

Reactive Dyes Development: A Review

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INTRODUCTION AND HISTORICAL BACKGROUND

Throughout the long history of the tinctorial arts, the dyer of textiles has been confronted with the problem of trying to match the performance of his colorants as closely as possible with the useful life of the fabric. The dyeing of cotton (cellulosics) with direct, vat, or azoic dyes depends on the adsorption of dye molecules into the fibre, while vat or azoic dyes, the dyes are first adsorbed onto the fibre followed by reaction to convert them into insoluble form, thus retained on the fibre(1). The possibility of attaching dyes to fibres by forming covalent bond has for long been attractive to dyestuff chemists because attachment by physical adsorption and mechanical retention have the disadvantages(2) of either low wet fastness or high cost.

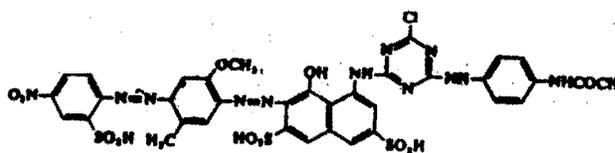
It must be pointed out that in this context "chemical reaction" implies the formation of a covalent bond between the dye and the fibre. In this respect, two approaches were known viz: by producing the dye onto the fibre, and by producing the dye and make it reactive towards the fibres. The first recorded covalently bound combination of a dye with cellulose was achieved in 1895 by Cross and Bevan(3). They treated soda cellulose with benzoyl chloride, to form a mixture of cellulose mono- and dibenzoate. Then nitrates was formed upon the reaction of these benzoates with a mixture of nitric and sulphuric acids. Reduction of these products produced aminobenzoyl cellulose derivatives. The latter were capable of diazotisation and coupling with aromatic amines and phenols to form colouring matters covalently bonded with the cellulose.

In 1906 Schroter(4) treated cotton with p-benzene-sulphonyl aminobenzene sulphonyl chloride in boiling chloroform and pyridine, thus obtaining a cellulosic material which was coupled slowly with the resulted para nitrobenzene diazonium salts in aqueous solutions of sodium acetate to form a yellow-coloured fibre having the following formula.



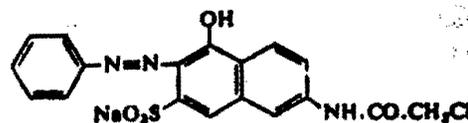
In 1920s the Society of Chemical Industry in Basle (later CIBA) began to work on the technology of cyanuric chloride, and produced chlorantine light green series as direct dyes. Their capacity of forming covalent bonds with cellulose

under certain conditions was not recognized(5). An example of this series is the chlorantine light blue BG of the following structure.



In 1922 Textilwerk Horn(6) discovered that cellulose could be pretreated with aromatic or heterocyclic sulphonyl chlorides. The reduction of nitroarylsulphonyl cellulose esters followed by diazotisation and coupling was mentioned. Peacock (7) in 1926 stated that cellulose nitrobenzoyl esters were treated with diluted solutions of p-nitro benzoyl phenyl dimethyl ammonium chloride containing stoichiometric quantity of sodium carbonate, followed by reduction, diazotisation and coupling to give dyeings fugitive to light.

In 1929 IG claimed(8) fast dyeings on wool from dyes containing chloroacetyl groups and in mid-1930s they were placed in the market as supramine orange R, the first genuinely reactive dye for wool of the following structure.

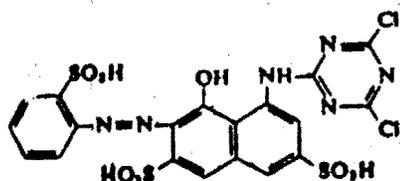


During 1930-1933 CIBA chemists, Haller and Hecken-dron, investigated the use of cyanuric chloride as acylating agent for cellulose, using the well known stepwise reaction which permits the three chlorine atoms to be replaced one at a time according to the reaction conditions. This patent is of most importance to the present study. During the late thirties and early forties efforts continued to search for the way of attachment of dyes to cotton through the covalent linkages, and work was carried out both by ICI and CIBA on dyes containing quaternary ammonium salts groups(11).

Some such dyes gave dyeings exceptionally fast to washing when padded onto cotton and afterwards subjected to baking. Of greater importance the experiments of Guthrie(12), who in 1952 found that by impregnating cotton with sodium hydroxide solutions of the sulphate ester of dyes containing alcoholic groups and subsequently baking at 100-110°C for

one hour or longer, fast dyeings could be produced. In 1948 Hoechst commenced research on vinylsulphone and β -sulphatoethylsulphones which led to marketing of the Remalan range of reactive dyes for wool in 1952 and later on, after the appearance of Procion dyes, to the Remazol range for cellulosic fibres. 60 years after the pioneer work of Cross and Bevan, the first commercial reactive dyes for cellulose came onto the market. A major factor(12) for the long delay was due to the belief that cellulose is a relatively inert material requiring drastic and probably anhydrous conditions to bring it into chemical reaction with the acylating agents.

An event(13) which had far reaching consequences was the discovery made by Rattee and Stephen in 1954, of dyes containing dichlorotriazinyl group which could be applied from aqueous solution and caused to form a covalent bond with cellulose by increasing the pH. This discovery resulted in the first commercial reactive dyes for cellulose, the procion dyes, being marketed in 1956, just a century after Perkin's Mauveine had appeared. The earlier members of the range, e.g.:



The appearance of procion dyes on the market gave a great impulse to the investigation of reactive systems other than S-triazine, and within few years several other ranges of commercial reactive dyes were available, particularly, Cibacron (CIBA), Reactone (Geigy), Drimarene (Sandoz), Remazol (Hoechst), and many others(14). All these dyes are characterised by the presence of reactive atoms or groups to react with certain functional groups of the fibrous material(14) forming the covalent bond. Reactive dyes form covalent bond (14) with fibres and this insures a high wet fastness. Other brands of reactive dyes then were followed. The following table shows the different commercial reactive dyes marketed (15), firms, and year of introduction.

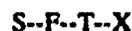
TABLE 1
INTRODUCTION OF COMMERCIAL REACTIVE
DYES

Commercial name	Firm	Year
PROCION M	ICI	1956
PROCION H	ICI	1957
CIBACRON	CIBA	1957
REMAZOL	Hoechst	1958

Levafix	Bayer	1958
Reacton	Geigy	1959
Drimaren	Sandoz	1959
Levafix E	Bayer	1961
Elisiane	Francolor	1963
Primazin	BASF	1964
Solidazol	Cassella	1964
Procilan	ICI	1964
Levafix P	Bayer	1966
Lanasol	CIBA	1966
Reactofil	Geigy	1968
Verofix	Bayer	1970
Drimalan	Sandoz	1970
Procion HE	ICI	1970
Procion T	ICI	1977
Procion H - EG	ICI	1979
Kayacelon	Nippon Kayaku	1984
Procilene	ICI	1987
Cibacron C	CIBA	1988

STRUCTURE OF REACTIVE DYES

There are many types of reactive dyes with different reactive group, i.e. with different reactive systems, that react with substrate to form covalent bonds. The chromophore of their molecules are very similar i.e. either azo, anthraquinone, phthalocyanine chromophore or others. The general formula for the reactive dyes structure is as follows(16):



Where S: Solubilising group

F: Chromophore

T: Bridging group

X: Reactive system

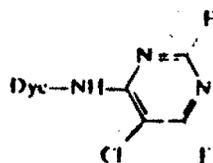
The dye structures consist of two parts(16); the chromogen and the reactive system, and it is convenient to discuss them separately. Since different ranges usually have similar chromogen, and only differ in reactive system.

Reactive systems

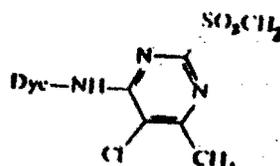
S-triazinyl systems were the first reactive systems used. They were derived from cyanuric chloride. It's significance lies on the specificity of the reactivity of it's chlorine atoms. Thus(16) the first chlorine atom of cyanuric chloride only can be displaced by a nucleophile at 0-5°C, the second at 35-40°C, and the third at 80-85°C. Much use of this relative reactivity is made in designing dyes for specific applications.

The dichloro-s-triazinyl system dyes (procion MX) are thus susceptible to nucleophilic attack at 35-40°C and it is at this temperature that reaction takes place with cellulose under alkaline conditions. The structure of the dichloro s-triazinyl dyes in general is as the following:

Other substituted pyrimidines which use other leaving groups than chlorine are also introduced to the market like Bayer's Levafix EA and Levafix P as follows:

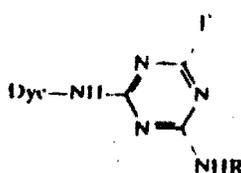


Levafix EA dyes



Levafix P dyes

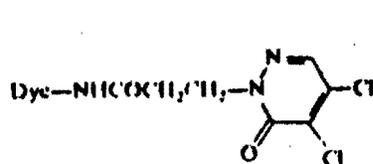
Both of these dyes have a relatively high level of reactivity similar to that manifested in Cibacron F dyes which use monofluoronyltriaziyl system.



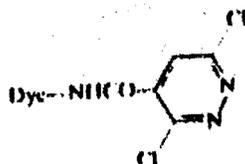
Cibacron F dyes

The Levafix EA and cibacron F dyes can both be applied to cellulose at 50 C.

Of the diaziyl systems available, pyrimidine has proved to be the most important commercially. Others have been used including quinoxaline, and phthalazine. However, the 1,2-diazine ring system was used in the Primazin P dyes (BASF) and the Solidazo dyes (Cassella):



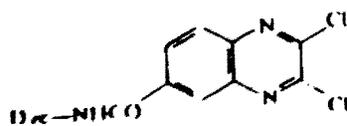
Primazin P dyes



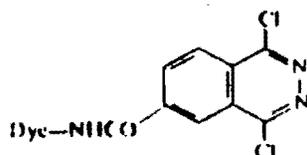
Solidazol Dyes

The quinoxaline reactive system was illustrated by Levafix E (Bayer), and introduced in 1961 with reactivity comparable with that of the dichlorotriazinyl dyes.

Phthalazine for instance, as reactive system, was used in the Eliasiane (Francolour) range:

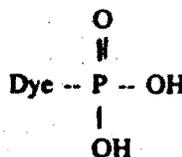


Levafix E dyes

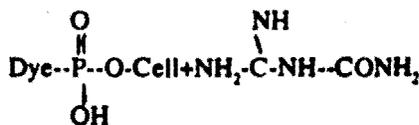
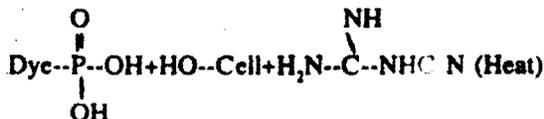


Eliasiane dyes

Reduction of a monochlorotriazinyl dyes with a suitable tertiary amine such as pyridine, nicotinic acid, or others, produces dyes sufficiently reactive for cold dyeing. An example for this is the Kayacelon react range (Nippon Kayaku)



A recent novel approach by ICI was the introduction of procion T dyes particularly for dyeing cotton in the cotton/polyester blends. The dyes contain phosphonic acid group which readily undergo esterification reaction in the presence of dicyandiamine and the fixation process involves baking at 200°C for 2-3 min. in acidic conditions. This could be conveniently illustrated by the following equation(17).

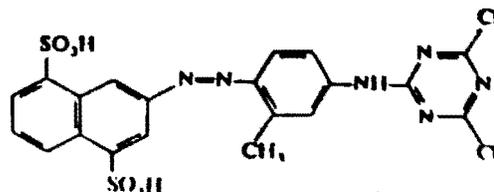


CHROMOGEN IN REACTIVE DYES

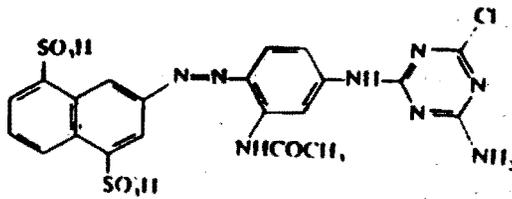
In practice, monoazo, diazo, metallized monoazo, metallized diazo, formazan, anthraquinone, triphenodioxazine, and phthalocyanine chromophores have been used for preparation of reactive dyes(16). However, the chromogen in use are frequently common to various ranges and only the reactive systems varies.

Azo reactive dyes

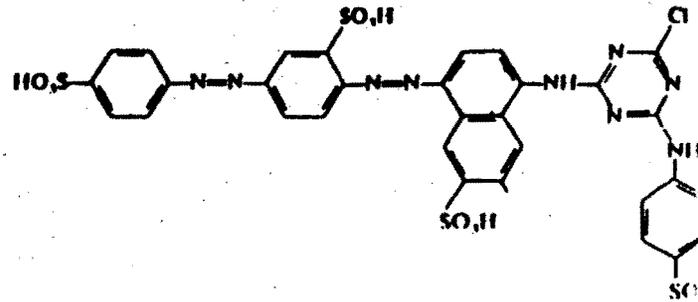
Yellow dyes are usually of simple monoazo type, particularly in the case of greenish yellows. From this chromophore so many dyes could be derived using different couplers and different reactive systems e.g.:



Procion Yellow MX-B; Cl Reactive Yellow 4



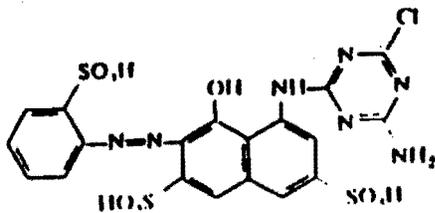
Procion Yellow H-A; CI Reactive Yellow 3



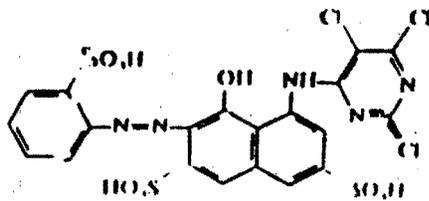
Procion Orange Brown H-G
CI Reactive Brown I

Anthraquinone reactive dyes

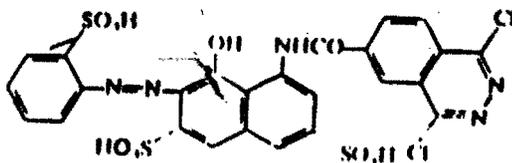
Anthraquinone dyes(16) are second only in the overall importance to azo dyes and the chromogen is commercially known in reactive dyes. The most common structure are derived from bromaminic acid (1-amino-4-bromoanthraquinone-2-sulphonic acid) and, by variation of substituents, give rise to bluish violet to bluish green colours with the reddish to mild blues being the most important. A typical example is the procion blue MX which was launched at the beginning of the reactive dyes era.



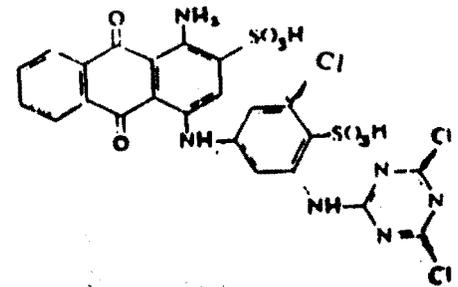
Cibacron Brilliant Red B
CI Reactive red 12



Drimarene Red Z-2B
CI Reactive Red 17



Eltane Brilliant Red B
CI Reactive Red 96

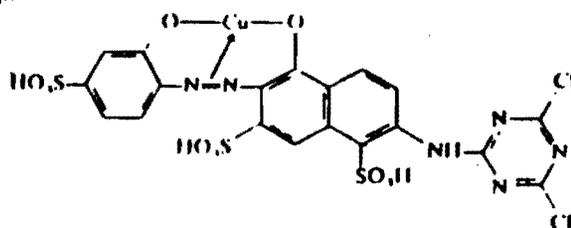


Procion Blue MX-B
CI Reactive Blue 4

Phthalocyanine reactive dyes

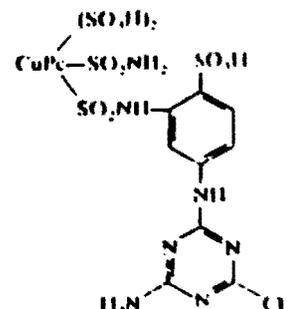
Solubilised phthalocyanine reactive dyes are used for bright turquoise hues, which can not be achieved using either azo or anthraquinone dyes. The most used dye in this group is the copper phthalocyanine of the following structure.

However, the most commonly coupling components used are aminonaphthols which can give hues from orange through black. Monoazo copper metallized reactive dyes are also cited e.g.:



Procion Rubine MX-B
CI Reactive Red 6

Brown hues can also be produced in diazo molecule by using one, two and often three naphthylamine molecules e.g.



Cibacron Turquoise Blue G-E
CI Reactive Blue 7

Triphenodioxazine and formazan reactive dyes

Recently, the domain of the blue reactive dyes has been infiltrated by the introduction of triphenodioxazines and by increased interest in the formazans. Since they offer bright hues are being tinctorially stronger, have marked commercial advantages over anthraquinone. The precise structure have not been officially disclosed and further research is actively going on.

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