Replacement of disperse anthraquinone dyes

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A INTRODUCTION

For some time, dye research has been making intensive efforts to replace anthraquinone (AQ) dyes with technically equivalent and more economical products. Though not yet concluded, this process has reached a point where it seems appropriate to make a critical evaluation of the results achieved to date.

Counterbalancing the well-known relatively low tinctorial strength of the AQ dyes are their unrivalled brilliance in certain red and blue regions and, apart from a few exceptions, their good dyeing properties and high fastness level. From a commercial standpoint, AQ dyes today are still the second most important class of dyes after the azo types [1].

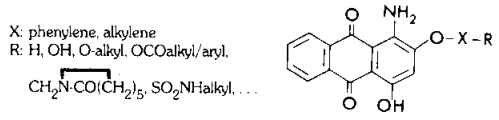
In the following we confine ourselves to research done in the particularly important area of brilliant red and brilliant blue disperse dyes for polyester fibres during the period 1967–1984. For the years 1967–75 use has been made of the comprehensive reviews of Clark, Dawson and Leverenz [2–4]. During the entire time span 1967–84 the patent literature reveals a great number of potential substitution products. In order to provide the reader with a comprehensive view of the major developments during this period, we have selected for the discussion of the chemical constitution classes presented, what is regarded as their representative prototypes.

In each case, following the discussion of the chemistry of non-anthraquinone disperse dyes we present a technical comparison of the most important AQ dyes with selected replacement products, taking into account their dyeing and fastness properties.

B BRILLIANT RED CHROMOPHORES

Anthraquinone dyes

Among the brilliant red AQ dyes, the most important is the 1-amino-4-hydroxy-2-oxy-subst.-anthraquinone type (1)

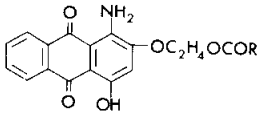


(1)

Depending on the bridge X, the hues range from neutral (alkylene) to bluish red (phenylene). Certain properties such as sublimation fastness and, to a slight extent, levelling characteristics can be varied by the appropriate choice of substituent R.

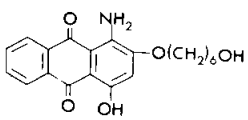
The following red AQ dyes were selected as 'standard' (Red I to VI):

Red I (neutral)

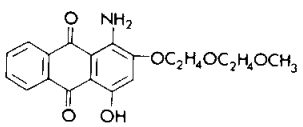


R: C_2H_5, C_6H_5

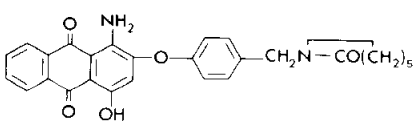
Red II (neutral)



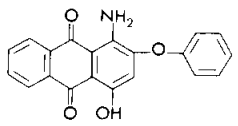
Red III (neutral)



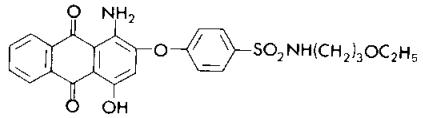
Red IV (bluish)



Red V (bluish)



Red VI (bluish)



This limited selection (Red I to VI) as well as representative examples of dyes from Sections B.1 to B.3 (Red VII to XX) are more closely characterised from a fastness and colorimetric standpoint and comparatively discussed in B.4 (Table 1 and Figure 1).

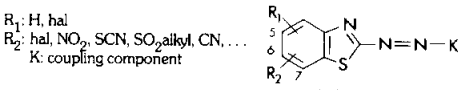
A partial replacement of the very brilliant but tinctorially weak red AQ dyes can be achieved by azo dyes with heterocyclic diazo components (B.1) – and to a lesser extent also with heterocyclic coupling components (B.2) – as well as by other chromophoric systems (B.3). The following discussion will focus on the most important types of structures, some of which have been developed into commercial products, as well as types which have been described in patents only. Included among these are systems which have been known for some time but which have attained new importance in recent patent literature.

B.1 Azo dyes with a heterocyclic diazo component

In addition to the high tinctorial strength generally characteristic of azo dyes, the brilliance of their dyeings can be increased in many cases by replacement of the aniline diazo component (see exception in B.3.1) by a heterocyclic amine. The synthesis and application of heterocyclic diazo components for the preparation of red disperse dyes has been reviewed by Weaver and Shuttleworth [141]. However, the brilliance of the anthraquinones with their narrow spectral absorption bands is attained by only a few heterocyclic-based azo dyes.

B.1.1 2-Amino-(4,5),6,(7)-(di)subst.-benzothiazoles; 4,5-heteroanellated-2-amino-thiazoles

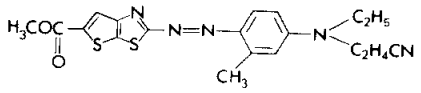
Various substituted benzothiazole-2-azo dyes (2) ranging from scarlet to bluish red have been on the market for some time [2,4] such as Red X, XI and XIV.



(2)

Although the brilliance of the red AQ dyes cannot be attained with benzothiazole components (see B.4, Figure 1), the various commercially established dyes of this type owe their success to their economy and good fastness level. In addition to the 6-nitro, 6-methylsulphonyl and 6-thiocyanate groups [2] and those with one or two halogens in various positions on the benzene ring [4b], substituents such as 4-trifluoromethyl [5], 5-nitro [6] and 5-cyano [7] have appeared in the recent benzothiazole patent literature dominated by Japanese authors. Strongly electron-attracting substituents in the 5-position produce a hypsochromic shift in hue and somewhat higher brilliance than 6-substituted dyes.

A recent Kodak patent application [8] describes the use of a 5-carboalkoxy-thieno-(3,2-d)-2-aminothiazole as a diazo component for orange to bluish-red hues, e.g. dye (3)



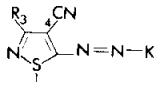
(3)

Thiazoles without an anellated benzene or heteroaryl ring have not attained any technical importance as red dyes to date.

B.1.2 5-Aminoisothiazoles

With 5-amino-4-cyanoisothiazoles as diazo components, brilliant red to violet dyes of the general type (4) [9,10] can be produced, depending on the coupling component K such as Red XVIII.

R: (subst.) alkyl, benzyl or aryl group



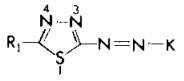
(4)

Dyes of this structure do not quite attain the brightness of AQ dyes (see B.4, Figure 1), and thus far have not been marketed. The economic feasibility of this system is open to question because of the formation of the unstable, so-called 'ortho' product (coupling in the ortho position to the tertiary amino group) which is produced during coupling with aniline coupling components in amounts up to 30% [11]. Nevertheless, numerous BASF patent applications [12] have appeared recently for azo dyes based on various 5-amino-4-cyanoisothiazole diazo components substituted in the 3-position. When isothiazole diazo components are substituted in the 4-position with a halogen [9] or sulphur bridge [13], a distinctly hypsochromic shift of hue occurs with the same coupling components.

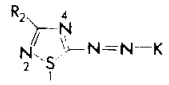
B.1.3 2-Amino-5-subst.-1,3,4-thiadiazoles; 5-amino-3-subst.-1,2,4-thiadiazoles

Aminothiadiazoles were among the first heterocyclic diazo components for disperse dyes to be described in the patent literature [2–4]. Depending on the substituent (R_1, R_2) in the diazo component and the coupler used, brilliant scarlet to bluish red dyes such as Red XV are obtained. These however still do not quite match the brightness of the AQ dyes. In spite of the great number of patent applications for structures with substituents such as aryl [2,3], halogen [4b,14,15], thiocyanato [16], cyano, trichloromethyl [17] and various substituted mercapto groups [4a,18,19], etc., these systems (5) and (6) have fallen short of expectations as far as their commercial exploitation is concerned.

R_1: S-(subst.)alkyl, $S(O)_n$alkyl, phenyl, CF_3, hal, SCN, CO_2alkyl, ...
R_2: (subst.)phenyl, S-(subst.)-alkyl, $S(O)_n$alkyl, CN, CCl_3, ...
n: 1 or 2



(5)



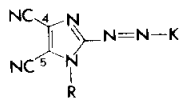
(6)

Among recent Bayer and Kodak patent applications, there are some with more unusual substituents R_1, e.g. substituted cinnamyl groups [20] or the thiocyanomethylene group [21]. Numerous applications of more recent date [22–24], most of them Japanese, with substituted mercapto groups (R_1, R_2) and various couplers testify to the still high interest in the thiadiazole system.

B.1.4 2-Amino-4,5-dicyanoimidazoles

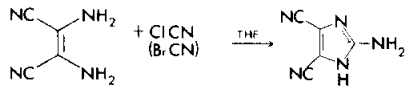
Dyes of structure (7)

R: (subst.) alkyl (e.g. CH_2CN), alkenyl, ...
K: coupling component



(7)

were discovered by du Pont [25] and later intensively investigated by Mitsubishi [26]. These are dyes of high tinctorial strength and very bright ranging from scarlet to bluish red, depending on the substituent R and coupling component K. From a brightness standpoint they practically attain the AQ level, but with cyanomethylene as R constituent they must be regarded as weakly resistant to hydrolysis and to reduction such as e.g. Red XVI. The preparation of this unusual diazo component proceeds according to the following scheme:



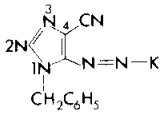
(8) (9)

After diazotisation and coupling, the imidazole ring nitrogen (NH) is alkylated.

A dye of this type been marketed by Mitsubishi.

B.1.5 5-Amino-4-cyano-1,2,3-triazoles

Dyes of the general type (10), based on 5-amino- 4-cyano-1,2,3-triazole such as Red XII are claimed by Sandoz [27]. They reach the level of the AQ dyes with respect to their general fastness properties and are extremely bright, their brilliant red hues being comparable with those of the AQ type.



(10)

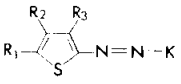
In addition to their excellent resistance to hydrolysis and reduction, also comparable to that of AQ dyes, they exhibit a very high level of light fastness.

B.1.6 Various heterocyclic diazo components

Of relatively low practical value are red dyes which are based upon certain negatively substituted 3-aminopyridines [28], 3-aminopyrazoles [29] and (4)5-aminopyrazoles [30–33] as diazo components.

Contrary to the blue region (see C.1.4), 2-aminothiophenes [34–36] substituted with various acceptor groups are without commercial interest as diazo components for red (violet) dyes of the type (11).

R_1: CO_2alkyl, CN
R_2: (H), alkyl, phenyl
R_3: CN, CO_2alkyl



(11)

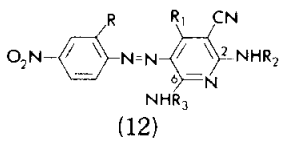
This is evidently due to their inadequate economic value and/or general fastness properties. The same is presumably true of heteroanellated aminothiophenes [37,38].

B.2 Azo dyes with a heterocyclic coupling component

B.2.1 2,6-diamino-3-cyanopyridines

Among the few heterocyclic coupling components in the red region, 2,6-diamino-3-cyanopyridines are the most important. Dyes (12) ranging from yellow to blue have been claimed in the patent literature since the beginning of the 1970s, mostly by BASF [3d,4b]. They have also become commercially important as brilliant reds [39] such as Red IX.

R: NO_2, CN, SO_2alkyl, SO_2aryl, CO_2alkyl, ...
R_1: alkyl, aryl, ...
R_2,R_3: H, (subst.) alkyl, ...



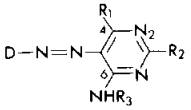
(12)

For such a red, the aniline diazo components must include strongly electron-attracting substituents. With appropriate disazo compounds, dyes ranging even into the navy blue region can be obtained [40]. In addition, 2,6-diaminopyridine coupling components with *N*-alkyl amino groups in the 4-position [41] as well as various substituents such as halogen, nitro, etc. [42,43] in the 3-position have also appeared in the patent literature.

B.2.2 2,4,6-trisubstituted-pyrimidines

Dyes (13) ranging from brilliant yellow to red (blue) are claimed in the patent literature [44,45]. Substituents in the 2- and 4-position of (13) may vary considerably.

R_1: hal, NHalkyl, S-alkyl, O-alkyl, ...
R_2: NH_2, NHalkyl, $N(alkyl)_2$, S-alkyl, aryl, ...
R_3: H, (subst.) alkyl, ...
D: diazo component



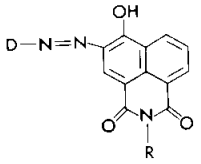
(13)

Here also the diazo component D is either an aniline derivative containing strongly electron-attracting substituents or is a heterocyclic amine, both of which provide a sufficient bathochromic shift of hue.

B.2.3 4-Hydroxynaphthalic acid imides

These brilliant red monoazo dyes (14) primarily investigated by Mitsubishi [46,47] approximate to the AQ level with respect to brightness such as e.g. Red VIII and XIII.

R: (subst.) alkyl, aryl, ...
D: diazo component



(14)

With appropriate disazo compounds as D, even blues can be obtained [48]. Other companies have also patented several modified structures [49]. Thus for example, a 4-aminonaphthalic acid imide substituted with two acceptor groups has been used as the diazo component [50] with which red-violet to blues can be attained.

In this connection it should be mentioned that brilliant scarlets can be obtained with 4-aminoazobenzene as the diazo component and specially substituted 2-hydroxynaphthalene-6-sulphonic amides as the coupling component [51] such as in Red VII.

B.3 Miscellaneous chromophores

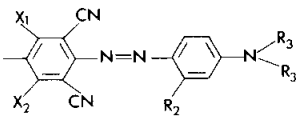
In addition to the commercially important class of azo dyes based on a heterocyclic diazo component (B.1) or – of considerably less importance – a heterocyclic coupling component (B.2), azo dyes which contain an isocyclic diazo component with a special substituent pattern (B.3.1) as well as non-azo chromophores (B.3.2) are also described in the patent literature as potential replacement products for red AQ disperse dyes.

With the exception of the brilliant benzodifuranones (B.3.2) discovered by ICI in the 1970s, and the extremely brilliant yellow to red fluorescent benzothioxanthene dyes (B.3.2) intensively investigated by Hoechst, it is probably true to say that the remaining non-azo chromophores found in the patent literature were not primarily designed as AQ replacement products. They have only attained limited technical importance, at least as textile dyes.

B.3.1 Azo dyes based on 4-subst.-2,6-dicyanoanilines as diazo components

First described at the beginning of the 1970s mainly by Bayer [52] and later also by BASF [53], ICI [54], Cassella [55] and Nippon Kayaku [56], disperse dyes of the general type (15) such as e.g. Red XVII,

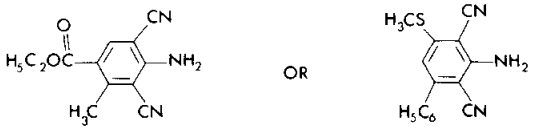
R_1: H, alkyl, hal, hetaryl, ...
R_2: H, alkyl, NHCOalkyl, $NHSO_2$alkyl, OH, ...
R_3: (subst.) alkyl
X_1X_2: H, alkyl, S-alkyl, aryl, ...



(15)

have high tinctorial strength and produce yellowish to bluish reds, depending on the type of the coupling component; they come close to the level of the AQ reds with respect to brightness.

The preparation of this type of dye can be achieved by cyano/halogen exchange [57]. Very recently, specific syntheses for 3-, 4- and 3-, 5-disubstituted-2,6-dicyanoanilines such as (16) or (17) have been described [58].



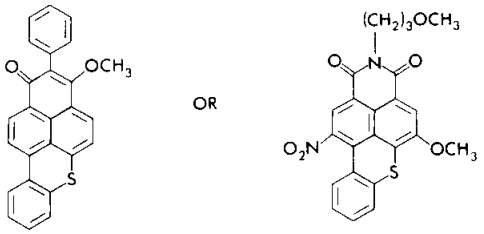
(16) OR (17)

B.3.2 Non-azochromophores

Besides the tricyanostyryl dyes, there are a number of polycyclic or polycondensed aromatic or hetero-aromatic ring systems described in the patent literature which lead to brilliant, often fluorescent red disperse dyes for polyester. As a result of the pigment-like character of some of these types of compounds, their dyeing properties and textile applications are limited; for this reason they can only be partially considered as true AQ replacement products.

The most important representatives are: benzothioxanthenes, coumarins, naphtholactams, triphenodioxazines, benzodifuranones and tricyanostyryls.

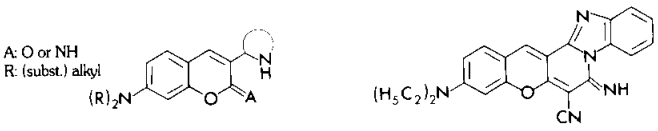
During the 1970s, Hoechst [59] brought out a number of fluorescent, brilliant and light fast yellow-orange benzothioxanthenes as disperse dyes. Through the inclusion of suitable substituents or ring anellation, the colour range can be further extended into the (bluish) red region [60] e.g. (18, 19):



(18) OR (19)

According to BASF [61], fluorescent but only moderately light fast red coumarin derivatives (21) can be obtained by condensation of the fluorescent 3-NH-hetarylcoumarins (20), commercially used as flavine dyes, with e.g. malodinitriles.

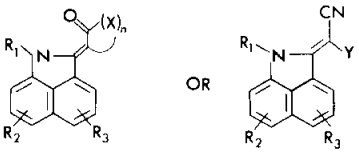
A: O or NH
R: (subst.) alkyl



(20) (21)

Unlike the commercially important cationic blue naphtholactam dyes, nonionic red naphtholactam compounds of the general type (22a, 22b) are claimed in the patent literature by Bayer [62], Ciba-Geigy [63] and particularly by BASF [64].

X: heteroatom
R_1: H, (alkyl), ...
R_2,R_3: H, COOalkyl, S-phenyl, ...
n: 1, 2
Y: heteroaryl

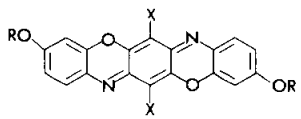


(22a) (22b)

In spite of their brilliance, tinctorial strength and relatively good light fastness, dyes such as Red XIX have remained technically rather unimportant.

The yellow to bluish red triphenodioxazines of type (23) claimed primarily by Mitsubishi [65],

R: (subst.) alkyl
X: hal, CN

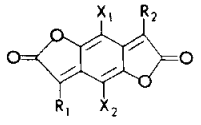


(23)

have not attained technical importance as disperse dyes, in contrast to the brilliant blue, water-soluble triphenodioxazine dyes for cotton [1].

Related to the above chromophoric system are the benzodifuranone dyes of type (24) discovered by ICI in the mid-1970s [66].

R_1, R_2: (subst.) phenyl
X_1, X_2: H, hal

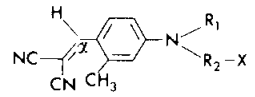


(24)

For a cross-conjugated quinone system, these brilliant red dyes such as Red XX exhibit a surprisingly high photochemical stability on the polyester substrate and a fastness level which is almost comparable with the AQ chromophore in a number of respects.

With the styryl dyes of type (25), which are technically very important as yellow chromophores,

R_1: (subst.) alkyl
R_2: alkylene
X: OCONH-(subst.) phenyl, O-(subst.) phenyl, ...



(25)

a strongly bathochromic shift of hue is observed through the introduction of a cyano group in the α-position. Red tricyano-styryl dyes, described by Ciba-Geigy as early as 1976 [67], have also been claimed quite recently in the patent literature by Sumitomo [68] and Mitsubishi [69].

B.4 Technical and fastness comparisons between the most important brilliant red AQ and selected replacement dyes

See Table 1 for data concerning sections B.4.1 to B.4.3 and Table 2, a summary of all chemical structures discussed.

B.4.1 Colour region, brilliance and tinctorial strength of red AQ disperse dyes and selected replacement products

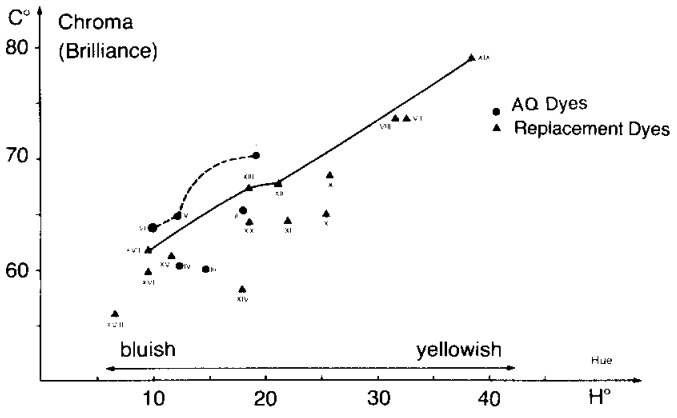


Figure 1 – Hue and chroma brilliance of red disperse dyes in 1/1 standard depth (CIELAB)

In the bluish red region the AQ elements (Red I, V, VI) exhibit distinctly superior brightness to the replacement products. The neutral to yellowish red region, however, is not covered by any AQ dyes known to the authors. Several non-anthraquinone dyes of high brilliance are found in this region (Red VII, VIII, IX, XII, XIX).

From the ε_{mol} values it follows that the replacement products exhibit a considerably higher molar tinctorial strength than the AQ dyes. Unlike the ε_{mol} values, the per cent concentration data for 1/1 standard depth are not a measure of the tinctorial strength, as the dyes are standardised with dispersants in different ratios.

B.4.2 Fastness comparison of AQ and selected replacement dyes
– Light fastness

Many replacement products attain the light fastness values of AQ dyes (xenon lamp 200 h, > 6) and are therefore fully adequate for application in the clothing and furnishing textiles sector. However, the replacement dyes do not yet reach the level of the best AQ products for special requirements such as high temperature light fastness for the automotive textiles sector.

– Sublimation fastness

The AQ disperse reds as well as their replacement products include examples with very low and very high sublimation fastness properties. However, due to the selection, more replacement dyes exhibit high to very high sublimation fastness properties (Red VII, IX, X, XIII, XIV, XVI), while those of the AQ dyes (with the exception of Red VI) are generally lower.

– Sensitivity to hydrolysis

Unlike the generally high stability of red AQ dyes to pH, the chemical stability (to hydrolysis) of certain replacement products (Red XIII, XVI) under HT dyeing conditions (130°C) is marginal (pH < 6).

– Reduction stability

With few exceptions (Red XII, XIX), the replacement products must be applied at approx. pH 5 in order to achieve reproducible dyeings under HT dyeing conditions in the presence of reducing compounds. Almost without exception, only the AQ dyes are stable in the special application sector of discharge printing on polyester (not included in Table 1) where the dye is applied in the presence of e.g. tin salt or zinc formaldehyde sulphoxylate.

– Thermomigration

After heat treatment (e.g. for dimensional stability) the fastness properties of dyeings on polyester may be reduced to a greater or lesser extent. This shows up, for instance, in the form of increased staining of the adjacent fabric in washing tests after thermal treatments. As given in Table 1 under staining of nylon in washfastness tests, among the AQ dyes Red I displays the best (but still unsatisfactory) behaviour in this respect, while replacement products Red XIV, XVI, XVII, XVIII and XIX attain this moderate level. By far the best results after heat treatment are shown by Red XX.

B.4.3 Application properties
– Migration

The migration of a dye helps to cover levelness differences such as are produced, for example, by incorrect temperature control during exhaust dyeing. Generally no major differences exist between the migration properties of the AQ disperse reds and the replacement products. Notable products in this respect are Red III (AQ) and Red XIV (azo).

– Coverage of barré

Temperature differences as well as various draw ratios during the manufacture of the polyester fibre lead to differences in dye uptake during dyeing. The AQ red dyes generally have a lower tendency to show these substrate-related differences than the replacement products. The advantages of the AQ disperse reds (e.g. Red I, III, V) are especially noticeable on polyester fibres with different draw ratios.

–Dyeing at 96°C with carrier

At atmospheric pressure (i.e. at temperatures of 96–99°C) the build-up of many disperse dyes is very limited, even when a carrier is used. Despite this drawback it is often necessary to dye polyester at these temperatures, e.g. in polyester/wool blends. Only few non-anthraquinone red dyes (e.g. Red XVIII) approach the build-up of the most suitable AQ disperse reds (e.g. Red III) at 96°C.

– Adsorption characteristics

Good dye build-up improves the reproducibility and economy of dyeings. For this reason, particularly in exhaust dyeing it is advantageous to select dyes that produce high yields and do not react sensitively to different dyeing conditions with respect to temperature and time. Today such dyes are often designated as 'rapid dyes'; a simple definition of their specific criteria is given in [70]. The high D values characteristic of AQ dyes are not in themselves a sufficient criterion for defining a rapid dye. The key value is the kinetic characteristic Z, for which, as in [70], the limiting value $Z \geqq 16 \times 10^{-5}$ is given. Unlike the AQ dyes, several replacement products in the brilliant red region attain or surpass this limiting value (see Table 1).

TABLE 1

Dye	Type	CIELAB		λ_{max}	ε mol	D value	Z value	1/1 SD	Xenon lamp	Dry heat	Hydrolysis stability	Reduction stability	Thermo-migration	Migration	Coverage of barré	Suitability for dyeing at 96°C with carrier
		H^0	C^*	[nm]	$\left[\frac{1}{Mol.cm}\right]$	$[10^{-10}\ cm^2\ sec^{-1}]$	$[10^{-5}]$	(% o.w.f)	200 h	180°C 210°C	[pH]	[pH]				
Red I	Anthraquinone (AQ)	19.1	70.1	517	14 240	7.3	14.1	4.6	>6	4 2	7	6	3	1–2	T 4 V 3–4	U 4 F 3
Red II	Anthraquinone (AQ)	17.9	65.4	516 552	14 700 13 380	9.1	12.7	5.3	6	4 2	7	7	2	2	T 4 V 3	U 4–5 F 2
Red III	Anthraquinone (AQ)	14.6	60.0	517 554	14 620 13 170	17.3	22.0	4.0	>6	3 1–2	7	7	2–3	3	T 3–4 V 3–4	U 5 F 4–5
Red IV	Anthraquinone (AQ)	12.3	60.3	521	14 100	2.4	6.0	5.2	6	4 2–3	9	7	2–3	1–2	T 2–3 V 2	U 2 F 1–2
Red V	Anthraquinone (AQ)	12.2	64.9	521 556	13 970 12 110	6.2	12.5	1.4	6	2–3 1	9	7	2–3	2	T 4–5 V 3–4	U 4 F 3
Red VI	Anthraquinone (AQ)	9.9	63.8	522 556	13 690 11 760	3.3	7.7	2.7	>6	5 4–5	9	7	2–3	2	T 4–5 V 2	U 3–4 F 1–2
Red VII	Azo (isocyclic)	32.6	73.6	505	28 470	2.6	13.5	1.2	4–5	5 4–5	7	5	2–3	1–2	T 4 V 1–2	U 3 F 2
Red VIII	Azo (heterocyclic CC)	31.7	73.4	519	24 600	2.2	11.9	1.8	>6	4–5 2–3	7	5	2–3	1–2	T 4–5 V 2–3	U 4 F 2
Red IX	Azo (heterocyclic CC)	25.8	68.4	520	49 340	1.8	9.7	1.3	>6	5 4–5	7	5	2–3	2	T 3–4 V 2–3	U 3–4 F 2–3
Red X	Azo (heterocyclic DC)	25.4	64.9	524	52 670	1.6	5.1	2.9	6	4–5 4	7	5	2–3	2	T 2 V 2	U 2–3 F 2
Red XI	Azo (heterocyclic DC)	22.0	64.3	532	51 665	1.7	13.0	1.2	5	3–4 2–3	7	5	2–3	1–2	T 3 V 2	U 2–3 F 1–2
Red XII	Azo (heterocyclic DC)	21.1	67.8	536	48 050	2.1	10.1	1.3	>6	4 2–3	9	7	2–3	1–2	T 3 V 2	U 3 F 2
Red XIII	Azo (heterocyclic CC)	18.5	67.3	530	29 850	1.4	4.5	1.9	>6	5 4	5	5	2	1	T 3 V 2	U 3 F 1
Red XIV	Azo (heterocyclic DC)	18.0	58.2	531	50 900	3.0	21.2	0.9	>6	5 4	7	<5	3	2–3	T 3–4 V 2	U 4 F 2–3
Red XV	Azo (heterocyclic DC)	11.6	61.3	533	55 390	2.7	20.3	1.0	5–6	3 1–2	7	6	2	1–2	T 3 V 2	U 4 F 1–2
Red XVI	Azo (heterocyclic DC)	9.6	59.8	531	51 500	0.6	3.5	1.3	>6	4–5 3–4	5	5	3	1–2	T 1–2 V 1	U 2 F 1
Red XVII	Azo (isocyclic)	9.5	61.8	527	42 120	2.0	20.7	0.8	>6	4–5 2–3	9	6	3	1	T 1–2 V 1	U 3–4 F 1–2
Red XVIII	Azo (heterocyclic DC)	6.6	55.9	539	48 200	2.0	25.0	0.8	>6	4–5 2–3	7	5	3	1–2	T 3 V 2–3	U 4–5 F 3–4
Red XIX	Naphtholactam	38.3	79.0	472 500	23 580 24 390	1.3	4.4	1.8	5	4 3	7	7	3	1	T 3 V 3	U 2 F 1
Red XX	Benzodifuranone	18.5	64.3	502	46 000	1.5	3.9	3.8	6	4 2	7	6	4	1	T 2–3 V 2	U 1 F 1

Footnotes to Tables 1 and 3

DC : diazo component
CC : coupling component

CIELAB
Cylinder coordinates H° (Hue) and C* (Chroma) as defined by the 'Commission Internationale de l'Eclairage' (CIE) and specified in CIE Publication 15.2. The term 'chroma' is equivalent to the better known expression 'brilliance'.

λ_{max}
Wave length of the absorption maximum in dimethylformamide + 1% glacial acetic acid. With dyes which exhibit two maxima, both values are given.

ε_{mol}
Molar extinction coefficient at λ_{max}.

D value
The diffusion coefficient D ($cm^2.sec^{-1}$) is assessed according to the method described by M Hammoudeh et al. [139]. A polyester film is rolled up on a glass rod and dyed for several hours at 130°C. The calculation of D is based on the concentration profile of the polyester film layers.

Z value
The kinetic value Z is a dimensionless parameter according to the kinetic study described by J Cegarra et al. [140]. It is defined as

$$Z = \frac{C^0}{RTT} \cdot \sqrt{D \cdot k} \quad \text{where}$$

C^0 corresponds to the indefinite concentration C_∞ obtained by extrapolation from the diffusion curve
RTT corresponds to the dyestuff concentration required to obtain standard depth (ISO Standard)
D is the diffusion coefficient
k $= 1\ cm^{-1}.sec\ 1/2$

1/1 Standard Depth (SD)
Determined according to method given in Textilveredlung, **20,** No 7/8, (1985) 244.

o.w.f.: on weight of fibre
Xenon lamp: ISO 105 B02
Dry heat: ISO 105 P01

Sensitivity to hydrolysis
Dyeings prepared at different pH values at 130°C are compared with one another and the highest pH value is given at which a change of colour and depth is still not yet visible.

Reduction stability
The dyeings are prepared as for determining sensitivity to hydrolysis, but in the presence of a reducing agent (glucose).

Thermomigration
A dyeing is prepared in 3 × 1/1 standard depth on texturised polyester woven fabric (130°C for 60 min), followed by a reduction clearing treatment. Afterwards the dyeing is given a fixation treatment for 30 s at 180°C.

Fastness test: Domestic Laundering CIS, 60°C, ISO 105 C06.
Assessment is made of the staining of polyamide adjacent fibre in a multifibre test strip using the Grey Scale.

Migration
Treat a polyester 1/1 standard depth along with an equal portion of undyed material at 130°C for 60 min. Evaluate the change of colour between the two materials using the Grey Scale (ratings 1 to 5).

Coverage of barré
This test is divided into two parts. The physical characteristic values of the test materials are described in Textilveredlung, **7** No. 8 (1972), 427–483. Polyester materials with different draw ratios (1 : 3.20 and 1 : 3.66) or preset at different temperatures (180°C and 205°C) are dyed in each case in the same bath at 130°C for 60 min and the change of colour assessed according to the Grey Scale.

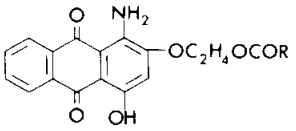
Suitability for dyeing at 96°C with carrier
Unset (U) and preset (S) spun polyester fabric is dyed at 96°C in the presence of a normal commercial carrier for 60 min and the change in colour compared with a dyeing prepared on unset spun polyester fabric (130°C without carrier) is assessed according to the Grey Scale.

(1) in 1/1 SD
(2) main component

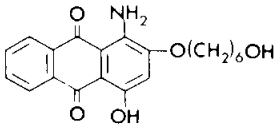
TABLE 2

Structures of red dyes

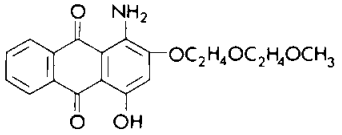
Red I
CGY; NSK
Japan P 14297 (1962)



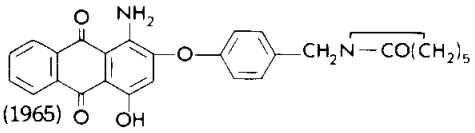
Red II
BASF
German P 1209680 (1962)



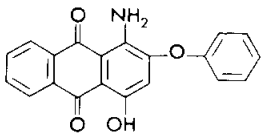
Red III
S
German P 1083960 (1955)



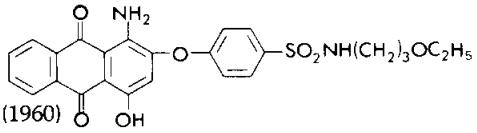
Red IV
BAY
German P 1644595 (1965)



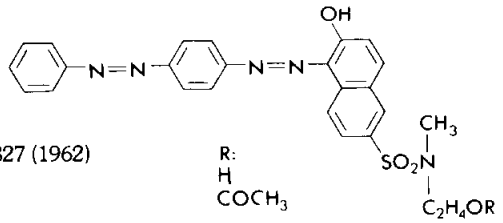
Red V



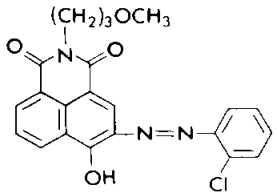
Red VI
BASF
German P 1271284 (1960)



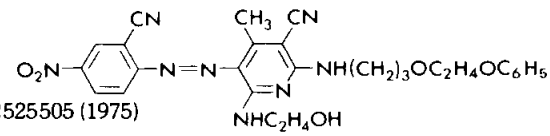
Red VII
Geigy
German P 1252827 (1962)



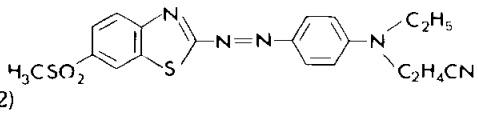
Red VIII
KYK
Japan P 60018776 (1973)



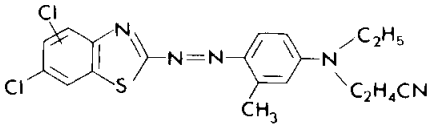
Red IX
BASF
German P 2525505 (1975)



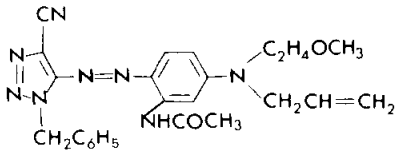
Red X
Kodak
USP2785157 (1952)



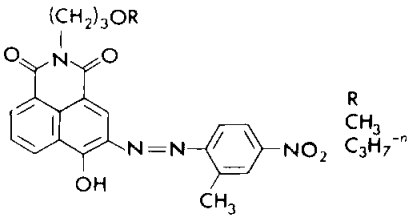
Red XI
Martin Marietta
USP3 502645 (1968)



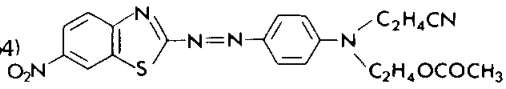
Red XII
S
German P 2856873 (1978)



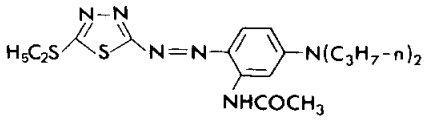
Red XIII
MCI
Japan P 49090327 (1972)



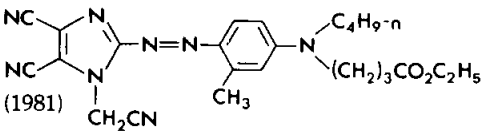
Red XIV
Interchem Corp
BP 813906 (1954)



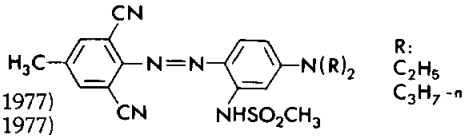
Red XV
Kodak
USP 3657215 (1972)



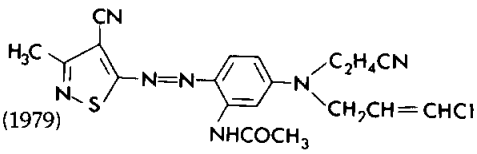
Red XVI
MCI
Japan P 58029859 (1981)



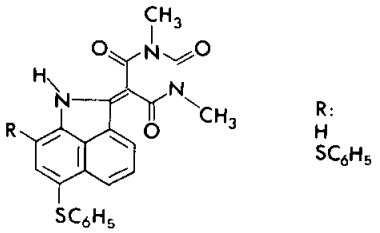
Red XVII
BAY
German P 2711130 (1977)
German P 2739842 (1977)



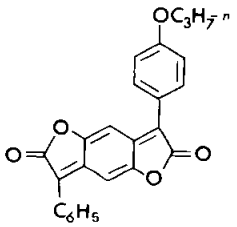
Red XVIII
S
German P 3001945 (1979)



Red XIX
BASF
German P 2428198 (1974)



Red XX
ICI
BP 2068402 (1980)



C. BRILLIANT BLUE CHROMOPHORES

Until about 1970, AQ dyes were the only types available for dyeing polyester to brilliant blues. Up till then the bathochromic region could only be covered with dull yet tinctorially strong blue compounds such as navy blue azo dyes based on 2,4-dinitro-6-haloanilines as diazo components and suitably substituted anilines as coupling components [71].

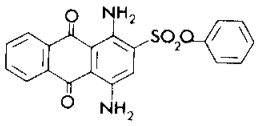
In the intervening period, novel combinations of substituents in aniline diazo components ('cyano/sulphinate exchange', see C.1.1) and the commercialisation of new heterocyclic diazo components (see C.1.2 to C.1.4), especially the thiophenes, have led to blue azo dyes. In a comprehensive review by Weaver and Shuttleworth [141] the use of the most heterocyclic diazo components for the preparation of (blue) disperse dyes has been described. With the exception of extremely reddish blues and turquoises, these azo dyes definitely attain the brilliance of the AQ dyes. However, only in the case of the polymethine chromophore Blue XX (C.3) can there be considered a substantial increase in brilliance on the part of these AQ replacement products.

As a result, the search for non-anthraquinone neutral to strongly greenish blue disperse dyes continues to be the object of intensive research efforts [72–74].

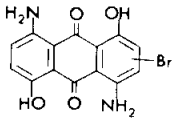
Anthraquinone dyes

The 'standard' AQ types selected for comparison purposes cover the reddish to greenish blue region with the following members (Blue I to VI):

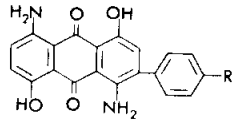
Blue I (reddish)



Blue II (neutral)

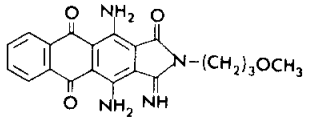


Blue III (neutral)

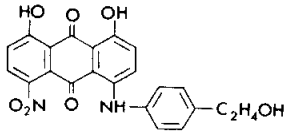


R: OH, OCH_3

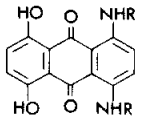
Blue IV (turquoise)



Blue V (greenish)



Blue VI (greenish)



R: CH_3, C_2H_4OH

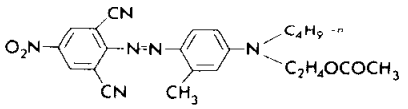
This limited group (Blue I to VI), together with the selected examples of dyes in Section C.1 to C.3 (Blue VII to XX) will be more closely analysed from the colour, physical properties and fastness standpoints (Figure 2, Table 3) and also comparatively discussed in section C.4.

C.1 Azo dyes with isocyclic and heterocyclic diazo components

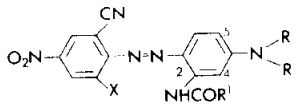
C.1.1 Aniline diazo components

The exceptional brightness of the reddish Blue I has not been attained by any dye based on azobenzene, even with types such as Blue VII

Blue VII (reddish)



However, since 1970 the neutral blue anthraquinone dyes such as Blue II or Blue III have been increasingly displaced by azobenzene derivatives which are similar in colour and in certain respects technically equivalent, tinctorially strong and therefore commercially interesting. These dyes are of the general type (26), examples of which are Blue XI, XIV, XVII and XV:



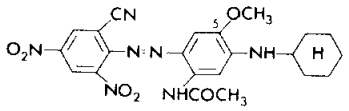
(26)

	X	R	R'
Blue XI (reddish)	Br	C_2H_5	C_2H_5
Blue XIV (neutral)	NO_2	C_2H_5	CH_3
Blue XVII (neutral)	CN	C_2H_5/C_3H_7-n	CH_3
Blue XV (neutral)	SO_2CH_3	C_2H_5	CH_3

Compared with the distinctly redder Blue XI, the neutral Blues XIV, XVII and XV are more elaborate from a synthetic standpoint (substituent X = halogen vs cyano with Blue XIV and XVII; halogen vs methylsulphonyl with Blue XV). Nevertheless, along with the AQ specialities, these 'conventional' isocyclic azo structures still dominate the neutral blue region. Recent patent activities claiming minor structural modifications in the 4-dialkylamino or 2-acylamino group [75] or the extension to toluidine/cresidine coupling component mixtures [76] confirm the still considerable importance of these azo types.

5-Alkoxy derivatives such as Blue XVIII investigated by Kodak [77] exhibit a considerable bathochromic shift of hue:

Blue XVIII (greenish)



Dyeings of Blue XVIII on polyester are comparable in hue with the greenish but somewhat dull AQ Blue VI (mixture). However, in this colour region and with respect to the shading possibilities for bright green tones, the thiophene-2-azo Blue XIX (see C.1.4) is still superior.

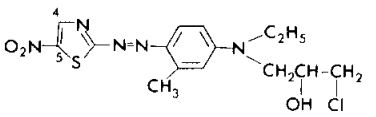
Finally, a recent patent application claims the use of 2,4-dinitro-5-thiocyanatoaniline as the diazo component in the preparation of strongly bathochromic absorbing azo dyes [78].

C.1.2 2-Aminothiazoles

For practical purposes thiazole-2-azo dyes are classified according to their acceptor groups in the 5-position of the thiazole ring; 4,5-heteroanellated dyes form a secondary group.

Beginning in 1954 [79], 5-nitrothiazole-2-azo dyes such as Blue VIII

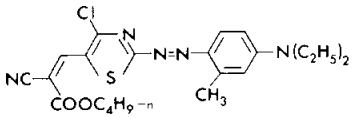
Blue VIII (reddish)



were the subject of numerous patent applications. Since 1980 a further 20 applications have appeared in which selected structures are claimed mainly for application in transfer printing and particularly as discharge printing dyes. These reddish to royal blue dyes with hydrogen or methyl in the 4-position of the thiazole ring do not attain anywhere near the brightness standard of the AQ structures Blue I to III. On the other hand, 4-phenyl-5-nitro or 4-chloro-5-nitro analogues, the latter being of interest from a shade point of view but difficult to synthesise, do not come up to the technical requirements [80]. 5-nitrothiazole-2-azo dyes are generally characterised by high tinctorial strength but above average sensitivity to pH and reduction.

5-Formylthiazole-2-azo dyes [81,82] do not produce bright blue dyeings on polyester until after condensation with methylene-active compounds such as malodinitrile or cyanoacetic esters. The dyeings then attain or even surpass the brightness level of AQ Blue II or Blue III, as e.g. Blue XIII:

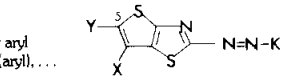
Blue XIII (neutral)



However, the Achilles' heel of these 'azomethine' structures of the Blue XIII type is primarily their lack of chemical stability under high temperature dyeing conditions (reverse Knoevenagel condensation to the aldehyde precursor).

5-arylazothiazole-2-azo dyes, especially 5-subst. phenylazo derivatives, were patented in 1976 [83] but have not yet achieved technical success. In addition, 4-(thienyl-2') substituted analogues were published in 1981 [84].

After 1975, thieno(2,3-d)thiazole-2-azo dyes of the general formula(27)



X: H, (subst.) alkyl oder aryl
Y: NO_2, CN, SO_2alkyl (aryl), ...

(27)

have supplemented the thiazole sector as a chromophore for blue dyes [85], followed by the 5-nitroderivatives [86] and bisazo dyes with isocyclic or heterocyclic aryl azo groups in the 5-position [87]. Structures of this type have not yet found commercial application.

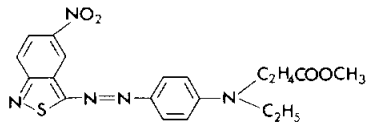
With the exception of the 5-nitroderivatives for discharge printing or dyeing acetate fibres, thiazole-2-azo dyes have so far achieved only secondary importance as bright blue dyes for polyester.

C.1.3 Anellated 3-aminoisothiazoles

Depending on the substituents and/or hetero-atoms in the fused ring, the isocyclic or heterocyclic anellation of the isothiazole produces strongly bathochromic shifts in the corresponding azo dyes.

Dyes of the benzoisothiazole series, developed by BASF since 1965, have become technically important, particularly 5-nitro-2,1-benzoisothiazole-3-azo dyes, e.g. Blue XII [88]:

Blue XII (reddish)

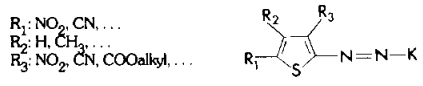


Azo dyes based on 3-amino-5-nitro-2,1-benzoisothiazole, in some cases additionally substituted with halogen, cyano, nitro, alkylsulphonyl, alkyl or alkoxy groups, have been the subject of a considerable number of dye patents up to the present [89]. The hue of these dyes can be readily varied from reddish to strongly greenish; however, the brightness of the dyeings is only average.

Isothiazolo(3,4-d)pyrimidine [90], isothiazolo(3,4-b)pyridine [91] or isothiazolo(3,4-d)pyridine [92] and finally thieno(3,2-c)isothiazole azo dyes [93] are newer variations involving more complicated syntheses. As a rule, the preparation of the corresponding diazo compounds is based on the oxidative ring closure of (hetero)aromatic thioamides with an amino group in the ortho position.

C.1.4 2-Aminothiophenes

Disperse dyes based on suitably di-(or tri-)substituted 2-aminothiophenes were comprehensively patented in 1972 primarily by ICI [94], but also by Kodak [95], Sandoz [96] and Gewald [97]:



R_1: NO_2, CN, ...
R_2: H, CH_3, ...
R_3: NO_2, CN, COOalkyl, ...

(28)

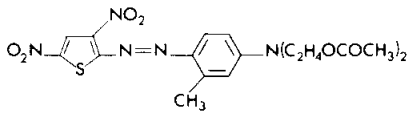
Although blue 3-nitro-5-acetylthiophene-2-azo dyes were already described in 1958 [98], this type (28) was again taken up from 1979 onwards [99] and expanded to include fluorinated 5-acyl [100], 5-methylsulphonyl [101], 5-(substituted)benzoyl [102] and finally 5-cinnamoyl groups [103].

Recently 2-aminothiophenes with carboxyl functions in the 4- and 5-positions including anellation to 4,5-dicarboximides [104] have also been patented as diazo components for (blue) dyes. During the same period patent applications have also been filed for blue 3,5-(difluorosulphonyl) [105] as well as 5-heteroarylthiophene-2-azo dyes [106].

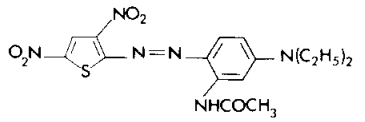
As described in the thiazole series (see C.1.2), for practical purposes blue thiophene-2-azo dyes are characterised according to various acceptor groups in the 5-position of the thiophene ring. For blues the 3-position must also bear a negative substituent (nitro-, cyano-, carboalkoxy-, etc.).

5-Nitrothiophene-2-azo dyes, as the most important class of this type to date, are represented by the two ICI-patented 3,5-dinitrothiophene derivatives Blue XVI [107] and Blue XIX [108]:

Blue XVI (neutral)



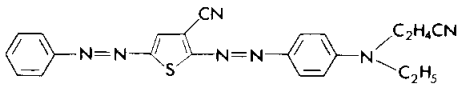
Blue XIX (greenish)



The extremely greenish blue of Blue XIX has so far not been attained by the AQ dye Blue VI or the azo benzene derivatives such as Blue XVIII (C.1.1) or other heterocyclic azo dyes (C.1.2 to C.1.4). This was undoubtedly the motive for renewed patent activities mainly on the part of Japanese dye manufacturers in the area of the 3,5-dinitrothiophene-2-azo dyes [109,110,111], and also in the field of 3-cyano-5-nitrothiophene-2-azo dyes [112,113].

5-Formylthiophene-2-azo dyes with hydrogen, alkyl or aryl in the 4-position were patented by ICI in 1977 [114]. It was not until six or seven years later that the condensation products were claimed [115], in which the aldehyde group was modified analogously to Blue XIII (see thiazoles C.1.2). A recent patent application describes the diazotisation of 3-negatively substituted-2-amino-5-formylthiophenes coupled to 2-*N,N*-dialkylamino-4-arylthiazoles [116]. Finally, 4-chloro-5-formyl(cyano)thiophene-2-azo dyes including derivatives of the aldehyde as blue chromophores have been described [117]. The substituent in the 3-position of the 5-formylthiophenediazo components is preferably cyano. This also applies to the following class of the 5-arylazothiophenes.

5-Phenylazothiophene-2-azo dyes such as the reddish navy blue of the structure (29)



(29)

have been intensively patented in Japan [118] since 1980 (approx. 30 applications). This 'renaissance' of 5-(substituted)-phenylazothiophene-2-azo dyes and their intermediates is somewhat surprising, considering the thiophene patent literature of the years 1972–73 [94–97] and especially in view of the relevant basic dye patent of Bayer [119]. The novel feature of the newer patents is merely the definition of various heteroaryl azo groups such as pyridyl-3, (benzo)thiazolyl-2 or 1,3,4-thiadiazolyl-2 [120]. The preparation of 2-amino-5-(2'-thienylazo)thiophenes as diazo components was published quite recently [121]. Alkylsulphonyl groups [122] and a wide variation of the carbonamide function [123] in the 3-position of these thiophene-bisazo dyes have also been claimed.

C.2 Azo dyes with heterocyclic coupling components

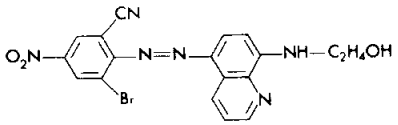
Until now, heterocycles have rarely been encountered as coupling components for blue disperse dyes. Over the past ten years, three

main classes of compounds have been described in the patent literature. With selected diazo components (isocycles and/or heterocycles), they can be converted into reddish to greenish blue azo dyes.

C.2.1 8-(N-alkylamino)quinolines

Coupling components based on 8-(*N*-alkylamino)quinolines have been patented in combination with isocyclic diazo components [124,125], such as Blue IX [124]

Blue IX (reddish)



and also extended to 5-nitrothiazole- and 3-cyano(nitro)-5-nitrothiophene-2-azo dyes [126]. No commercial dyes of this type are known.

C.2.2 2-Aminothiazoles

Coupling components based preferably on 2-*N*,*N*-dialkylamino-4-arylthiazoles have attained technical importance as terminal coupling components for blue bisazo dyes for polyester/cellulose blended fabrics [127]. Monoazo dyes with heterocyclic [128] and isocyclic [129] diazo components have also been patented, especially those based upon 2,4-dinitro-6-cyano(halo)anilines as diazo components [131]. Finally, heterocyclic groups have been introduced into the 4-position of the thiazole coupling components [130].

C.2.3 2-Aminothiophenes

2-*N*,*N*-dialkylaminothiophenes with various substituents in the 3-position and occasionally alkyl or phenyl groups in the 4-position, coupled with isocyclic as well as heterocyclic diazo components, are claimed in recent Japanese patent applications [132]. These compounds were already disclosed by BASF in 1977 as terminal coupling components of bisazo dyes [133]. However, 2-aminothiophene coupling components have to date remained technically unimportant.

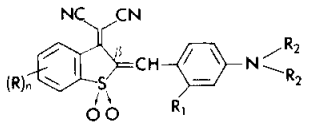
C.3 Miscellaneous chromophores

Unlike the non-azo red chromophores of various types described in section B.3.2, only the class of the modified styryl dyes (C.3.1) has attained any technical significance as blue disperse dyes besides the AQ types.

C.3.1 Modified styryl dyes

The styryl dyes of the general type (30) were discovered by Sandoz [134] at the end of the 1970s:

R: alkyl, alkoxy, hal, . . .
R_1: H, alkyl, . . .
R_2: (subst.)alkyl
n: 0, 1, 2



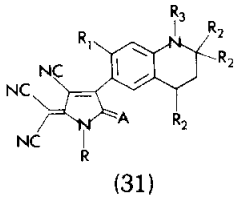
(30)

The formal replacement of the two cyano groups in the β-position of the technically important yellow chromophore (styryl dyes) with the novel 3-dicyanovinylidene-2,3-dihydrobenzothiophene-1,1-dioxide ring produces a drastic bathochromic shift (ca 450 nm → 600–630 nm).

The reddish to greenish blue dyes of this structure are distinguished by their high tinctorial strength and hitherto unattained brilliance such as Blue XX. Variations of the above chromophoric system were later claimed by Sumitomo [135].

Further variations are represented by the blue pyrrole dyes recently described by Sumitomo [136] of general type (31)

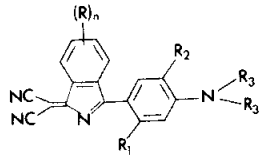
R: H, (subst.) alkyl, . . .
R_1: H, alkyl, NHCOalkyl, . . .
R_2: H, alkyl
R_3: (subst.) alkyl
A: O, S



(31)

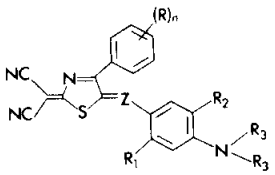
and the isoindole [137] and thiazole [138] dyes of types (32) and (33) primarily claimed by BASF.

R: alkyl, alkoxy, hal, . . .
R_1: H, alkyl, NHCOalkyl, . . .
R_2: H, alkoxy
R_3: (subst.) alkyl
n: 0, 1, 2



(32)

Z: CH, N



(33)

C.4 Technical and fastness comparisons between the most important brilliant blue AQ and selected replacement dyes

See Table 3 for data concerning sections C.4.1 to C.4.3 and Table 4, a summary of all chemical structures discussed.

C.4.1 Colour region, brilliance and tinctorial strength of blue AQ disperse dyes and selected replacement products

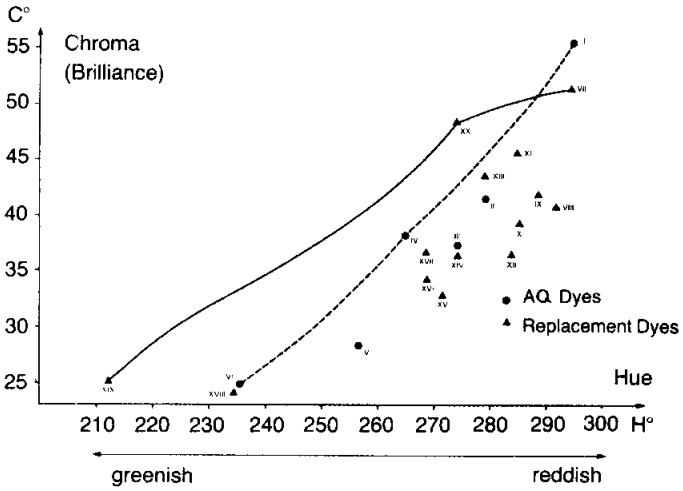


Figure 2 – Hue and chroma (brilliance) of blue disperse dyes in 1/1 standard depth (CIELAB)

Over a wide region the two non-anthraquinone dyes Blue XIX and XX and their mixtures surpass all known AQ disperse blues in brilliance. However, both replacement products exhibit only moderate light fastness and therefore cannot be used for many applications. With higher light fastness requirements the AQ Blues I and IV still produce the most brilliant dyeings. In the neutral blue region, on the other hand, the important AQ Blues II and III are equalled or surpassed in brilliance by the non-anthraquinone dyes Blue XIII, XIV and XVII.

Compared with the AQ blues, the replacement products exhibit considerably higher molar tinctorial strengths.

C.4.2 Fastness comparison of AQ and selected replacement dyes

– Light fastness

Certain replacement products (Blue VII, XIV, XV and XVII) attain the light fastness values of the best AQ dyes and are therefore fully adequate for application in the clothing and furnishing textiles sector.

However, as in the brilliant red region, replacement dyes do not reach the level of the AQ derivatives with respect to high temperature light fastness which is decisive in the automotive textiles sector; here dyes of the type Blue IV and V are mostly used.

– Sublimation fastness

Blue dyes of high sublimation fastness are found equally among the

TABLE 3

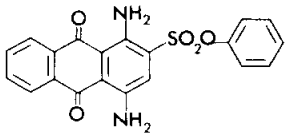
Dye	Type	CIELAB		λ_{max}	ε mol	D value	Z value	1/1 SD	Xenon lamp	Dry heat	Hydrolysis stability	Reduction stability	Thermo-migration	Migration	Coverage of barré	Suitability for dyeing at 96°C with carrier
		H^0	C^*	[nm]	$\left[\frac{1}{\text{Mol.cm}}\right]$	$[10^{-10}\ \text{cm}^2\ \text{sec}^{-1}]$	$[10^{-5}]$	(% o.w.f)	200 h	180°C 210°C	[pH]	[pH]				
Blue I	Anthraquinone (AQ)	294.5	55.4	589	11 950	3.7	12.4	2.8	6	3-4 2	7	6	2-3	1-2	T 4 V 1-2	U 4 F 2-3
Blue II	Anthraquinone (AQ)	279.3	41.5	636 594	23 540 19 610	4.7	20.4	1.9	>6	2-3 1-2	7	7	2	2	T 4-5 V 3-4	U 4-5 F 3
Blue III	Anthraquinone (AQ)	274.4	36.6	639 595	26 800 21 800	2.3	14.0	2.3	6	5 3-4	7	7	1-2	2	T 4 V 2	U 4-5 F 3
Blue IV	Anthraquinone (AQ)	264.6	38.2	659 674	16 700 14 900	4.3	4.7	10.7	>6	3 2	7	7	2[1]	2	T 4-5 V 2	U 2-3 F 2
Blue V	Anthraquinone (AQ)	256.3	28.3	615[2]	12 090[2]	1.7	8.2	4.7	>6	4-5 3-4	6	6	2	2	T 3 V 2	U 3-4 F 1-2
Blue VI	Anthraquinone (AQ)	235.3	24.8	677 622	34 200 22 600	3.4	2.8	5.3	3-4	3-4 2	7	7	1	3-4	T 3-4 V 2-3	U 3 F 1-2
Blue VII	Azo (isocyclic)	294.3	51.3	600	50 100	2.0	33.0	0.7	>6	4-5 3	7	5	3	1	T 2 V 1-2	U 2-3 F 2
Blue VIII	Azo (heterocyclic DC)	291.7	40.7	607	59 300	4.9	9.4	3.0	5	4 2-3	5	5	2-3	2	T 2-3 V 2	U 4 F 2
Blue IX	Azo (heterocyclic CC)	288.5	41.8	600	37 570			1.7	4-5	5 3-4	6	<5	2	2	T 2-3 V 2-3	U 3-4 F 2
Blue X	Azo (isocyclic)	285.2	39.1	592	44 250	1.1	4.8	1.1	5-6	5 4-5	6	<5	2	2	T 3-4 V 1-2	U 4-5 F 1-2
Blue XI	Azo (isocyclic)	285.1	45.5	591	48 700	1.5	13.4	0.6	5-6	4 2	7	5	2-3	1-2	T 4 V 1-2	U 3 F 2
Blue XII	Azo (heterocyclic DC)	283.8	36.3	603	43 490	2.6	47.1	0.7	5-6	4-5 2-3	7	5	3	1-2	T 2 V 2	U 2 F 1-2
Blue XIII	Azo (heterocyclic DC)	277.4	43.4	650	62 760	1.2	4.3	0.8	5-6	3 1-2	5	5	2-3	1	T 4 V 1-2	U 3-4 F 1
Blue XIV	Azo (isocyclic)	274.5	36.4	613	64 890	1.1	12.9	1.0	>6	4-5 2-3	6	5	3	1	T 3-4 V 2	U 4-5 F 3
Blue XV	Azo (isocyclic)	271.4	32.7	617	70 190			1.2	>6	5 4	5	<5	2	1-2	T 2-3 V 1	U 3-4 F 1
Blue XVI	Azo (heterocyclic DC)	268.9	34.2	647	56 400	2.3	16.0	1.5	5	5 3-4	5	5	3	2-3	T 3-4 V 2	U 4-5 F 2
Blue XVII	Azo (isocyclic)	268.6	36.3	619	75 100	1.0	11.8	0.9	6	4 2-3	7	5	2-3	1	T 2 V 1-2	U 3-4 F 2-3
Blue XVIII	Azo (isocyclic)	235.0	24.6	625	84 260	0.9	13.7	1.1	5-6	4 2	7	<5	2	1	T 2 V 1	U 2 F 1-2
Blue XIX	Azo (heterocyclic DC)	212.2	25.1	644	87 400	1.7	7.6	2.1	4	4-5 2	6	5	2	1	T 4-5 V 3	U 5 F 4
Blue XX	modif. Styryl	274.1	48.4	619	59 200	1.1	2.3	2.8	3	4 2	6	5	3	1	T 2-3 V 2	U 1 F 1

(1) in 1/1 SD
(2) main component

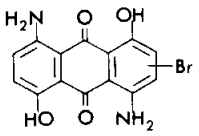
TABLE 4

Structures of blue dyes

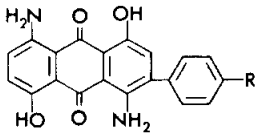
Blue I
BAY
German P 1644587 (1965)



Blue II
BAY
German P 1029506 (1955)

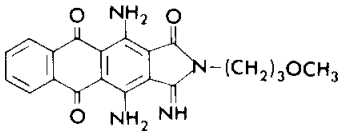


Blue III
S
German P 1144578 (1958)

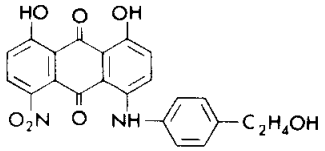


R: OH
OCH_3

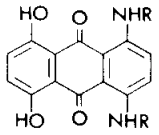
Blue IV
BASF
German P 1918696 (1969)



Blue V
Kodak
USP 2641602 (1950)

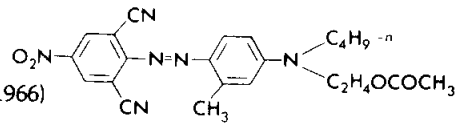


Blue VI
ICI
B105987, S161 (IC 1931)

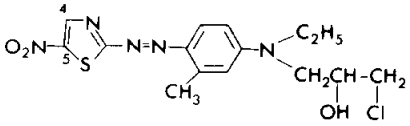


R: CH_3
C_2H_4OH

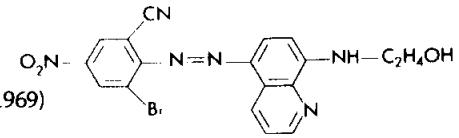
Blue VII
BAY
German P 1644777 (1966)



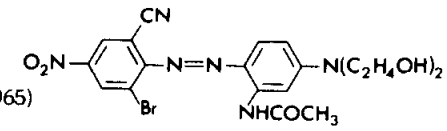
Blue VIII
ICI
BP 840903 (1958)



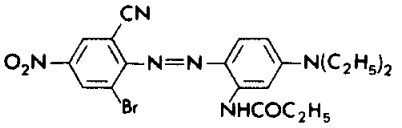
Blue IX
HOE
German P 1929573 (1969)



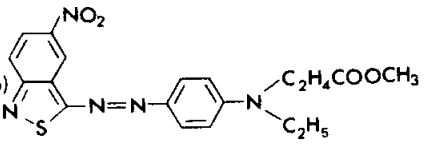
Blue X
BASF
German P 1544373 (1965)



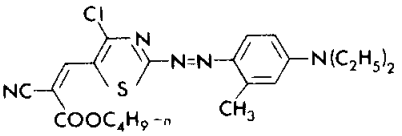
Blue XI
S
German P 1248190 (1963)



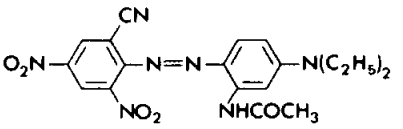
Blue XII
BASF
German P 1544375 (1965)



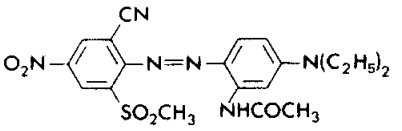
Blue XIII
S
German P 3108077 (1980)



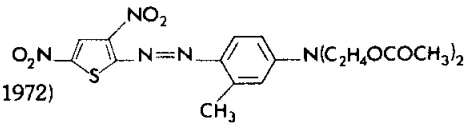
Blue XIV
Kuhlmann
French P 1458333 (1965)



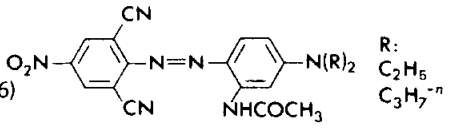
Blue XV
CFM
German P 1719066 (1968)



Blue XVI
ICI
German P 2304202 (1972)

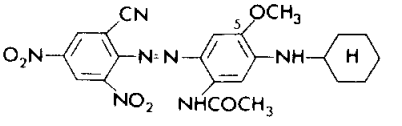


Blue XVII
BAY
Belgian P 694264 (1966)

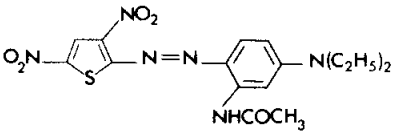


R:
C_2H_5
C_3H_7-n

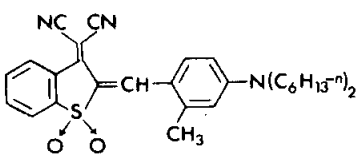
Blue XVIII
Kodak
German P 2341109 (1972)



Blue XIX
ICI
German P 2304218 (1972)



Blue XX
S
German P 2929001 (1978)



AQ derivatives (Blue III and V) and the replacement products (Blue X, XV and XVI).

– *Sensitivity to hydrolysis*

While practically all AQ blue dyes are stable over a wide pH range, for many of the replacement products it is essential to maintain a pH of approx. 5 under HT dyeing conditions in order to achieve reproducibility. However, pH-stable dyes can be found among the replacement products (Blue VII, XI, XII, XVII and XVIII).

– *Reduction stability*

Unlike the situation with the brilliant red products, all the blue non-anthraquinone replacement dyes, without exception, must be applied at pH 5 in order to achieve reproducible dyeings under HT dyeing conditions in the presence of reducing substances. It goes without saying that only AQ compounds are stable in the special application sector of discharge printing on polyester (not included in Table 3).

– *Thermomigration*

Most of the blue replacement products are superior to the AQ dyes with respect to thermomigration fastness. Although their tendency to accumulate at the fibre surface during heat treatment is not much less than that of the AQ dyes, the replacement dyes exhibit considerably less staining of nylon in washing tests.

C.4.3 Application properties

– *Migration*

The migration power of most blue AQ and replacement dyes is moderate. The best product in this respect is Blue VI (AQ).

– *Coverage of barré*

As in the case of the brilliant red dyes, the AQ blue dyes generally have a lower tendency to show up substrate-related differences than the replacement products. The advantages of the AQ disperse blues (e.g. Blue II) are especially noticeable on polyester fibres with different draw ratios.

– *Dyeing at 96°C with carrier*

When dyeing preset polyester at temperatures below 100°C, build-up problems are encountered with most blue dyes. Unlike with the red disperse dyes, only a few suitable components can be found among both the AQ dyes (e.g. Blue II and III) and the replacement products (e.g. Blue XIX).

– *Adsorption characteristics*

As in the red region, several replacement products in the blue region exhibit a medium to high kinetic Z value. As a result, for the selection of dyes with rapid-dyeing character more suitable compounds are found among the replacement products (e.g. Blue VII, XII, XVI) than among the AQ dyes (Blue II).

D. CONCLUSIONS AND OUTLOOK

Has success been achieved in the replacement of brilliant anthraquinone red and blue disperse dyes with technically equivalent and more economical replacement products? The question can only be answered in a qualified manner, taking into account the specific requirements (whether from a chemical-technical or applicational-fastness standpoint) in each case.

– *Technical aspects*

As far as economy is concerned, the above question can be answered in the affirmative, as can be seen merely from the considerably higher molar tinctorial strengths of the replacement products compared with those of the AQ dyes.

The replacement process has been more successful in the red region than in the blue; there now exist heterocyclic/isocyclic based azo dyes (1,2,3-triazoles, 2,6-dicyanoanilines) such as Red XII or XVII which nearly attain both the brilliance and the fastness level of the AQ dyes. In the bluish red region, none of the replacement products discussed exhibits quite the level of brightness of the AQ dyes. In the neutral to yellowish red region, however, which is not covered by the AQ dyes, there exist several non-anthraquinone dyes of exceptional brightness and adequate fastness level, for example Red VIII.

In the neutral blue region, AQ dyes have for some time been replaced by various azobenzene derivatives such as Blue XIV or XVII for applications where the highest fastness properties are not required.

The replacement of the established AQ turquoises of the Blue IV type is a much more difficult matter; it seems unlikely that this will take place in the near future. The brilliant hue of this dye, coupled with its outstanding fastness level (particularly light fastness) is extremely difficult to attain on an azo basis, if at all.

Among the blue heterocyclic azo dyes, the thienyl-2-azo dyes are the most important. 2-Aminothiophenes can be more widely varied, depending on the substituent pattern, than 2-aminothiazoles. Even the extremely greenish blue region can be covered with thienyl-2-azo dyes; moreover, their hues are generally brighter than those of the thiazole analogues.

The brightest dyes, both in the red as well as the blue sector, e.g. *Blue XX*, are most likely to be based on new chromophores. However, the alternative systems often exhibit weaknesses with respect to (photo)chemical stability, dyeing behaviour, technical accessibility, etc., which makes successful marketing difficult if not impossible. For this reason, the chances of successfully competing with the well-established AQ dyes or their azo replacement products, will probably remain limited.

– *Application and fastness aspects*

Considering the substrates dyeable with disperse dyes, the replacement of the AQ dyes has had a greater success on polyester, which is by far the most important substrate for this class of dyes, than e.g. cellulose acetate or polyamide, where AQ dyes still predominate.

There are, on the other hand, certain limitations in the application of replacement products even in the polyester sector, for example to meet extremely high light fastness requirements (for very pale colours or in the automotive sector), or to achieve resistance to hydrolysis and reduction stability. As far as these criteria are concerned, the status attained by the replacement products is more favourable in the red than in the blue region. From the standpoint of stability to reduction for discharge printing on polyester, only AQ dyes can be used, virtually without exception. In transfer printing also, AQ dyes are mostly used by virtue of their ease of sublimation.

The better covering of AQ dyes for substrate-related barré is no longer the important factor it was a few years ago, thanks to the quality improvements achieved by yarn manufacturers.

The dyeing behaviour of disperse dyes at atmospheric pressure using a carrier is still of some importance. In the brilliant blue region the AQ and the replacement dyes suitable for this application are about evenly balanced, but only a few of the non-anthraquinone brilliant red dyes are suitable.

The generally lower tendency to thermomigration and more favourable rapid-dyeing behaviour are examples of properties where many replacement products are superior to AQ dyes. In the so-called rapid dyeing method, levelness is primarily ensured by correct process control. Here the relatively modest migration power of most disperse dyes is of secondary importance. A few dyes with above-average migration property can be found among the AQ as well as the replacement dyes.

In conclusion, it cannot be overlooked that a certain consolidation of the 'competitive situation' of AQ dyes vs replacement products has taken place, as Renfrew has recently observed [1]. Nevertheless, based on the continuing intensity of the patent activities of the major dye manufacturers in the disperse dye sector, the process of gradual replacement of AQ dyes will continue, although the AQ speciality dye can be expected to retain its position in preferred applications for a long time to come.

ACKNOWLEDGMENT

We would like to thank Prof. E J Moriconi for helpful discussions and valuable advice.

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