# Recent Advances in Disperse Dye Development and Applications

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**P** olyester fiber production in the U.S. fell markedly in 1990. Staple production fell by 12.3% and filament production by 8.7% compared with 1989 (1). In 1991 some recovery is expected as the country comes out of recession with increases in consumer spending and housing purchases. On a world basis, the forecasts are much more optimistic. Latest estimates put the long term growth rates for polyester fiber at 5% per annum against 3% for all fibers. The highest growth rates are predicted in Asia and the Far East where over 8% per annum is forecast for the period 1990-2000. Over the same period a growth rate of just 0.5% per annum is predicted in the U.S.

It is against this background of a significant global growth rate in polyester fiber that major dye manufacturers continue to devote substantial resources to the development of new disperse dyes for the coloration of polyester and its blends, particularly with cellulose.

Disperse dye development has to be directed towards satisfying a number of

The commercial development of new disperse dyes for 100% polyester and polyester/cellulose blends is reviewed. The deficiencies of traditional anthraquinone disperse dyes for bright red and bright blue shades are highlighted from the standpoint of today's requirements for higher wetfastness and more economical processing. More acceptable alternative dyes are described with emphasis on exhaust dyeing of 100% polyester microfibers and one-bath dyeing of polyester/cellulose blends. Some aspects aimed at reducing environmental pollution, namely alkali-clearable disperse dyes and choice of formulating agents, are discussed.

## **KEY TERMS**

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Anthraquinone Dyes Benzodifuranone Dyes Disperse Dyes Polyester/Cellulose Polyester Fibers Polyester Microfibers obvious needs. Firstly, there is a need for new dyes to be tailored to satisfy shorter, reproducible and more economical dyeing processes. Secondly, with the increasing use of polyester and its blends in leisurewear and sportswear, there is a clear demand for dyes of higher wetfastness. This requirement has been exacerbated by the introduction of fabrics based on polyester microfibers where higher depths of shade have to be dyed to obtain the same visual vield as conventional polyester. Last, but by no means least, new disperse dve development has to be directed towards minimizing pollution of the environment

These objectives are not mutally exclusive but interrelated, and all need to be taken into account in any dye development program.

## Properties of Anthraquinone Disperse Dyes

Anthraquinone disperse dyes were developed more than 60 years ago for the coloration of cellulose acetate. They were subsequently found suitable for the coloration of other such synthetic fibers as nylon, cellulose triacetate and polyester.

It was the phenomenal growth of polyester fiber production during the 1950s and 1960s that signaled an extensive research and development program for new disperse dyes for polyester. Research was largely concentrated on substituted anthraquinone and substituted benzenoid mono-azo structures.

The anthraquinone disperse dyes developed over this period had some clear benefits.

• Brightness of shade (particularly blues and reds)

- Very good lightfastness
- Good level dyeing properties
- Good coverage properties
- Good reproducibility

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A further attraction of anthraquinone dyes was the fact that many gave good yields with carriers and enabled satisfactory dyeings to be achieved at the boil, in nonpressurized machinery at a time when atmospheric dyeing machines were more common.

During the past 20 years, however, the following deficiencies of anthraquinone disperse dyes have come forward.

Tinctorially weak

- Poor wetfastness
- Expensive

• Environmental problems in manufacture

Compared with many other dye types, anthraquinone disperse dyes are tinctorially weak. Furthermore, with the introduction of detergents and multifiber strips to evaluate wetfastness, they have been found to have, in the main, poor wetfastness, being particularly poor with respect to staining adjacent nylon. For dye users they are expensive relative to mono-azo disperse dyes; for dye manufacturers they are environmentally problematical.

Many key anthraquinone disperse dyes are derived from sulphonation of anthraquinone itself, which for most manufacturers requires the use of mercury catalysts. Hence, there has been a clear need to find replacements for anthraquinone dyes to counter these deficiencies. This does not mean that anthraquinone disperse dyes do not still have their place. They do. They are still seen as essential to satisfy the lightfastness requirements for automotive outlets. They are still used extensively for such nonpolyester synthetic fibers as acetate, triacetate and nylon, together with blends of these substrates with polyester. Probably their main use today is in pale shade trichromatic dyeing where their good coverage, good reproducibility and good leveling properties are still needed, and their obvious deficiencies of expense and poor wetfastness can be largely discounted.

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Some developments have continued. Japanese manufacturers have devised and successfully operated mercury-free processes for anthraquinone intermediates. Ciba-Geigy has recently added a completely new anthraquinone disperse dye to its range: Terasil Brilliant Blue FFL (C.I. Disperse Blue 361), a bright mid-blue of high lightfastness.

However, with few exceptions, recent developments in disperse dyes have concentrated on other types of dye structures. Many projects have been aimed at improving on and replacing anthraquinone disperse dyes and satisfying demands for the highest quality performance.

## Replacements for Anthraquinone Disperse Dyes

Bright Blues. In the late 1960s and early

1970s bright blue mono-azo disperse dyes started to appear and be offered as potential replacements for anthraquinone disperse dyes. Typical of these dyes was C.I. Disperse Blue 165 (Fig. 1). This dye possesses a significant improvement in tinctorial strength, being more than three times stronger than the popular anthraquinone C.I. Disperse Blue 56 (Fig. 2).

As shown in Table I, the wetfastness of the dye was also superior when subjected to the ISO 105 C06/C2 washfastness test, with much lower staining of nylon adjacent fabric.

However, while the deficiencies of low tinctorial strength, low wetfastness and cost ineffectiveness had been largely overcome, the new mono-azo dye was more easily reduced during a high temperature dyeing cycle and as a consequence was less reproducible, particularly in tertiary shades. The dye found great acceptance in continuous dyeing outlets on polyester/ cellulose blends owing to its higher heat and wetfastness, but in batchwise dyeing it has been only moderately successful.

The shade of C.I. Disperse Blue 165 is also considerably greener than C.I. Disperse Blue 56. On shade grounds alone, it could not convincingly be offered as a viable alternative. This last objection has been largely overcome in the last two to three years by the development of a new dye with a closely related structure, C.I. Disperse Blue 366 (Fig. 3).

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This dye is very much redder than C.I. Disperse Blue 56 but mixtures containing this dye are now being marketed which are similar in hue to the anthraquinone dye. Typical mixtures are C.I. Disperse Blue 165/366 or C.I. Disperse Blue 367/366. Both are close in shade to C.I. Disperse Blue 56 but slightly duller. As might be expected, they show much inferior resistance to reduction in the dyebath.

Very recently, ICI has developed a new mono-azo thiophene bright blue, slightly redder in shade than C.I. Disperse Blue 56 but marginally brighter. This dye finally explodes the myth that mono-azo blue dyes cannot achieve the brightness of C.I. Disperse Blue 56. Furthermore, it is far



Fig. 1. C.I. Disperse Blue 165.



Fig. 4. C.I. Disperse Red 60.

Disperse Dye	ISO 105	
Preparations <sup>a</sup>	CO6.CE Wash Test	
C.I. Disperse Blue 56 C.I. Disperse Blue 165	Р <sup>ь</sup> 4 4	N <sup>c</sup> 2-3 4

<sup>a</sup>Dyes were applied at 1/1 standard depth and heatset for 30 seconds at 180C. <sup>b</sup>P = stain on polyester. <sup>c</sup>N = stain on nylon.

superior to other azo blues in its resistance to decomposition during high temperature dyeing. Its reproducibility is of the same order as C.I. Disperse Blue 56 and with its superior heatfastness and wetfastness, and good cotton reserve, it is ideally suited for batchwise dyeing, continuous dyeing and printing of 100% polyester and polyester/ cotton blends. It is being marketed as Dispersol Blue C-RN 200 Grains.

• Bright Reds. A very similar line of development has been followed in the replacement of the popular bright bluishred anthraquinone dye, C.I. Disperse Red 60 (Fig. 4). Like the anthraquinone blue, it is still widely used in pale tertiary shades owing to its excellent reproducibility. But for medium to heavy shades it has been largely replaced by the introduction in the late 1970s of the mono-azo Bayer dye, Resolin Red F3BS (C.I. Disperse Red 343). This dye has superior heatfastness and wetfastness compared with anthraquinone dye, and tinctorially it is more than three times stronger. Hence, it is a far more economical reddening component although it is significantly duller.

ICI's approach to replacing the tinctorially weak anthraquinone reds, C.I. Disperse Red 60 and 91, led to the development of a completely new class of disperse dyes, the benzodifuranones. In the 1970s ICI researchers were pondering how they could increase the tinctorial strength of anthraquinone dyes and still retain their brightness of shade.

One factor which affects the tinctorial strength of a molecule is the number of

conjugated double bonds it possesses.-Amobious approach was to try to synthesize new molecules similar in structure to anthraquinone dyes but containing an increased number of conjugated double bonds.

A search of the literature revealed that Junek (2) in 1960 had reported the formation of a novel red lin-pentacenequinone from the reduction of benzoquinone with cyanoacetic acid. Greenhalgh (3), at ICI, repeated this work but could not confirm the reported structure. After extensive analysis and spectroscopic studies, the dihydroxybenzodifuranone structure was proposed and confirmed as correct. This particular dye was very dull bluish red and of no commerical value. But as a new chromogenic system, it was of great significance.

#### Commerical Development Of Benzodifuranone Dyes

ICI has since developed two very bright red dyes based on benzodifuranone chemistry—Dispersol Red C-BN and Dispersol Brilliant Scarlet D-SF. Both are being marketed in solid and liquid forms for exhaust and continuous dyeing outlets. The same two dyes have also been specially formulated for use in discharge printing of 100% polyester and polyester/cellulose blends as Dispersol Red BN PC Liquid and Dispersol Brilliant Scarlet SF PC Liquid, making a total of six sales products in all. It is also planned to extend the range of benzodifuranone dyes to other shade areas.

• Properties of Benzodifuranone Dyes in Relation to Industry Trends. The two benzodifuranone dyes developed to date can be applied by conventional application techniques. However, for exhaust dyeing of 100% polyester or polyester/cellulose blends, it is preferable to use top temperatures of 135-140C rather than 130C to ensure consistency of color yield and rapid diffusion of the dyes into polyester. This slight deviation from established practice is more than outweighed by the unique wetfastness characteristics possessed by the dyes.

Throughout the 1980s there was a



Fig. 2. C.I. Disperse Blue 56.



Fig. 3. C.I. Disperse Blue 366.



Fig. 5. Questionable formation of pentacenequinone.



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Table II. Wetfastness of Dispersol Red C-BN vs. Other Disperse Dyes on Polyester Microfiber

Disperse Dye	Marks and Spencer C-4A Wash Test (60C)		
	Pª	Cp	N°
Dispersol Red C-BN Grains	5	5	5
C L Disperse Red 127	4-5	4-5	3-4
C   Disperse Red 146	4-5	4-5	3-4
C   Disperse Red 92	4-5	4-5	2-3
C   Disperse Red 343	4-5	4-5	3-4
C1 Disperse Red 190	4-5	4-5	3
C1 Disperse Red 206	5	4	3-4
C   Disperse Red 359	4	4-5	3

 $^{a}P$  = Stain on polyester.  $^{b}C$  = Stain on cotton.  $^{c}N$  = Stain on nylon.

worldwide growth in blends of polyester and cellulosic fibers, particularly for sportswear and leisurewear. There was also greater popularity for contrast color panels in the same garment or white effect trim adjacent to deep shades. Furthermore, more stringent washfastness tests became the norm—e.g., Adidas Wash Test, Marks and Spencer C-4A Wash Test (60C). National and international bodies introduced similar tests which became widely adopted, such as AATCC Test Method 61-IIA and IIIA and the ISO 105 C06.C2 detergent wash tests.

Conventional disperse dyes have great difficulty satisfying these tests, particularly when the dyed fiber has been subjected to a heat setting and/or finishing treatment. During heat setting, thermomigration occurs and the dye moves out of the polyester and accumulates on the fiber surface. Subsequent washing of the dyed fiber in the presence of a multifiber strip causes staining of one or more of the adjacent fibers. Adjacent nylon is usually the most affected by disperse dyes. Obviously the heavier the depth of shade the worse the resultant staining.

By far the best performance in the tests is achieved by the new benzodifuranone dyes. They are clearly superior to all other red disperse dyes. Experience has shown it is often possible simply to rinse the dyed fabric or yarn after dyeing and still satisfy these stringent tests, thereby saving a clearing treatment. The uniqueness of these dyes was recognized in the UK in 1990 with The Queen's Award for Tech-



Fig. 6. The first benzodifuranone dye.

nological Achievement which acknowledged the outstanding contribution these dyes are making to the coloration of polyester and its blends.

• Benzodifuranone Dyes Applied to Polyester Microfibers. Conventional filament polyesters are normally considered to be within the range 2-6 dtexpf, weightreduced polyesters between 1.2-1.6 dtexpf and polyester microfibers on the order of 0.3 and 0.99 dtexpf.

As early as 1944, Fothergill (4) pointed out that the dye concentration required to achieve a given depth of shade was inversely proportional to the square root of the fiber denier as follows:

$$\frac{C_1}{C_2} = \sqrt{\frac{dtexpf_2}{dtexpf_1}}$$

where:

 $C_1 = \%$  dye applied to fiber 1

 $C_2 = \%$  dye applied to fiber 2 dtexpf<sub>1</sub> = decitex per filament of fiber 1 dtexpf<sub>2</sub> = decitex per filament of fiber 2

Subsequent studies have largely confirmed this relationship, but it is known to be affected by a number of factors, particularly the shape of the fiber cross section (5).

Hence, to achieve the same visual depth of shade on a polyester microfiber as on conventional polyester it is necessary to apply considerably more dye. Application of much heavier depths of shade on polyester microfiber leads to a significant deterioration in the wetfastness of microfibers compared with conventional polyester.

Work at ICI with benzodifuranone dyes and microfibers has shown that the benefits of these dyes are even more exaggerated on microfibers. They continue to exhibit acceptable levels of wetfastness while most other disperse dyes deteriorate markedly (Tables II, III).

$$R_1 - N = N - (R_2 - COOR_3)_2 \xrightarrow{aikaii} R_1 - N = N - (R_2 - COO^-)_2$$

Insoluble

Affinity for Polyester

Fig. 7. General structure of Dispersol PC dyes.

Soluble

No affinity for Polyester

## vs. Other Disperse Dyes on Polyester Microfiber

Table III. Wetfastness of Dispersol Brilliant Scarlet D-SF

	Marks and Spencer C-4A Wash Test (60C)			
Disperse Dye — Preparations	Pa	Cp	N°	
Dispersol Brilliant Scarlet				
D-SF 200 Grains	5	5	5	
C.I. Disperse Red 352	4-5	5	3	
C.I. Disperse Red 135	4-5	4-5	3-4	
C.I. Disperse Red 200	4-5	4-5	3	
C.I. Disperse Red 151	4-5	4-5	3-4	
C.I. Disperse Red 153	4-5	4-5	3	

 $a^{\text{P}}$  = Stain on polyester.  $b^{\text{C}}$  = Stain on cotton.  $c^{\text{N}}$  = Stain on nylon.

## Disperse Dyes Designed To Reduce Pollution

All new dyes which are to be imported by or manufactured in the U.S., Western Europe, Japan, Canada, Australia or New Zealand have to satisfy stringent regulations pertaining to their possible toxicity, including their toxicity to fish. Any dye failing these requirements is not allowed to be freely imported or sold.

Until recently, with few exceptions, there was less attention paid to the possible pollution caused by coloration processes and how the structure or formulation of a dye might reduce this.

#### **Discharge Printing**

One notable exception was the development of Dispersol PC dyes in the late 1970s which was designed for the discharge printing of 100% polyester. Up to about 1976, the technique used was to pad the ground shade with an azo disperse dye followed by drying. The azo dye was chosen so that it could be easily destroyed by reduction.

The discharging (reducing) agent together with any illuminating dye was printed and the fabric dried again. Finally, during the fixation process—steaming or dry heat—those parts of the ground shade in contact with the discharge agent were destroyed and the illuminating dye, if present, was fixed in its place. Obviously the illuminating dyes were chosen so that they were stable to reduction by the discharge agent. Usually these were anthraquinone based.

The common reducing agents employed in this process were all heavy metal salts, namely, stannous chloride, zinc formaldehyde sulfoxylate, cuprous acetate or similar salts. Even at the time, effluent containing heavy metals from the washing off process was widely regarded as unacceptable.

This concern was one of the factors which led to the development of Dispersol PC disperse dyes which allowed the ground shade to be discharged by simple alkali. These novel dyes were characterized by the presence of diester groups (Fig. 7).

In its diester form a Dispersol PC dye acts like a conventional disperse dye. It is insoluble, with an affinity for polyester. By treatment with dilute alkali, it can be converted into a water soluble species with no affinity at all for polyester.

Thus if a Dispersol PC dye is used for the ground shade and an illuminating dye is chosen which is stable to alkali, then the ground shade can be discharged by simply using alkali. No heavy metal salts are needed.

## Exhaust Dyeing

Dispersol PC dyes are alkali-clearable dyes, as they are solubilized by alkali. This property can be used to advantage in exhaust dyeing of both 100% polyester and polyester/cellulose blends.

Most disperse dyes have a high exhaustion on polyester, often achieving 95% or higher. However, to achieve the best levels of wetfastness, it is necessary to remove the residual dye from the polyester surface after dyeing to prevent it from staining other fibers. This is normally achieved by a reduction clearing treatment using caustic soda and hydros (sodium dithionite), which reduces the surface dye. Hydros, as a strong reducing agent, places a very high Biochemical Oxygen Demand on any effluent system. On the other hand, alkaliclearable dyes completely obviate the need for hydros and should significantly reduce the cost of effluent treatment.

ICI has a wide range of alkali-clearable disperse dyes, some based on the diester chemistry of the Dispersol PC dyes, some on novel thiophene chemistry, as exemplified by Dispersol Navy C-MSA Liquid, and some based on our new benzodifuranone dyes.

## Select II Process

The advent of alkali-clearable disperse dyes has enabled highly productive onebath, two-stage processes to be developed for such exhaust dyeing of polyester/ cellulosic blends as the Select II Process (Fig. 8).

This method has been widely promoted throughout the world by ICI (6). Compared with the conventional two-bath dyeing method, improved productivity of 30% can be achieved. Both the disperse dye for the polyester component and the reactive dye (Procion H-E dye) are introduced at the start of the dyeing cycle. The polyester component is dyed first and, on cooling back, alkali is added. This clears any residual disperse dye from both the polyes-



Fig. 8. The Select II process.

ter and cotton and effects fixation of the reactive dye.

## **Formulation Aspects**

Throughout this paper there have been many references to Colour Index names. There is often a mistaken belief that dyes possessing the same C.I. name are identical in every respect. This is not the case. The C.I. name only refers to the colored species in a dye and in the case of disperse dyes may represent as little as 10% of the actual dye as sold. The rest of the dye is loosely classified as formulating agents.

Formulating agents are necessary to convert what is an insoluble dye into a preparation that can be evenly applied to polyester and its blends from an aqueous medium. Thus, for high temperature dyeing, the formulating agents must be able to provide the overall preparation with good, high temperature dispersion stability.

The choice of formulating agents is crucial to good and reproducible dyeing performance. An injudicious choice can lead to dye restraining, fiber staining, lower fastness, excessive foaming and adverse interaction with other chemicals commonly used in the dyebath. Indeed, where a dye is sensitive to the reduction or hydrolysis, the formulating agent can greatly influence to what extent this occurs. Hence, there are many reasons why disperse dyes, classified by the same C.I. name can perform markedly different in the dyebath, or for that matter in continuous dyeing or printing.

One aspect which has received little attention is the contribution formulating agents make to the effluent. In a typical exhaust dyeing, virtually all the dye is taken up by the polyester substrate and its presence in the resulting effluent is minimal. The formulating agents, however, being water soluble are not adsorbed by the substrate to any significant extent and virtually all become part of the effluent.

Reputable manufacturers of formulating agents have begun to provide data for the formulation chemist on the properties of their products in effluent. For example, Borregaard Industries, a major supplier of formulating agents, has has its major products independently assessed for toxicity to fish, toxicity to micro-organisms and biodegradability by the Batelle-Institute, Frankfurt. This type of data is becoming increasing important to the dye manufacturer who wishes to minimize adverse effects on the environment.

## Conclusion

The growth of polyester fiber in the textile industry, the development of new fibers and fabrics, the need for economical and shorter processing methods and ever changing fastness requirements all signify an increasing market for new disperse dyes.

The new thiophene based azo bright reddish blue Dispersol Blue C-RN should find widespread acceptance due to its benefits over existing products. The new benzodifuranone dyes—Dispersol Red C-BN and Dispersol Brilliant Scarlet D-SF—have outstanding levels of wetfastness, ideally suited for polyester microfibers. Alkali-clearable disperse dyes simplify polyester and polyester/cellulose dyeing and printing as well as making a significant contribution to reducing pollution from dyehouse effluent, as can the choice of their formulating agents.  $\infty$ 

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