to that extinction of parochialism and of conservatism. I hope also that the greater range of topics covered in this book on color chemistry does not influence unfavorably the depth of treatment of fundamental phenomena. This book, it is hoped, will be a tool for chemists in the context of another recent and critical statement written by two well-known technologists, Davies and Weisz (1981): "Color science and technology have become different, but chemists haven't noticed the opportunities."

In order to keep the size of the book within reasonable limits, it was necessary to concentrate on major colorants of the past and present. Coverage also had to be given to new areas, as well as to promising, future-oriented projects – even if their scientific or technological success is still an open question. The literature mentioned was chosen on the basis of these principles, whenever possible, in the form of recent books and reviews. Key research papers are discussed, in some cases even if they are 20, 50 or more years old, but still relevant. Patents are mentioned too, but only for recent inventions if they have had an impact on industrial products. There is a total of some 800 references; 35 % of these were published in and after 1981.

A problem for every author of a book or review covering industrial colorants is the unfortunate fact that dye and pigment manufacturers do not publish the structures of their products. This is a serious obstacle for any scientist who is working with such compounds. I did not choose the solution of this problem which is usually applied by review authors working in industry who mention many patents, but do not indicate which example of which patent is really a commercial product! (Here Sandoz Ltd. should be commended for publishing the structure of Foron Brilliant Blue S-R, a disperse dye with a fundamentally new chromogenic system, in 1982 immediately after bringing it onto the commercial market; see formula 3.20 in Sec. 3.3.)

With very few exceptions, I include only commercial products with known structures in this book. I thank my senior coworker Dr. P. Skrabal, who has elucidated some structures of important dyes for publication in this book.

In the preparation of this book I am indebted to several friends, colleagues and coworkers. First of all, I would like to thank Prof. W. Lüttke (University of Göttingen) and Prof. T. Iijima (Tokyo Institute of Technology), who were patient critics of the text of some chapters, as they evolved and who made many suggestions and prevented many errors. For advice and discussions of specific problems, I am indebted to Dr. G. Back, Dr. H. H. Bosshard and Dr. D. Reinecke (Ciba-Geigy A.G.), Prof. L. Dulog and Prof. H. E. A. Kramer (University of Stuttgart), Dr. D. H. Dybvig and his coworkers (3M Research Ltd., Harlow, England), Prof. E. Fischer, Prof. A. Grinvald and Prof. V. A. Krongauz (Weizmann Institute of Science), Prof. M. Grätzel (EPF Lausanne), Prof. G. W. Gray (University of Hull), Dr. W. Koch (Sandoz A.G.), Dr. H. H. Kuhn (Milliken Research Corp.), Dr. B. S. Nagar (Indian Dyestuff Ind., Kalyan), Prof. E. S. Olson (Clemson University). Parts of the manuscript were written during my stays as a Visiting Guest at the Weizmann Institute of Science in Rehovot, Israel, at Kyushu University in Fukuoka and at the Tokyo Institute of Technology. I thank my hosts Profs. Y. Mazur, D. Samuel, H. Taniguchi and T. Iijima for their hospitality.

I thank also Drs. P. Ball, M. D. Ravenscroft and G. Tovstiga, research assistants at ETH Zurich, for improving the English style of my manuscript and Dr. M. Gisler and S. Müller for their help in literature work for this book.

My association with VCH Verlagsgesellschaft has not been the usual type of business relationship. Dr. H. F. Ebel suggested I write this book, and Dr. Christina Dyllick-Brenzinger read and improved the typescript with respect to language and content. I am very thankful to both of them for their friendly collaboration.

I hope that this monograph will arouse the interest of chemists in academia and in industry for an old but still fascinating field of chemistry.

Zurich, March 1987

Heinrich Zollinger

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# 1 Introduction

## 1.1 Classification of Colorants

Colorants are characterized by their ability to absorb visible light (400 to 700 nm); in fact it is for this reason that they appear to be colored. Natural organic and inorganic colorants have been used by man since prehistoric times. However, it was the discovery of Mauve by W. H. Perkin in 1865 which marked the start of the synthetic dye industry (see Sec. 1.2). In the last 130 years several million different colored chemical compounds have been synthesized and about 10 000 of these were or are produced on an industrial scale. Some form of classification of this enormous family of compounds is clearly necessary.

Two large groups of colorants have already been mentioned, these being the inorganic and organic colorants. Each of these groups can be subdivided further into natural and synthetic compounds. This second differentiation is, however, generally not meaningful, as there are colorants which originally had a natural source, but which are today produced synthetically.

A very important differentiation of colorants is the following: Colorants are either *dyes* or *pigments*. These terms are often used indiscriminately, in particular, pigments are quite often considered to be a group of dyes. Ideal pigments are characterized by being practically insoluble in the media in which they are applied (for details see Sec. 12.1). Pigment particles have to be attached to substrates by additional compounds, e.g. by a polymer in a paint, in a plastic or in a melt. Dyes, on the other hand, are applied to various substrates (textile materials, leather, paper, hair *etc.*) from a liquid in which they are completely, or at least partly, soluble. In contrast to pigments, dyes must possess a specific affinity to the substrates for which they are used.

The often rather inaccurate distinction made between pigments and dyes has several origins. Firstly, the words "dye" and "dyeing" are much better known by the general public than the more technical term "pigment" or even the word "colorant". Furthermore, most organic pigments are closely related to dyes with respect to their chemical structure, and, finally, there are dyes which become pigments after application (vat dyes).

In this book only organic colorants are described. In Chapters 3 to 9 dyes and pigments are arranged according to their chemical structure. The content of these chapters follows basic concepts on the color of organic compounds, introduced in Chap-

ter 2. The discussion begins with polyenes, *i.e.* compounds whose visible light absorption is based only on a sequence of methine groups ( $-\text{CH}=\text{}$ ), and with polymethines, *i.e.* polyenes with an electron donor and an electron acceptor at the respective ends of the conjugated system. Increasingly more complex structures are treated in the following chapters, namely, those containing ring systems of methine groups, and colorants in which one or more methine groups are replaced by nitrogen atoms. Here we find the

largest class of colorants, those containing azo groups ( $-\text{N}=\text{N}-$ ). Finally, dyes and pigments are discussed for which—in addition to conjugated systems—carbonyl groups or sulfur bridging units are characteristic.

An alternative method of classification is that by area and method of application (coloristic classification). Chapter 11 discusses the physicochemical basis of the classical application of dyes, mainly that on textile fibers. In Chapter 12 the application of pigments is treated, and Chapters 13 to 16 deal with applications involved in physical and technical processes (*e.g.* dyes for lasers, liquid crystal displays, solar energy conversion, dyes in photography and in reproduction techniques). Furthermore, applications in analysis, biochemistry, biology, medicine and food technology are discussed.

A compound which absorbs radiation takes up energy which can be released in various ways. One possibility is fluorescence, *i.e.* the emission of light from singlet excited states at longer wavelengths than absorption (see Sec. 2.4). This effect is used in fluorescent colorants and, particularly, in optical brightening agents. The latter are compounds which absorb near-ultraviolet light and release energy by fluorescence in the visible light range. They can be applied to various substrates and cause emission of visible light from the surface of these substrates (see Chap. 10).

There are also proposals by Griffiths (1976), Dähne and others to classify colorants according to the type of electronic excitation occurring on light absorption (summary: Klessinger, 1982). Lüttke (1985) classifies colorants as absorption colorants, fluorescent colorants and energy transfer colorants, depending on whether the light energy absorbed is dissipated predominantly (*i.e.* with high quantum yields) by internal conversion, by fluorescence or by intersystem crossing (see Fig. 2–8).

The two classifications based on chemical structure and on area and method of application overlap, *i.e.* there is hardly a chemical class of dye which occurs solely in one coloristic group, and *vice versa*. Furthermore, some coloristic groups can be applied to two or more substrates, whilst others are specific to a single substrate. Reactive dyes, for example, are classified chemically as colored compounds having a group capable of forming a covalent bond with a substrate. The colored parent substance can, in principle, be derived from all classes of Chapters 3–9, but in practice the compounds of interest are mainly of the azo, anthraquinone and aza annulene types (Sec. 7.12, 8.6 and 5.2, respectively).

When classified according to the dyeing method, one speaks of anionic, direct or disperse dyes, depending on whether they are intended for use on protein, cellulose or polyamide fibers. Moreover, certain reactive dyes with a particular type of chemical structure can be used for several substrates, whilst others (with the same type of structure) are suitable for only a single substrate.

Both classifications are used by the *Colour Index* (3rd Ed., 1971), which lists all

dyes and pigments used commercially for large-scale coloration purposes, *i.e.* dyeing of textile fibers, for pigment coloration of plastics, paints, printing inks and for the coloration of liquids (solvents *etc.*). It does not list dyes for those applications discussed in Chapters 13 to 15 of this book. In Part 1 of the Colour Index dyes are grouped in the following classes: acid, mordant, basic, disperse, natural dyes and pigments, food, leather, direct, sulfur, vat, reactive, an ingrain section including ingrain dyes, azoic diazo components, azoic coupling components, azoic compositions, oxidation bases, optical brighteners, intermediate products, developers and reducing agents. The various classes of dyes are subdivided according to color, *viz.* yellow, orange, red, violet, blue, green, brown and black.

Part 1 also gives methods of application, usage, the more important fastness properties and other basic data.

Part 2 gives the structural formulae (where known) of the dyes, methods of manufacture and literature references, including patents.

Part 3 includes abbreviations of manufacturers' names, and Generic Names and commercial names indexes. In 1976 and 1982, respectively, two supplementary volumes to the third edition and a separate volume on pigments and solvent dyes were published.

In the Colour Index each dye or pigment is given two reference numbers on the basis of the coloristic and the chemical classification, respectively. One refers to the area of application and method of coloration; it is called the C.I. Generic Name (*e.g.* C.I. Vat Blue 4 for indanthrone, Sec. 8.9 in this book). The other is termed the C.I. Constitution Number (*e.g.* C.I. 69800 for indanthrone). All commercial names under which the colorant is sold (a total of 35 for indanthrone, *e.g.* Indanthren Blue RS, Cibacron Blue RSN, Caledon Blue XRN, Nikanthrene Blue RSN *etc.*) are also listed in Part 1.

Under a C.I. Generic Name all commercial dyes or pigments are mentioned which have the same chemical structure. They should not be called 'identical' as they may differ significantly with respect to crystal structure (important for pigments), particle size (pigments, disperse and vat dyes), additives and impurities (all dyes and pigments). Schmid (1985) has given a series of examples for the limited equality of commercial dyes having the same C.I. Generic Name.

The Colour Index is edited jointly by the Society of Dyers and Colourists (Great Britain) and the American Association of Textile Chemists and Colorists. To date, some 8000 C.I. Generic Names and more than 40 000 names of commercial products have been registered in the Colour Index. The past, present and future of the classification of colorants in the Colour Index have been discussed by Burdett (1982) and by Schmid (1985).

For all colorants mentioned in this book and registered by the Colour Index, the C.I. Generic name is given as well as one of the commercial names – either the first name historically or a name under which the colorant is well known. The C.I. Constitution Number is not mentioned here because the constitution is given in a structural formula for practically all colorants discussed in this book.

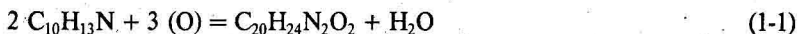
## 1.2 History of Dyes and Pigments

Prehistoric man had already dyed furs, textiles and other objects with natural substances, mainly of vegetable, but also of animal origin. Ancient Egyptian hieroglyphs contain a thorough description of the extraction of natural dyes and their application in dyeing. Cave-drawings such as those in Altamira (Spain) demonstrate that (inorganic) pigments were used also in prehistoric time (Brunello, 1973).

Further developments extending over many thousands of years led to rather complicated dyeing processes and high quality dyeings. Among these the following deserve special mention: Indigo, which was obtained both from dyer's woad, indigenous in Europe, and from *Indigofera tinctoria*, a native plant of Asia; Ancient purple, which was extracted from a gland of the purple snail by a process developed by the Phoenicians; Alizarin, on which Turkey Red is based, which was obtained from madder Campeachi wood extract imported from Africa.

Picric acid, which was obtained by P. Woulfe in 1771 by treating indigo with nitric acid, was subsequently occasionally used for dyeing silk yellow, but did not attain any significance.

In 1856 the young and talented English chemist William Henry Perkin worked under the direction of the German chemist August von Hofmann at the Royal College of Chemistry in London. He suspected that the natural product quinine, at that time the only known treatment for malaria, might be produced by the oxidation of allyltoluidine, which von Hofmann had obtained from coal tar (1-1). As an oxidizing reagent he used potassium dichromate. In 1856 only molecular formulae, not structural formulae of organic compounds (including allyltoluidine and quinine) were known.



He was of course not successful in synthesizing the complex heteroalicyclic structure of quinine, but he became interested in studying the reaction of other coal tar bases, including a mixture of aniline and toluidines. He found that the crude bases produced an intense bluish purple solution with methanol and that it dyed silk in a rich color that did not wash out nor fade upon exposure to sunlight over a week. Perkin decided to patent his discovery and to manufacture it commercially. The British Patent Nr. 1984 was issued to the 18-year old W. H. Perkin on August 26, 1856, and with the financial help of his father the dye firm Perkin and Sons was established some months later in a London suburb. Production started in 1857. The name Mauve or Mauveine was given to Perkin's product by Poirrier from St. Denis in France (Welham, 1963; Farrar, 1974; and others).

The brilliant hue on silk immediately attracted much attention and stimulated other chemists to carry out similar experiments. In this way, in 1859 E. Verguin in Lyon discovered Fuchsine, whilst the discovery of diazo compounds by P. Griess in England laid the foundation for the development of the currently largest class of synthetic dyes, namely the azo compounds. The first true azo dyes were developed in 1861 and 1863 (see Sec. 7.1).

It is astonishing that in 1856, the year in which Perkin discovered Mauve, another dye was obtained by C. H. G. Williams, namely the first polymethine dye, cyanine. This dye is hardly mentioned in the historical chapters of books on dyes. This omission is probably due to the fact that cyanine did not become a commercial dye for coloration purposes immediately after its discovery. Much later, however, its sensitizing power for silver halide photography became important (see Sec. 3.3, and Hamer, 1964).

After the fundamental work by August von Kekulé on the quadrivalence of carbon (1858) and on the constitution of benzene (1865), the way was open for the planned preparation of synthetic dyes, as well as for the artificial production of natural dyes. The first success was the elucidation of the constitution (1868), and the synthesis immediately afterwards, of alizarin (1,2-dihydroxyanthraquinone), the basis of the metal complex dye Turkey Red, by Graebe and Liebermann (see Sec. 8.1). The structural elucidation and the synthesis of indigo (A. von Baeyer, 1883; K. Heumann, 1890) involved research work extending over several decades (Sec. 8.1 and 8.3). Shortly before the turn of the century, Vidal opened up the field of sulfur dyes (Chap. 9), whilst the year 1901 was characterized by the discovery of indanthrone; the first anthraquinoid vat dye, by R. Bohn (Sec. 8.9).

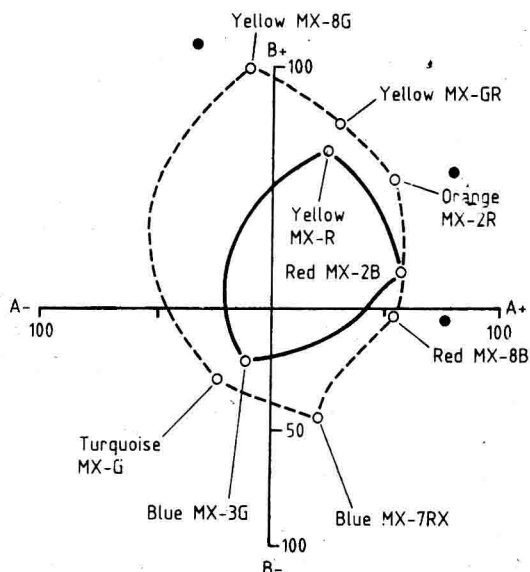
In the domain of metal complex dyes, the first half of the 20th century yielded important contributions (Neolan dyes, 1915; phthalocyanine pigments, 1936; Irgalan dyes, 1949; Secs. 7.10 and 7.11). In the 1920s the problem of dyeing hydrophobic fibers was solved with disperse dyes (Secs. 7.7 and 8.7). The era following the second World War was characterized by the development of pigments (e.g. quinacridone, 1958, Sec. 8.12) and reactive dyes (wool dyes, 1951, dyes for cellulosic fibers, 1956, Sec. 7.13).

Reactive dyes, for example, clearly show the general tendency of dyestuff research to move away from purely empirical syntheses of colored molecules to the study of the mechanisms of interaction of substrates and dyes with already known chromogens (e.g. azo, anthraquinone and cyclic azo compounds).

The fact that nowadays thousands of colorants of different constitution are commercially available clearly shows that a thorough knowledge of synthetic organic chemistry (leading to the preparation of new dyes and pigments; the discovery of new reactive groups, etc.), of the reaction mechanisms (leading to the optimization of manufacturing processes) and of the techniques needed to apply the results of research on colorants can ultimately bring success.

As an example of the influence of organic synthesis, Figure 1-1 shows the restricted gamut of shades obtainable from the first three reactive dyes for cellulose (Procion dyes, 1956, solid line), whilst the extension of the gamut obtainable as the result of later additions to the Procion dye range is shown by the dashed line\*. The three black dots indicate fluorescent dyes which produce dyeings lying beyond the limits of Procion dyes.

\* The basis of Fig. 1-1 is the ANLAB color system which is related to the CIELAB color space described in Sec. 2.7.



**Figure 1-1.** Gamut of shades obtainable with Procion reactive dyes in 1956 (solid line) and in 1976 (dashed line). Location of three fluorescent dyes ●. With permission of Imperial Chemical Industries (Technical Information D 1466, 1976).

Since the 1970s colorant research has not concentrated predominantly on the development of new structures with which to extend the shade gamut (although there is still progress in this direction, e.g. the extremely bright Foron Brilliant Blue S-R, 1982, see Sec. 3.3). More emphasis has been placed in the optimization of manufacturing processes and in more economic methods of application. In addition, the use of dyes and pigments for coloration of new substrates, their use for purposes other than coloration *per se*, as well as ecological problems of colorant manufacture and application have become more important. For this reason new applications and ecological aspects will be discussed in more detail in this book than in earlier books on colorants (Chaps. 13 to 15 and 16, respectively).

### 1.3 Production of Colorants

The manufacture of dyes and pigments has always been characterized by its concentration in several large firms. Whilst before the first World War the world's requirements of synthetic dyes were manufactured almost entirely in Germany (apart from Germany, only Switzerland contributed a significant proportion of world production),

nowadays manufacture is spread over a larger number of countries. Production or sales statistics are available only for a few countries, but total world colorant production is now estimated to be of the order of 700 000 tons. A little more than half of the production concentrates on textile dyes and some 15 per cent are used for other substrates dyed in a similar manner to textiles (leather, paper *etc.*). 25 per cent of the production is devoted to organic pigments. Inorganic pigments, including delustrants ( $\text{TiO}_2$ ) for man-made fibers, have a production volume which is several times higher than that of organic pigments. Fluorescent brightening agents and dyes for other applications (as discussed in Chaps. 10 and 13–15, respectively) have a share of about 6%.

With respect to countries and manufacturers only gross estimates are known of worldwide colorant production. The tonnage produced in USA is probably the highest, but most of it is manufactured by West European subsidiaries. The largest companies (including subsidiaries) with respect to worldwide production of colorants are, in the sequence of tonnages produced, Bayer, Ciba-Geigy, Imperial Chemical Industries, Sandoz, BASF and Hoechst. With respect to sales value Ciba-Geigy is the largest. The Japanese industry has grown in recent decades. The five major manufacturers in Japan (Mitsubishi, Sumitomo, Nippon Kagaku, Mitsui Toatsu and Hodogaya) manufacture about 10 per cent of the world production. Further data on the coloration industry have been summarized by Booth (1984).

The marketing of new dyes can be followed in the entries of Generic Names in the Colour Index. As shown by McLaren (1982), the annual average of entries was about 100 in the 1950s, 200 in the 1960s, followed by a decrease to 60 in 1981. This decrease is clearly a consequence of the change in perspective demonstrated by colorant producers, as discussed at the end of Sec. 1.2. The Colour Index also allows one to detect changes in the popularity of various classes of colorants. In the period 1974 to 1982 the largest increase in new products was observed for disperse dyes (41.5%), followed by reactive dyes (39.4%), solvent dyes, fluorescent brighteners, cationic dyes and pigments. For all other classes of the C.I. classification the number of withdrawals was larger than the number of newly-introduced compounds (acid, azoic, direct, vat and mordant dyes).

Estimates on the worldwide production volume in the various classes of colorants vary greatly. Accurate figures are only obtainable for the USA and Japan, but they are not representative of worldwide production. As an example, the share of sulfur dyes in the production of dyes (not including pigments) in Japan was 6% in 1983; in the Soviet Union it is estimated to be about 50% (worldwide probably about 20%).

Information on industrial research activities can also be obtained from colorant patents recorded in Chemical Abstracts. For a three-month period in 1983 48% of all abstracted patents on colorants originated in Japan, 22% and 15% from Western and Eastern Europe, respectively (Zollinger, 1985). Even more interesting are the branches of colorant technology in which the Japanese chemists are most active. In synthesis alone, 25% of all patents belong to Japanese companies (43% to Western Europe). The Japanese industry is, however, clearly dominant in non-conventional applications. For photographic and similar reproduction techniques, lasers, liquid crystal displays, jet-printing inks and other processes Japan's share is 73% of all patents!