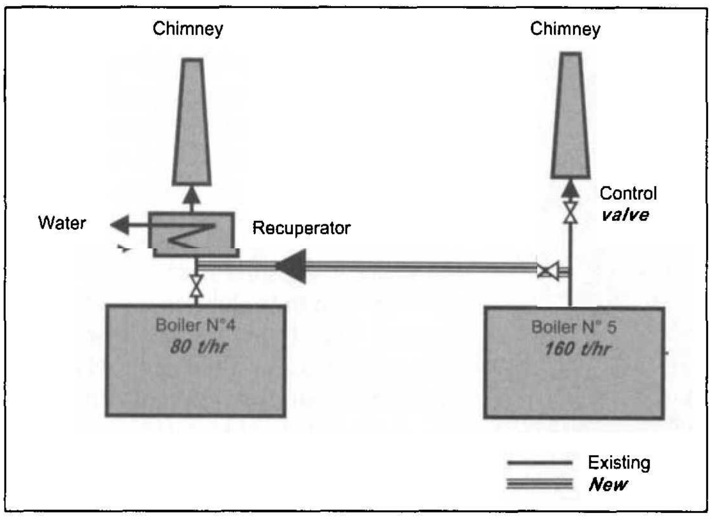

Fig. 1. Skeleton diagram

Technical data

The technical data of the recuperator, given for a maximum load, are as follows:

Heating surface	3000 m^2
Temperature of exhaust gas at entry	130 °C
Temperature of exhaust gas at exit	approx. 45 °C
Exhaust gas stream	50 000 m^3 (n)/h
Pressure loss exhaust gas stream	20 mbar
Water temperature at entry	20 °C
Water temperature at exit	approx. 60 °C
Recovered heat	3.8 MW

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Ecotoxicological Issues and their Influence on the Development of New Dyestuffs

Reinhard Pedrazzi*, Jürgen Geiwiz, Manuel Golder, and Roland Grimm

Abstract: Up to the time of the First World War, synthetic dyes were manufactured mainly in Europe. Nowadays dyes are produced all over the world. About 50% of dyes are used in the textile industry. Some of the most urgent challenges now being faced by dyestuff manufacturers and users are those related to environmental and toxicological issues. Over the past years, tougher regulations, standards and laws have been enacted. These will exert legal pressure during the coming years, with the goal of removing critical products from the market and compelling the dye manufacturing industry to offer only ecotoxicologically sound products. The purpose of this paper is to point out certain consequences for research that might take place due to the regulations, and to describe recent developments towards overcoming this challenge, which has already led to considerable benefits for the environment.

Keywords: Azo dyes · Environment · Green chemistry · Regulations · Research

Azo Dyes

Azo dyes are compounds containing at least one azo chromophore group (–N=N–) which is linked to sp^2-hybridised carbon atoms. To produce this azo chromophore, one begins with an aromatic amine which is converted into a diazonium ion. This relatively weak electrophilic reagent reacts with aromatic species that carry electron donor substituents. Azo dyes account for the largest portion of all synthetic dyes in terms of number and volume of production. They include approx. 70% of all organic dyes currently on the market. Therefore, the class of azo dyestuffs plays an exceptionally important role, particularly for economic reasons.

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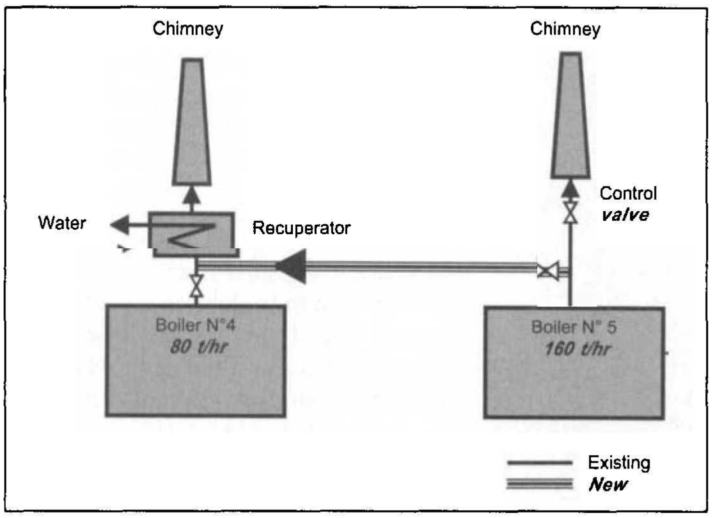

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Table: *Banned amines*

Amine	CAS RN
4-Aminobiphenyl	99-67-1
Benzidine	92-87-5
4-Chloro-o-toluidine	95-69-2
2-Naphthylamine	91-59-8
o-Aminoazotoluene	97-56-3
2-Amino-4-nitrotoluene	99-55-8
p-Chloroaniline	106-47-8
2,4-Diaminoanisole	615-05-4
4,4-Diaminodiphenylmethane	101-77-9
3,3-Dichlorobenzidine	91-94-1
3,3-Dimethoxybenzidine	119-90-4
3,3-Dimethylbenzidine	119-93-7
3,3-Dimethyl-4,4-diaminodiphenylmethane	838-88-0
p-Cresidine	120-71-8
4,4'-Methylene-bis(2-chloroaniline)	101-14-4
4,4'-Oxydianiline	101-80-4
4,4'-Thiodianiline	139-65-1
o-Toluidine	95-53-4
2,4-Toluylenediamine	95-80-7
2,4,5-Trimethylaniline	137-17-7

120 to 150 of the more than 2000 dyes currently in use, are strongly suspected to cause cancer. Particularly azo dyes based on benzidine and benzidine derivatives seem to be among the major causes of cancer. The first dyes based on the benzidine molecule were synthesised more than 100 years ago. A wide spectrum of colours could be achieved by varying the molecule's chromophores and this facile and productive synthesis resulted in many excellent dyes. The variety of dyes based on benzidine is exemplified by the fact that 258 benzidine-based dyes were listed in the third edition of the Colour Index. The wide range of different azo dyes shows, however, that sufficient alternatives exist with a much lower risk potential.

For the judgement of the risk potential of a dyestuff, one must not only consider the dyestuff itself, but also the potential metabolites. On July 15, 1994, the German government amended its regulation on consumer goods. This banned the use of azo dyestuffs that could split into any of 20 named amines (see Table).

These amines are classified by the German Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area (MAK Commission) as Group III A1 or III A2 carcinogens – that is, substances that have been unequivocally proven to be carcinogenic according to the Commission. Benzidine was one of the first chemicals for which an association of occupational exposure and increased cancer was recognised for humans. Since occupational exposure to benzidine-based dyes has been most frequently associated with co-exposure to benzidine, it has been difficult to clearly establish their carcinogenicity in humans. You *et al.* [1] observed no increased incidence of tumours in workers exposed almost exclusively to benzidine-based dyes, whereas Bi *et al.* [2] reported that cancer incidences were elevated for workers exposed to both benzidine and benzidine-based dyes. The IARC (International Agency for Research on Cancer) evaluation of these results reached the following conclusion: 'Although the epidemiological data were inadequate to evaluate the carcinogenicity to man of individual benzidine dyes, they, together with the presence of benzidine in the urine of exposed workers, provide sufficient evidence that occupational exposure to benzidine-based dyes represents a carcinogenic risk to man'.

3,3'-Dimethylbenzidine and 3,3'-dimethoxybenzidine are structurally similar to benzidine. 3,3'-Dimethyl-benzidine-based dyes that are metabolised to 3,3'-dimethylbenzidine are reasonably anticipated to be human carcinogens based on the facts that 3,3'-dimethylbenzidine is carcinogenic in male and female rats (IARC 1972; NTP 1991b, 1998) and that metabolism of 3,3'-dimethylbenzidine-based dyes to release free 3,3'-dimethylbenzidine is a generalised phenomenon, occurring in all species studied [3][4]. A representative dye is C.I. Acid Red 114, which is carcinogenic in male and female rats. Further, the pattern of tumours observed with C.I. Acid Red 114 [5] is similar to that observed with the structurally similar chemical 3,3'-dimethoxybenzidine and the 3,3'-dimethoxy-based dye C.I. Direct Blue 15 [6]. Meanwhile most of the members of ETAD (Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers) have stopped manufacturing and selling dyes that could, through cleavage of one or more azo group(s), form the specified amines listed in the Consumer Goods Act. This created the necessary awareness to impose stricter rules on a global basis.

Very recently all manufacturing companies have been confronted with inquiries from customers or associations on the general topic of 'prohibition of azo dyes' based on uncertainty on the assessment of the carcinogenic risk potential of azo dyestuffs. Several newspaper articles, which gave the impression that azo dyes as a group are likely to be banned from use, have been published. However, a scientific and non-emotional analysis of this topic shows clearly, avoiding critical building blocks, azo dyestuffs will remain major elements of coloration in the future. There might be the need for a new generation of ecotoxicologically less harmful products with properties that will necessitate a certain re-thinking of their applications.

Toxicological Issues

The amendment is a result of the presumption that all azo compounds are reduced *in vivo* to their corresponding amines by azo-reductase. This generalised hypothesis, which is postulated by the authorities, must however be more precisely investigated in the individual case. For soluble dyes, this breakdown has been demonstrated experimentally both in the gastro-intestinal tract and in the respiratory tract. Hydrazone dyes, *e.g.* based on 3,3'-dimethylbenzidine, are ranked as animal carcinogens, whereas a corresponding dye which exists in the azo form and which is derived from the same benzidine diazo component, has been reported not to be an animal carcinogen [7].

For a pigment, which is defined as a substance which is practically insoluble in the application medium, it is assumed that this very low solubility in water and solvents prevents breakdown in the organism. The toxicological studies conducted to date have, however, been carried out almost exclusively with oral intake, a mode of intake which is of subordinate importance for the workplace. Workplace-related exposures to such pigments are normally inhalative, for which the methods of chemical analysis used displayed too low a sensitivity to exclude any release with sufficient reliability.

For the time being too little information exists to allow a general statement regarding the relationship between molecular structure and carcinogenic activity. Therefore, economically interesting amines, which have not been tested in dyes and pigments and without indication in the literature as to their carcinogenic potential, must be submitted to ecotoxicological assessment before adoption of new products based on such amines. It is probably the case that reductive-cleavage is not the important metabolic pathway in the mutagenesis of certain azo dyes, and that the actual mutagen probably has an intact azo linkage. While both the use of nonmutagenic amines and the design of azo dyes having nonmutagenic potential reductive-cleavage products are important considerations in the development of new dyes, it is clear that using *in vitro* assays other than the standard Ames test may be the key to future success.

With careful forethought and strategic molecular modification, it is often possible to reduce or even eliminate the toxicity of a substance without affecting its technical or commercial usefulness. It is clear that systematic research to establish relationships between azo dye structure and carcinogenicity would be essential. One very successful application was reported for the design of metallised azo dyes [8][9]. Historically, chromium was a metal of choice, because it imparts the desired colour and fastness. Cr(VI) is a known human carcinogen, and its commercial use is strictly regulated and highly discouraged by environmental authorities. An alternative metal to chromium, iron in premetallised azo dyes would have to have the same colour and properties.

In far-ranging studies, it has been observed for example that azo dyestuffs that carry at least one sulfo group on each fragment can be classified as non-carcinogenic [10][11]. In 1991, sulfonated diaminobenzanilides were reported [12] to be useful alternatives to benzidines in the synthesis of direct dyes with the same desired properties. However, this manner of consideration limits the selection of aromatic amines as building blocks for new dyestuffs considerably. In addition to the chemical structure of a dyestuff, of particular relevance for the toxicological rating is that a dye should have a high technical performance, *e.g.* a high affinity to the fibre, which will not always be the case with to the above-mentioned benzanilides.

C.I. Acid Red 114, a brilliant red dyestuff for application on polyamide, was widely used in the industry. It became obvious that such a brilliant red shade could not easily be replaced. On this occasion, close co-operation with paper dyes research proved to be very helpful. A newly developed red dye for the paper industry showed very promising results on polyamide. It not only possesses a very similar shade to C.I. Acid Red 114 but also equal or, in some cases, even higher fastness than the banned product. This new product was recently released and was rapidly introduced in the textile industry. With this new dye, research has greatly reduced the risks in polyamide dyeing. This example proves that more stringent restrictions with respect to environmental issues are not only a burden but also a challenge to the industry.

After all, when designing a new chemical, synthesis yield is no longer the only consideration for a chemist. It is strongly expected today that toxicity, biodegradation, aquatic toxicity, pollution effects and others are considered as part of the design strategy for chemicals. Therefore research chemists need to familiarise themselves with as much toxicity information as possible.

Ecological Issues

Companies need to be focused not only on issues of process and product safety, but also on recycling. That means research chemists have to consider the total process. This is due above all to the fact that research, working in close collaboration with marketing, has recognised and accepted from the outset that these demands have achieved a special degree of importance particularly in the textile and paper industry.

The importance of designing dyestuffs that can be decolourised by using environmentally acceptable agents like hydrogen peroxide, ozone *etc.*, has increased. Unfortunately up until now investigations show that only a few dyestuffs are known which can be destroyed under practical conditions [13]. Studies concerning the relationship between dyestuff structure and peroxide bleachability are still at an early stage.

To meet the requirements of the environment, the dyestuff producers are not only developing chemically new and better dyestuffs but they are offering new formulated product forms as well. Reactive dyes which require a chemically active group to establish a chemical link between dyestuff chromophore and the fibre may, however, cause irritation when inhaled. Today a dust-free and easily dosed dyestuff enables a trouble-free handling. Thanks to new technologies [14] such as fluidised-bed spray granulation or compacting of powders, the dust problem can be reduced dramatically, although these drying techniques are more expensive than the conventional methods to produce powders. The producers of such dyes have therefore developed new granulated forms. A very successful and innovative advantage are the new *cold dissolvable granules* which do not need hot water to create a true solution stable for application in the dyehouse [15].

Sulphur dyes, another example, are coloured pigments in their oxidised form, which can be transformed through reducing agents into soluble forms with a high affinity to cellulosic fibres. To avoid problems with dust whilst handling the sulphur dye powder and to eliminate the complicated process of reducing the dyes, pre-reduced liquid forms have already been available for a long time. To keep these pre-reduced sulphur dyes in a stable form for transport and storage, large amounts of caustic soda and reducing agents have to be used which lead to restrictions and risks in transportation. A new innovation was introduced into the market which consists of a stable liquid suspension of the oxidised dyestuff and, at the same time, a new application procedure. This new commercial form allows unrestricted transportation and eliminates all aggressive chemicals during storage and transportation of the sulphur dyes. The more important innovation, however, includes new application procedures that allow considerable reductions in the time, water and chemicals used for the dyeing process.

Further developments are now imperative as research is confronted with more challenges due to the changing ecological requirements of today. Modern trends, *e.g.* toward continuous dyeing, rather than batch dying, has led the way to use dyes in concentrated liquid form. However, the preparation of liquid dyes has led to the use of solubilising auxiliaries, examples of which are urea, various alcohols, amides and organic acids. These additives are not adsorbed by fibres and therefore remain in the effluent, where they accumulate. Furthermore big efforts are necessary to substitute additives by newly developed biodegradable auxiliaries which allow the wastewater to be purified biologically without problems.

New techniques like ultrafiltration (or reverse osmosis) have been introduced to avoid the addition of auxiliaries by lowering the salt content of liquid dyes. The omission of *e.g.* urea, used previously to aid dyestuff solubility, achieves significant reduction in both oxygen demand and nitrogen content in the backwater circuits. Further advantages include decreased risk of bacterial and algae growth. The ultimate goal for dyestuffs chemists is to receive a liquid product which should consist of the active substance which is adsorbed by the fibre material completely, and water only.

Summary and Outlook

Without doubt, only a dye range which meets stringent ecotoxicological conditions has good chances in the future. To reach this goal, however, extensive and cost-intensive studies are necessary, especially in order to replace older, possibly critical dyes with modern individual products. Nevertheless, research can only overcome the hurdle of commercial acceptance if the user is sensitised by the manufacturer's information and emphasis on advan-tageous products. It is therefore very important that the user and consumers get the correct message surrounding this issue. The prerequisite is not least a more intensive dialogue, which will help to put an end to the myth that all azo dyes are hazardous. Dyestuffs research is facing up to this challenge where scientifically rooted toxicological findings only can serve as guideline to future new products.

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