
# ASDC Dyeing of Synthetic Fibres

## 6.11 Dyes Used – Acrylic Fibres

**Acrylic fibres**

As discussed, PAN fibres are *ternary copolymers*[1] for which several comonomers are commonly employed in order to modify the thermoplasticity, aid fibre processability and improve mechanical, structural, and dyeing properties; as such, PAN fibres vary markedly depending on the manufacturer. PAN and MAC fibres are dyed predominantly using basic dyes using similar dyeing methods.

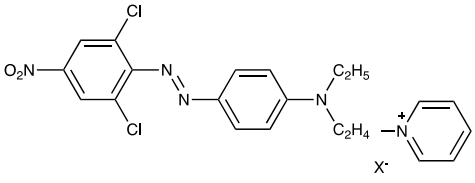
*Basic dyes*

A basic dye is '*a cationic dye characterised by its substantivity for the acidic types of acrylic fibre and for tannin mordanted cotton'* (61), which reflects the former importance of this class of dye in the dyeing of cotton. As basic dyes form coloured *cations* in aqueous solution, they are also referred to as *cationic dyes*. Although the latter term has been often used to denote dyes that were developed specifically for use on PAN fibres, in the Colour Index, all dyes that form cations in water belong to the application class known as *basic dyes*; nonetheless, in this discussion, the terms *cationic dye* and *basic dye* are used interchangeably.

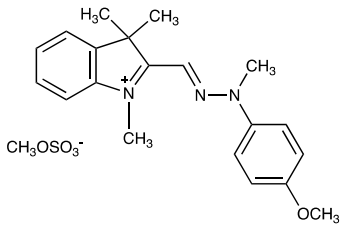
The dyes belong to several different chemical classes and are divided into two chemical types:

*(i)* *localised dyes* (aka *pendant dyes*): the positive charge is localised on one atom (eg *N*) as exemplified by C.I. Basic Orange 30:1;

*(ii)* *delocalised dyes*: the positive charge is delocalised over the entire dye molecule (eg C.I. Basic Yellow 28).

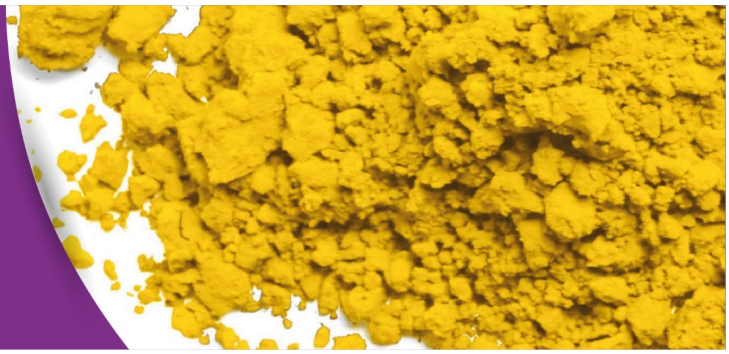



C.I. Basic Orange 30:1




C.I. Basic Yellow 28

[1] eg acrylonitrile:methyl acrylate:2-acrylamido-2-methylpropane sulfonic acid (AMPS)



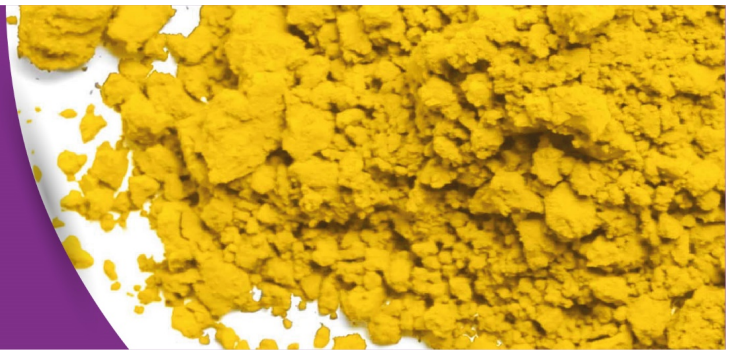
As many earlier types of basic dye (aka *conventional* basic dyes) exhibited low migration on PAN fibres, *migrating cationic dyes* were developed that were of lower molecular size and greater hydrophilicity and, consequently, display lower dye-PAN fibre substantivity, which thereby promotes dye levelling (ie dye migration). Both migrating cationic dyes and conventional cationic dyes intended for application to PAN fibres provide a wide range of characteristically brilliant hues, dyeings generally display excellent all-round fastness which can be attributed to both the polymer's $T_g$ (~70-90°C) being above the temperatures that are encountered during domestic laundering, and the fibre's intrinsic hydrophobicity.

The dyeing of PAN fibres with basic dyes is dominated by two fibre characteristics namely the presence of acidic (aka anionic) dye sites and $T_g$. As mentioned, the fibre contains sulfonate groups, $-SO_3^-$, and/or sulfate groups, $-OSO_3^{2-}$ derived from the polymerisation initiator; sulfonate groups can also be present owing to the comonomers employed, as can be comonomer-derived weakly acidic carboxy groups, $-COO^-$. Both the nature and number of the acidic groups varies markedly for different commercial types of PAN fibre (Table 5). Whilst the anionic charge carried by the fibre remains essentially unchanged as a function of pH in the case of strongly acidic sulfonate groups, the charge on the fibre is pH-dependent in the case of carboxy groups.

Table 5 Acidic group content of PAN fibres (83)

| fibre | acid group content/ m eq $g^{-1}$ | |
|---|---|---|
| | strongly acid | weakly acid |
| *Courtelle E* (Courtaulds) | 0 | 154 |
| *Acribel* (Fabelta) | 28 | 30 |
| *Acrilan 16* (Chemstrand) | 31 | 21 |
| *Orlon 42* (Du Pont) | 46 | 17 |
| *Dralon* (FBy) | 48 | 53 |
| *Beslon* (Toyo) | 70 | 44 |

Indeed, in terms of the mechanism by which basic dyes are adsorbed on PAN fibres, it is widely held (84) that the fibre acts as an *ion-exchange medium* insofar as, colourless cations (eg $Na^+$, $K^+$, $H^+$) which are associated with the anionic sites ($-SO_3^-$; $-OSO_3^-$, $-COO^-$) in the undyed fibre, are replaced during dyeing by coloured cations, $D^+$ (ie basic dye molecules), as illustrated by Figure 13, where *F* represents the PAN fibre.



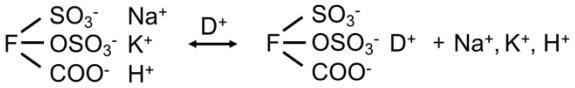



Figure 13 representation of ion-exchange mechanism for basic dyes/PAN fibres

As both the presence of such anionic dye sites and fibre $T_g$ markedly influence the rate of dye diffusion within the substrate, strict regulation of dyeing temperature, coupled with precise control of dyeing pH, preferably in the range pH 4-5.5 using a buffer system to secure optimum dye and fibre stability, as well as the use of both added inorganic electrolyte (eg $Na_2SO_4$) and a specialised dyebath auxiliary known as a *retarder*, (aka *retarding agent*) are required in order to control the rate of exchange of the dye cations with cations associated with the anionic sites in the fibre (ie achieve level dyeing).

**Retarding agents**

Several types of retarding agent are available [see (1)]:

*(i)* *conventional cationic retarding agents*: such low molar mass, colourless, quaternary ammonium compounds enhance dye migration by competing with dye cations for the anionic sites within the fibre; once adsorbed, they are gradually displaced by adsorbing dye cations;

*(ii)* *polymeric cationic retarding agents*: these quaternised polyamines do not expedite dye migration but instead are adsorbed at the fibre surface and provide an electrical barrier to dye uptake by reducing the *zeta potential*[2] (aka ζ-potential) at the fibre surface;

*(iii)* *anionic retarding agents*: these expedite dye migration via the formation of a dye-retarding agent complex that displays low diffusion in the substrate at low temperatures but which gradually breaks up at higher temperatures, releasing dye cations for adsorption.

**Added inorganic electrolyte**

Although various electrolytes can be used to impart cationic dye retardation and thus promote level dyeing, the two most commonly employed examples are NaCl and $Na_2SO4$, mostly for reasons of cost. It is generally thought that the mobile $Na^+$ ions compete with the dye cations, $D^+$, for the anionic sites in the fibre, thus displacing the equilibrium depicted in Figure 13 to the left.

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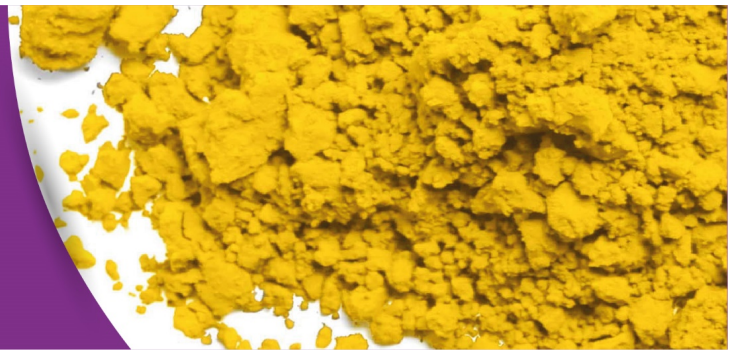
[2] zeta potential '*provides an indication of the likely electrostatic interactions that can occur between fibres and dyes within the dyebath/fibre system*' and is usually negative for all common textile fibres because of the negative charge developed at the fibre surface. 1. Burkinshaw SM. Physico-chemical aspects of textile coloration. Chichester: Wiley; 2016.



**Dyes in admixture**

When basic dyes are used in admixture on PAN fibres, level dyeing will be expedited if dyes of similar dyeing behaviour (substantivity, migration behaviour, diffusional characteristics, etc.) are employed. This approach has resulted in the concept of the *compatibility value*, *K* (aka *C* or *CV* value) (85) of a particular cationic dye for PAN fibres, where *K* quantifies the adsorption behaviour of cationic dyes in terms of both affinity and diffusion coefficient and ranges from 1 to 5. Generally, when a combination of dyes is used, that of lowest *K* value will exhausts most rapidly; wherever possible, dye mixtures should comprise dyes of the same compatibility value, or differ by ≤ one value of *K*. Compatibility values of dyes are altered by both anionic and cationic retarding agents.

Basic dyes are applied under acidic conditions (pH ~3.0-6.0) to avoid dye decomposition, in the presence of a
retarding agent (amount recommended by the dye maker), 2-2.5 $gl^{-1}$ $Na_2SO_4$; the dyebath temperature is brought to just below $T_g$ and then slowly raised to 96–102°C depending on the particular dye/fibre combination in use; temperatures >98°C are utilised to promote dye migration and expedite dye exhaustion. At the end of dyeing, the dyebath is cooled slowly and uniformly to ~60°C to avoid crease marking and a loss of handle and bulk.

Cationic dyes can also be applied using a pad→steam process in which the PAN fibre is impregnated with an acidic solution of dye, wetting agent and thickening agent and is then steamed at 100-110°C for 5-30 min. Furthermore, wet-spun PAN yarns can be produced in coloured form by passing the fibre in its *gel state* (ie amorphous state of little orientation) through a cationic dye dyebath; the advantages of this *gel dyeing* process are its speed and the fact that dye uptake is independent of $T_g$, thereby markedly reducing problems associated with dye selection and compatibility in admixture.

*Disperse dyes*

Disperse dyes enjoy little usage on PAN fibres, on which they mostly furnish pale depths of shade that display moderate fastness; application is carried out under acidic conditions in the presence of a non-ionic dispersing agent at ~98°C.