Dye-Fibre-Interrelations in Acrylic Fibres*

Ian Holme**

Department of Textile Industries, The University of Leeds, England

Abstract

The fundamental role of the physicochemical structure of acrylic fibres in relation to the development of satisfactory methods of coloration is critically reviewed with particular reference to the dye-fibre-interrelations that occur in cationic and in disperse dyeing systems.

1. Introduction

Within the brief space of thirty years acrylic fibre production has grown to become the third largest synthetic fibre capacity in the world [1–3]. This dramatic growth rate could not have been possible without satisfactory methods of coloration being developed, for these have expanded greatly the range of potential end uses for acrylic fibres.

The development of satisfactory methods of coloration for acrylic materials in their many diverse forms has resulted from much imaginative research and innovative development work in many countries. This has involved fibre producers, dye manufacturers and academic institutions, often working in close collaboration. The fruits of this success have led to a more rational view of the theoretical foundation upon which the dye-fibre interrelationships are based and upon which more satisfactory commercial processes will be evolved in the future.

* Lecture presented at the 7th International Colour Symposium at Interlaken, Switzerland, September 24–27, 1979.

** Dr. I. Holme, Lecturer in Textile Industries, Dept. of Textile Industries, Leeds LS2 9JT, England

The elucidation of the structure of acrylic fibres and of the complex web of relationships encompassing the physicochemical aspects of coloration processes has taxed the resources of fibre scientists, colour chemists and technologists. In particular, the modification of the fibre structure through copolymerization [1–3] and the synthesis of novel cationic dye structures [4] have played major roles. This has enabled a wide gamut of very bright colours on acrylic fibres with excellent fastness properties to be produced.

With these points in mind, the object of this paper is to review the considerable advances that have taken place in the coloration of acrylic fibres. The theoretical principles involving the dye-fibre interrelations will be expounded and their development, especially for coloration processes involving cationic and disperse dyes, will be considered in detail.

2. Acrylic fibres

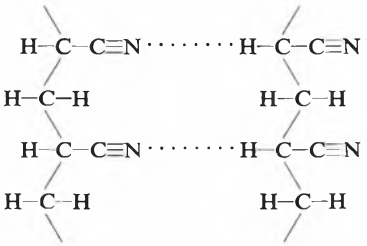
The development of acrylic fibre production from the original discovery of acrylonitrile by *Moureu* [5] in 1893 through to the pioneering work of *Rein* [6] and of *Houtz* and their coworkers [7] has grown dramatically to a total production capacity for 1979 of 5784 m lb, produced by some 59 organizations in 32 countries [2, 8]. These early developments are documented in detail elsewhere [1, 2, 7].

Considerable difficulties in the coloration of homopolymer fibres based on polyacrylonitrile led to the

use of copolymerization to improve the dyeability [1–3]. As a result an acrylic fibre is now defined as a manufactured fibre in which the fibre-forming substance is any long chain synthetic polymer composed of at least 85% acrylonitrile units [9]. In contrast to polyester and nylon fibre production the amount of acrylic continuous filament produced is extremely small [8].

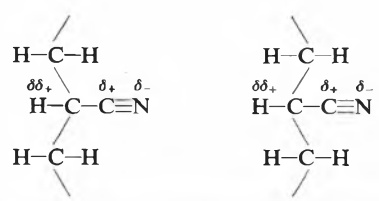
2.1. The structure of polyacrylonitrile

Initially the physical properties of polyacrylonitrile e.g. a high melting point (c. 330 °C) and poor solubility suggested to earlier workers [7] either a crosslinked structure or that the polymer chains were linked through intermolecular hydrogen bonding [10–13] between CN nitrogens and hydrogens on carbons alpha to the CN group, viz.



This view was paramount in initial discussions of the physical properties of polyacrylonitrile but subsequent studies using infrared spectroscopy did not substantiate this suggestion for the value of the ν (CN) mode was not significantly lower than that usually found in other nitriles [14].

A second point of view asserted that the predominant effect is due to dipole interaction between a given CN group and several nearest neighbour CN groups, termed random dipole interaction [15, 16]. However it has subsequently been suggested as a result of a very detailed analysis of the properties of liquid organic primary, secondary and tertiary nitriles that the intermolecular forces leading to the formation of dimers involved dipole interactions between closely associated pairs of CN groups, the so-called CN dipole-pair bond [17]. The energy of interaction between two CN groups is high, about 33.5 kJ.mole^{-1}. It has been assumed that these conclusions similarly hold for polyacrylonitrile. *Davidovits* [18] has also pointed out that hydrogen bonding is usually found when a hydrogen atom is near two electronegative atoms, but that in polyacrylonitrile only one such atom is present, namely the nitrogen of the cyano group. Further, this is adjacent to a carbon atom that is electrophilic owing to the inductive effect (–I) of the nitrogen

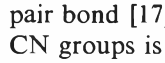


This had led *Davidovits* to suggest that only *Van der Waal*'s forces exist between the polymer chains [18]. The free space between chains was estimated to be 2.7 Å and an isotactic structure was assigned to the crystalline sections of the macromolecular micelle and a syndiotactic structure to the amorphous regions. The evidence for such a model however is by no means confirmed and the results of other workers [19–21] suggest that the fibre structure may be mesomorphic containing regions with a pronounced lateral arrangement of the chain molecules, together with small crystalline regions with a three-dimensional periodic arrangement of chain segments which appear to have a syndiotactic structure.

The many X-ray diffraction studies are difficult to summarise because of the different physical forms in which polyacrylonitrile has been studied e.g. drawn and undrawn fibres, oriented and annealed films and solution-grown crystals [22, 23]. Agreement between unit cell parameters and polymer density is not exact so that a conflicting picture emerges. However, the distance between the polymer chains is believed generally to be in the region of 5–5.3 Å which has been considered to be shorter than expected for *Van der Waals*'s forces [24, 25], and the presence of syndiotactic and/or isotactic polymer arrangements has been discussed, the formation of atactic polymer chains being rarely considered [23]. Clearly there will be a distribution of crystalline order ranging from the highly crystalline to the extremely disordered in most acrylic fibres, and the effects of the conditions of spinning and of subsequent treatments, particularly thermal and mechanical treatments, will have a pronounced effect on the fibre structure [26].

From the foregoing discussion the picture that emerges is by no means unequivocal and further work on the nature of the intermolecular forces in commercial acrylic fibres is required to resolve the diverse nature of the results and conclusions obtained in other physical forms of polyacrylonitrile.

The molecule of polyacrylonitrile:



is often described as a rod-like molecule, and as *Hearle* and *Greer* have shown, because of the influence of the bulky dipolar –C≡N side group, it takes up a helical form [27]. The chain however is quite flexible as was demonstrated in the way the model chain could bend. It is believed [28] that the electrical dipolar forces cause strong intermolecular attraction, but that this occurs without the specific localization that gives rise to a regular three-dimensional crystal lattice. Thus although the molecules try to pack together in a regular close-packed order, there is no register in the side-by-side position. This leads to the ordered regions being only pseudocrystalline, and if atactic sequences are present it becomes impossible to maintain a regular helix. Hence there will be regions of greater and of

lesser order and some polarization of the distribution between regions of high and low order must be expected, but in any event some disorder remains.

Bohn et al. [28] have pointed out that the X-ray diffraction patterns of oriented fibres show diffraction along the equator but only diffuse scattering along the meridian and in the quadrants indicating a regularly repeating chain-to-chain (lateral) spacing and the absence of a definite longitudinal repeat spacing. Indeed the X-ray diffraction results for polyacrylonitrile suggested that the material behaved as if it were all ordered and contained no amorphous regions, since there was a lack of a definite amorphous halo in the X-ray diagram. The large dipole moment of the nitrile groups together with their close proximity in space leads to very large intramolecular dipolar and steric repulsions. *Krigbaum* and *Tokita* [29] have calculated and plotted as a potential energy contour map the summation of these contributions for both an isotactic or a syndiotactic sequence in the polymer. Without such repulsion forces it was conjectured that a polymer molecule would most probably assume the extended planar zigzag configuration, although there was no information available as to what the tacticity of the nitrile groups would be. The repulsion forces thus give rise to a violent kinking and twisting of the molecule which takes on a random character even for a stereoregular polymer. Such strong repulsion forces are restrained only by the primary valence bonds along the polymer chain, thereby leading to an internally braced stiff structure. The net result is a kinked chain that resembles a more or less symmetrical rod with a diameter $\sim$ 6 Å.

As a result of this distortion the nitrile groups are distributed over a variety of angles to the rod axis which was in accord with the observed low infra-red dichroic ratios and optical birefringence. Deformation of the rigid kinked structure is small, although a slight tendency for the chains to become less kinked has been noted at high draw ratios [28]. In addition the kinking leads to a contraction along the chain axis from the normal length of an extended zigzag chain, and to a slightly higher polymer density than that calculated on the basis of hexagonal lateral packing.

Bohn et al. conclude that the very high average interchain attraction of dipoles that occurs in simple nitriles cannot occur in polyacrylonitrile because optimum pairing of all nitrile groups cannot occur [28]. Firstly, the protrusion of the nitrile groups will occur randomly owing to the irregular kinking of the chain, so that there may not be available a corresponding nitrile group to pair with on a neighbouring chain. Secondly even in the event of such a pair of groups being present, the various angles at which the groups are fixed may well not be at the optimum for maximum interaction. They concluded that a low average intermolecular force was more consistent with the well-known tendency of oriented films of polyacrylonitrile to fibrillate readily.

2.2. Copolymerization

Acrylic fibres are produced by addition polymerization processes and contain in addition to acrylonitrile 5–10% of one or more co-monomers to increase the polymer solubility in the limited number of solvents available [3]. These may also reduce the fibre compactness and improve the diffusion rates of dyes into the fibre [26]. Thus the high melting point of polyacrylonitrile is lowered by the introduction of neutral co-monomers such as methyl acrylate (the most widely used), methyl methacrylate and vinyl acetate [2]. Small amounts of other ionic or nonionic co-monomers may be included to enhance the dyeability [2, 3, 30, 31] and these are mainly based on the following:

Table 1: Co-monomers used in acrylic fibre production

Nature	Co-monomer	
Neutral	Vinyl acetate	$CH_2 = CH(OOCCH_3)$
	Methyl methacrylate	$CH_2 = CCH_3(OOCCH_3)$
	Methyl acrylate	$CH_2 = CH(COOCH_3)$
Acidic	Acrylic acid	$CH_2 = CH(COOH)$
	Allyl sulphuric acid	$CH_2 = CH(CH_2OSO_2OH)$
	Itaconic acid	$CH_2 = C(COOH)CH_2COOH$
Basic	Vinyl pyridine	$CH_2 = CH(C_5H_4N)$
	Ethyleneimine	$CH_2—CH_2$ $\diagdown\ \diagup$ NH

In practice therefore acrylic fibres may contain [3, 26]

(1) Acidic monomers conferring substantivity for cationic dyes. (e.g. sulphonic, phosphoric or carboxylic acids)

(2) Basic monomers conferring substantivity for acid and direct dyes (e.g. compounds containing amino or pyridino groups)

(3) Polar non-ionisable monomers containing functional groups capable of forming complexes with dyes (e.g. alcohols, ethers or ketones).

(4) Monomers that contain no reactive groups but alter the crystalline structure of the fibre (e.g. hydrocarbons).

The introduction of hydrophilic groups can also increase the substantivity of acrylic fibres for dyes. Epoxy compounds, urea and certain quaternary ammonium compounds have been cited in this connection [3].

2.3. Fibre extrusion in relation to the structure of acrylic fibres

2.3.1. Spinning systems

Effective solvents for polyacrylonitrile must break the intermolecular nitrile-nitrile attraction and hence highly polar aprotic compounds are used [2]. The principal solvent used is dimethyl formamide (used in both wet and dry spinning) followed by dimethyl acetamide. In general, wet spinning systems, employing aqueous solutions appear to be preferred [1–3].

Some of the principal advantages and limitations of wet spinning and dry spinning are summarized [32] in Table 2.

Table 2:

Parameter	Wet spinning	Dry spinning
Polymer concentration (%)	10–30	20–40
Range of solvents	Any	Only volatile
Number of filaments per position	Very high	Low
Take-up speed	< 100 m/min	About 1000 m/min
Drawing	Integrated	Separate
Most suitable product	Tow/staple or coarse fibres	Filament yarn and fine fibres
Solvent recovery	Easy and cheap	Expensive and complicated
Heat input in spinning	Low	Very high
Hazard	Toxic	Toxic and explosive

Fibres produced via dry spinning generally have kidney or dogbone shaped fibre cross-sections, while wet spun fibres have roughly circular cross-sections. Accordingly dry-spun fibres have a better cover, good lustre, softer handle and better soil-hiding properties [1–3]. While the fibres are almost homogeneous in cross-section a severe disadvantage from the viewpoint of subsequent coloration processes is the almost negligible internal surface, for in dry spinning the apparent density of the filament is inversely proportional to the amount of residual solvent present in the filament when it leaves the spinning chamber [33].

In wet spinning the extrusion speed of the polymer solution into the coagulation bath is limited by the breakage of freshly coagulated filaments as a result of the stresses from the higher drag forces involved [1, 2, 34]. In the coagulation process the precipitant molecules are generally less bulky than the polymer solvent molecules so that the precipitant penetrates more rapidly into the extruded filaments than the solvent can diffuse outwards. Thus microvoids are produced in the fibre structure which lead to a more heterogeneous structure than in dry spinning. The formation of voids in wet spinning is thus controlled by skin formation and the solvent diffusion rate which ultimately depends upon the type of polymer and solvent used, the coagulation conditions and the presence of surfactants [1, 2, 32–34].

Void formation in acrylic fibres is considered to be an important factor for coloration processes, and significant differences in fibre dyeability are apparent between fibres produced via the wet-spun or dry-spun routes. Thus surface area measurements on wet-spun fibres [33] have given values in the range of 200–300 m^2/g, while the dry-spun fibres give values of less than 1 m^2/g.

Dry-jet-wet spinning processes which combine both dry and wet spinning by extrusion into air or an inert gas followed by passage through a coagulating bath have been discussed [35, 36] and attempts to improve the speed of production and also the physical and mechanical properties of the drawn fibres have been made at spinning speeds in excess of 200 m/min. Current research work at Leeds University into dry-jet-wet spinning has evaluated the effects of some process parameters upon the physical properties of the fibres with interesting results [32].

2.3.2. Structure formation in acrylic fibres

It has been concluded [27, 33] that the general development of fibre structure in a wet-spun fibre follows the sequence:

(i) freshly coagulated fibre-unoriented fibre network, permeable to liquids and gases, area ratio 2.0 or higher, surface area typically 100 m^2/g.

(ii) Stretched uncollapsed fibre-oriented fibrillar network, permeable to liquids and gases, area ratio 2.0 or higher, surface area at least 50 m^2/g, increasing with stretch ratio, bulk density higher than unoriented fibre.

(iii) Dried collapsed fibre-oriented fibrillar network without residual pores, area ratio 1.0.

Dry-spun fibre at the tower exit does not have a readily distinguishable fibrillar structure, the area ratio is low and usually less than 1.5 and the internal surface area is not measurable. The initial differences between dry-spun and wet-spun fibres are reduced when unoriented dry-spun fibres are stretched, for an oriented fibrillar structure indistinguishable from stretched wet-spun fibres develops. This change in the apparent morphology is accompanied by a loss in density and the establishment of a measurable surface area. The development of a coarse fibrillar structure is evident in electron microscopical examination of filaments which have been broken in torsion [27, 37] or subjected to special peeling techniques [38].

The net result of the fibrillar structure and the nature of the coagulation process is thus the development of a microporous structure. Clearly the spatial arrangement, size and distribution of the pores and their modification by physical, chemical, mechanical and thermal treatments are of importance in determining the diffusion of dyes and other reagents within the fibre structure.

In a series of very interesting papers, *Sotton* et al. [39–43] have elegantly demonstrated the presence of radial cracks and fine micropores using optical or electron microscopical examination of fibres treated to produce the deposition of silver sulphide in the fibres. Optical microscopical examination of fibre cross-sections reveals significant differences between wet-spun, dry-spun and bicomponent acrylic fibres [40]. Generally the porous fraction revealed is made up of radial diffusion paths which may or may not be associated with a peripheral distribution of fine micropores. It is probable that these radial paths are related to the

manner in which the solvent was removed from the polymer solution during the spinning process.

Two observations are of particular interest [40]. Especially for wet-spun samples it appears that close to the surface the radial paths in numerous places split the skin and cuticle i.e. the first portions to become coagulated on the interface between the spinning bath and the polymer solution. Secondly the radial paths always originate from microlobes or faults which are visible on the surface and are probably caused by minor imperfections in the spinneret holes. In between these perforations more drastic swelling reveals a very great number of isolated fine microvoids inside the fibre skin.

Sotton et al. have recorded the subtle changes in this pore structure as a result of treatments in dry heat under an inert gas (nitrogen) and in saturated steam with fibres held either at constant length or in the relaxed state [39, 40]. Dry heat treatments strongly affect the spatial distribution of the porous zones but saturated steam treatments up to 140 °C do not appear to affect it. Above 140 °C the saturated steam treatment eliminates the initial porosity but leaves many fine micropores which are localized in the periphery of the fibres i.e. a skin effect.

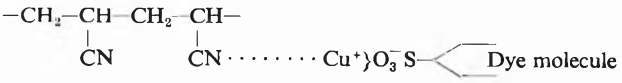
In dyeing tests with two cationic dyes the rate of dyeing and the substantivity of these «skin effect» fibres are greatly increased but they are more or less decreased for the dry heated fibres [41]. The higher the temperature of the wet treatments, the greater the dye uptake of the fibres, but in the case of dry heated fibres a slight decrease in dye uptake is observed. The slope of the kinetic curves for these samples changes specifically after ten minutes of dyeing. This change is often very pronounced, and proposals were advanced to interpret the changes observed [41]. The porous structure of an acrylic fibre treated in a mixture of solvent-cosolvent (perchloroethylene-dimethyl sulphoxide) at 100 °C is the same as that obtained by a hydrothermal treatment at high temperature [41]. Dramatic changes were also observed in fibres subjected to mechanical fatigue (10,000 extensions), and to thermomechanical fatigue [42–43].

2.4. Early attempts to dye acrylic fibres

Fibres made from 100 % polyacrylonitrile are difficult to dye [44] because of the lack of affinity for dyes and the high glass transition temperature (104 °C). Orlon fibres were modified to include acidic end groups, while basic groups were introduced into Acrilan fibres through copolymerization with vinyl pyridine etc. conferring dyeability with acid dyes [45]. Copolymerization with other neutral comonomers created a more open structure and a lower glass transition temperature leading to a greater dyeability with disperse dyes and in some instances an affinity for direct, vat, sulphur and azoic dyes [1, 2, 46].

In summary then, around 1957 it would appear that Acrilan could be dyed with selected dyes from the following classes-disperse, basic, neutral premetallised, acid premetallised, acid, chrome, soluble sulphur, vat, vat ester and azoic dyes [46, 47]. Orlon, Courtelle, Acrilan 16 and Dralon were dyeable only with disperse, basic and vat dyes and with acid dyes by the cuprous-ion technique [46, 48–51].

In the cuprous-ion technique 1–2 % of cupric sulphate (o.w.f.) was added to the dyebath, followed by half this weight of reducing agent and finally the acid dye [52–54]. Various reducing agents were suggested [46] e.g. zinc sulphoxylate formaldehyde, hydroxylamine sulphate, and even metallic copper was used which formed the basis of the original Sandocryl process (Sandoz) [55, 56]. On boiling the liquor, the cupric ions were reduced to cuprous ions which were rapidly absorbed by the acrylic fibre.



For homopolymer fibres a plot of the copper concentration in the fibre $(Cu_f)^2$ against copper in the bath (Cu_s) gave a linear relation [59] suggesting that moderately strong coordination complex formation between the cuprous-ions and the nitrile groups occurred, viz.

$$\tfrac{1}{2}\,Cu^{2+} + N{\equiv}C\text{-Polymer} \rightleftarrows Cu^{+}, N{\equiv}C\text{-Polymer}$$

Thus the absorption of the metallic cation led to the exchange of a simple neutralizing anion for a dye anion from the dyebath.

$$\text{Fibre.cation}^{+}\text{anion}^{-} + \text{dye}^{-} \rightleftarrows \text{Fibre.cation}^{+}\text{dye}^{-} + \text{anion}^{-}$$

The metallic copper process generated cuprous ions more slowly making it easier to produce level dyeings. There was always the possibility of reduction of azo dyes with reducing agents leading to duller colours [57, 58] and the practical details of the cuprous-ion technique generated great interest, as evidenced from the number of publications concerned with this method [52–59].

However, difficulties in application led to a revival of interest in the commercial development of basified acrylic fibres. Meanwhile the discovery of cationic dyes with improved light fastness on acrylic fibres finally stimulated intense research and development effort which has culminated in cationic dyes being the major class of dyes used for acrylic fibres. There is no doubt that the broad gamut of brilliant colours coupled with high light and wash fastness has contributed to the emergence of acrylic fibres as a major generic class. Disperse dyes are now the only other class of dyes of importance for acrylics and are used less frequently as improvements in methods for levelling cationic dyes continue to emerge.

3. Cationic dyes on acrylic fibres

3.1. Classification of cationic dyes

A basic dye is defined as 'a cationic dye characterized by its substantivity for the acidic types of acrylic fibre and for tannin-mordanted cotton' [60]. However in this paper these will be referred to as cationic dyes as these are defined [60] as dyes that dissociate in aqueous solution to give a positively charged coloured ion (cation). The first synthetic dye from coal tar, Perkin's Mauveine, was a cationic dye and many such dyes based on acridine, azine, oxazine, thiazine, azo, triarylmethane and xanthene chromophores were prepared for use on natural fibres [61].

While cationic dyes have always been characterized by their brilliant colours their general low light fastness almost caused their demise as a class of dyes and mitigated strongly against their use except for brilliant colours on silk [62]. However, in 1952 Du Pont's Basic Yellow OL became the prototype for the later developed Sevron range with improved light fastness on acrylic fibres [63]. The revival of the Astrazone range by Bayer and the production of new ranges of cationic dyes by other companies led to the introduction of some 80 new cationic dyes within a decade, of which 50 were claimed to be chemically different [62]. The production of deep dyeings of superior fastness using cationic dyes has been a major factor in the continuing expansion in acrylic fibre production.

The fastness to light of modern cationic dyes on acrylic fibres is extremely good, even in pale depths. The reasons for the high light fastness of such dyes on acrylic fibres, rather than on other classes of fibre, are complex and systematic studies on homologous series of compounds are rarely encountered. Correlations between dye structure and light fastness have however been the subject of a few studies, and some general conclusions have been formulated [62].

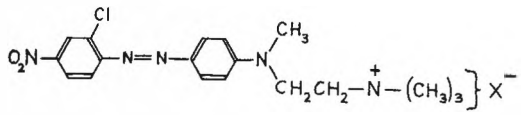
In cationic dyes the positive charge is associated with the chromophore part of the molecule [4, 64]. The accompanying anion is believed to have little effect on the dyeing properties but is often important because of its influence on the solubility characteristics of a dye and the ability to isolate a pure dye [4]. *Baer* [4] has divided cationic dyes into three distinct classes.

3.1.1. Pendant cation (non-resonating charge)

These dyes are similar in structure to disperse dyes except that a cationic charge has been added, insulated from the chromophore, enabling the dye to be adsorbed by fibres containing acidic dye sites like acrylic fibres. The colour, strength and fastness properties are generally similar to the disperse dyes and have been designed to give high light fastness. However, these dyes are not as brilliant or tinctorially strong as, for example, triarylmethane derivatives.

The cationic function is generally a substituted quaternary ammonium salt because this is easy to prepare and stable over a broad *p*H range, but sulphonium, hydrazinium and thiouronium salts are known derivatives. Typical examples are shown in Fig. 1.

Blue Anthraquinone Cationic Dye



Red Azo Cationic Dye

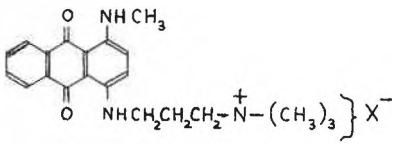


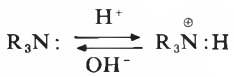
Fig. 1: Localized charge cationic dyes

3.1.2. Delocalized positive charge (resonating charge)

This class of cationic dyes yields dyes which are generally the brightest and strongest tinctorially and include modified oxazine, triarylmethane, azacyanine, polymethine and polyazamethine types. Here the positive charge in the molecule participates in the chromophoric system but many delocalized (or distributed) dyes are either too fugitive to light or do not possess sufficient stability to hydrolysis for application to acrylic fibres.

3.1.3. Amine salts (cation formed by protonation under acidic conditions)

Cationic dyes that develop a positive charge under acidic conditions are suitable for dyeing acrylic fibres because the latter are normally dyed within the *p*H range 4–5.5. Under neutral or akaline conditions this class of dyes behaves more like disperse dyes, since an equilibrium reaction occurs under normal dyebath conditions.



While good levelling properties are obtained, the disperse dye character often provides substantivity for fibres other than acrylics, leading to considerable staining of wool, nylon and polyester, where blends are to be dyed [4]. Pendant amino alkyl disperse dyes are the most important high light fastness group within this class of dyes.

It is to be noted that the excellent wash fastness of cationic dyes on acrylic fibres is due largely to the compact hydrophobic physicochemical structure of the fibre which requires higher temperatures for dyeing than are normally encountered in conventional washing cycles [4].

4. Mechanism of dyeing acrylic fibres with cationic dyes

The mechanism of the dyeing of acrylic fibres with

cationic dyes has been described in terms of an ion-exchange [65–69] or as a simple ion distribution [68]. *Glenz* and *Beckmann* [70–72] have proposed that the process can be considered in terms of three main steps:

(i) Adsorption of dye on the fibre surface.
(ii) Diffusion of dye from the surface into the fibre structure.
(iii) Interaction of the dye with sites in the fibre.

As *Beckmann* has succinctly pointed out, the equilibrium position of step (i) and the rate of step (ii) collectively determine the rate of dyeing, while step (iii) influences the dyeing equilibrium [73]. These three steps will now be considered in more detail.

4.1. Adsorption

The electrokinetic potential (zeta potential) which is established between the surface of an acrylic fibre in water is large and has been determined [74] to be −44 mV for Orlon in 0.01 N KCl. In an aqueous dyebath containing cationic dye this negative charge attracts the positively charged dye cation to the surface of the fibre where adsorption occurs. The fibre gradually loses its negative potential at low concentrations of dye in the liquor (approx. 20 mg/l pure dye), and becomes slightly positive as a result of the accumulation of dye cations at the fibre surface [13, 70–73, 75]. The diffusion of the dye within the fibre structure leads to the potential becoming negative again and the cycle is then repeated.

Experimental studies by *Glenz* and *Beckmann* [70–72, 75] demonstrated that a further increase of the dye concentration in the liquor altered the potential only very slightly, indicating that the quantity of absorbed dye remains almost constant. *Beckmann* has however pointed out that other intermolecular forces other than electrostatic attraction may also be involved e.g. dispersion forces or dipole forces, so that in practice this dependence on the zeta potential may well be too simplistic [73]. Clearly the zeta potential for different acrylic fibres may well vary in magnitude according to the polymer composition while the forces of attraction will differ according to the nature of the chemical constitution of the dye where polar and stereochemical considerations could play an important role.

The extent of dye uptake is independent of the liquor: goods ratio, the rate of dyeing, and the temperature, when this is below the second-order transition temperature of the fibre [13]. The dye uptake is however dependent upon the *p*H of the dye liquor because of the competition effects between dye cations and hydrogen ions on neutralisation of the potential of the fibre surface while additionally the nature of the acrylic fibre and the basicity of the dye also exert effects [13]. The changes in the magnitude and sign of the electrokinetic potential with concentration of various electrolytes in which the cation and anion were systematically changed have been determined [70–72, 76]. Univalent cations first increase the negative electrokinetic potential, but decline in value after reaching a maximum value. Divalent cations produced a slow decrease with increase in electrolyte concentration but trivalent ions such as aluminium even in small concentrations rapidly give rise to a charge exchange on the fibre surface. This confirms the law that the potential-reducing action of cations increases with their valency. Sodium sulphate in common with other electrolytes causes an initial increase in electrokinetic potential which gradually declines thus giving a peak in the curve against concentration [76]. When equimolar quantities of the chlorides of various metals were added to a cationic dye liquor, the retarding effect increased in the series sodium < potassium < caesium, but electrokinetic phenomena were not measured [73].

4.2. The effect of dye concentration on the rate of dyeing of cationic dyes

The relationship between the rate of dyeing and dye concentration is complex although it is well-established that level dyeing is promoted by increase in dye concentration [13]. *Beckmann* has discussed the difficulties in some detail and proposed empirical relationships to explain the phenomena observed in the case of single dyes [71, 73] and for dye mixtures [72, 73]. However both adsorption and saturation phenomena complicate the situation and this dichotomy has so far precluded an integrated treatment.

An expression for the rate of dyeing V gave reasonable agreement [73] with experimental results viz.

$$V = a\left(C_1 + \frac{Z}{a}\right)(S - C_f)$$

where S is the dye concentration to saturate the fibre,
C_f the dye concentration in the fibre
C_1 the dye concentration in solution
and $\frac{Z}{a}$ is a measure of the influence of the zeta potential.

However S, Z and a are dye-dependent and the equation is therefore not simple to use in practical situations.

However if the dyeing rate constant k is plotted against the initial dyebath concentration, where $k = \frac{C_t}{t^{1/2}}$, it has been shown that k increases rapidly in the initial stages and then remains nearly constant with further increases in concentration [13]. As a result the equilibrium exhaustion is attained rapidly when the initial dyebath concentration is low and, because of the high substantivity of cationic dyes, levelling problems occur particularly with pastel colours. At higher dyebath concentrations, although more dye is absorbed initially, the dye remaining in the bath is absorbed slowly and this may help in covering up any irregularities.

4.3. Dye-fibre interactions and site mechanisms

The use of a potassium persulphate-sodium bisulphite redox catalyst system for polymerization results in the

introduction of sulphate and sulphonate groups at the ends of the polymer chains which impart substantivity for cationic dyes to the fibre [1, 13, 73, 78, 79].

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{-}. + SO_4^{2-} + Fe^{3+}$$
$$HSO_3^{-} + Fe^{3+} \rightarrow HSO_3{\cdot} + Fe^{2+}$$
$$M + SO_4^{-}. \rightarrow -O_3SOM{\cdot}$$
$$M + HSO_3{\cdot} \rightarrow HO_3SM{\cdot}$$

where M = polyacrylonitrile chain.

The presence of such anionic groups has been confirmed using radioactive tracer studies with S^{35} labelled initiators [80] and by differential infra-red spectroscopy [81, 82]. The addition of small amounts of acrylic acid or alkyl hydrogen sulphate during polymerization or the hydrolysis of nitrile groups are other possible sources of acid groups in the fibre [83]. Early acrylic fibres contained only a limited number of the strongly acidic sulphate or sulphonate dye sites, which although conferring a high degree of substantivity for cationic dyes, precluded dyeing to heavy depths and caused difficulties in colour matching [13]. The use of acidic co-monomers containing weakly acid substituents e.g. carboxyl groups such as itaconic acid, however, solved these problems and the number and nature of the acidic groups in commercial acrylic fibres vary widely [13, 30, 31, 79]. In general, values between 50–150 m.eq/kg have been determined; strongly and weakly acid groups may be present in roughly equal proportions, or one of two types may predominate [79]. This is illustrated in Table 3.

The assumption was made in initial trials with cationic dyes that these were bound, as in a salt, to acid groups, although at the time the precise nature of the acidic component in the fibre was not known [48, 84, 85]. An acidic copolymer or an acidic hydrogen atom adjacent to the nitrile group were assumed to be involved [48, 85].

Table 3: Acid group content of acrylic fibres

Fibre	Acidic group content m.eq/kg Strongly acid	Weakly acid
Acribel (Fabelta)	28	30
Acrilan 16 (Monsanto)	31	21
Beslan (Toyo Rayon)	70	44
Courtelle E (Courtaulds)	0	154
Dralon (Bayer)	48	53
Orlon 42 (Du Pont)	46	17

The first systematic study of the nature of the dye-fibre bond was reported by *Glenz* and *Beckmann* [70]. Equilibrium studies using ten cationic dyes applied at 80–100 °C established that Dralon absorbed approximately the same amount (37 m.moles/Kg of fibre) of each dye. This fact coupled with the shape of the measured equilibrium isotherms of dye absorption led them to conclude that the dyes were bound to a definite number of available acidic groups in the fibre, probably at the ends of the polymer chains. Using a special non-aqueous titration method with sodium hydroxide as well as quantitative studies on the adsorption of the free carbinol base of Malachite Green, *Glenz* and *Beckmann* thus estimated the acidic group content and found a fairly close degree of correlation between the maximum extent of dye sorption and the number of acidic groups in the fibre. The latter was in close agreement with the number of chain ends calculated from the molecular weight of the fibre [70].

Further evidence in favour of this mechanism is to be found in the work of *Vogel* et al. [86] on Orlon 42 who found that the sulphur content (0.09%) corresponded to the number of acidic groups present (32 m.moles/Kg). *Weltzien* and *Fester* [87] with improved techniques confirmed that Dralon and Orlon 42 contained $-SO_3H$ groups at the chain ends capable of forming a bond with cationic dyes and the results of *Rosenbaum* [66] are in general agreement with this conclusion. Indeed cationic dyes have no substantivity for basically-polymerized acrylonitrile [88].

Remington and *Schroeder* [89] have pointed out that in the undyed fibre the acidic groups are neutralized by colourless cations, so that the fibre could be considered to act like an ion-exchange resin during dyeing, absorbing dye cations which displace colourless cations already in the fibre [79, 89]. The colourless cations are usually sodium [13, 79], but potassium, calcium and $[(CH_3)_2NH_2]^+$ cations have also been found [90] in other commercial acrylic fibres, so that, as will be discussed later in relation to the uptake of cationic retarders, the different rates of desorption of the cations are important.

Removal of the colourless cations by an ion-exchange process yielded acid group contents equivalent to the *Langmuir* saturation values [79]. Further correlation was obtained by estimating acidic group content by determining the sulphur content and from calculations of the reciprocal of the number-average molecular weights. Further experiments on polymer-dye systems in which the polymer had first been freed of metallic cations demonstrated that addition of electrolytes caused a decrease in dye uptake, due to competition with the dye for acid groups in the polymer [79]. The practical use of this technique to promote levelling will be described in due course.

Cegarra [13] has proposed the following reaction scheme for the dyeing of acrylic fibres containing anionic (i.e. acidic) sites with cationic dyes.

Fibre $\quad F{-}A(M,H) \rightleftarrows F{-}A^- + (M,H)^+$

Fibre and dye in liquor (1)

Dye $\quad D{-}X \rightleftarrows D^+ + X^-$

$\uparrow\downarrow$

$F{-}AD + (M,H)^+ + X^-$

Dye-fibre + ions in solution (2)

where FA = acrylic fibre, D = dye
M = metallic cation (usually Na^+), X = dye anion

Three important conclusions can therefore be derived:
(i) the number of dye sites depends on the number of acidic groups and on whether these groups are dissociated and accessible to enable interaction between the dye and the fibre to occur,
(ii) the dye must be dissociated for interaction to occur, and
(iii) factors which influence the degree of ionization of the fibre or of the dye will affect the dye uptake.
The amount of dye absorbed by acrylic fibres is often slightly higher than that expected from the number of acidic groups. This anomaly has been attributed to dissolution of a small amount of dye in the fibre [70, 91]. The work of *Sand* [67] confirmed the ionic interaction between cationic dyes and acrylic fibres but the affinity of 58.6 kJ.mole^{-1} on Orlon 42 dyed at equilibrium was higher than would be expected, and it has been suggested that other forces must play a part in the interaction.
Cegarra, Puente and *Valldeperas* [92] attempted to establish whether a cationic dye combines first with the strongly acidic groups and afterwards with the weak acidic groups, or whether simultaneous combination occurs. However, it was concluded that a certain amount of dye was adsorbed by a solution mechanism and this factor precluded the clarification of the mode of interaction of the dye with specific sites. In equilibrium dyeings, possible hydrolysis of some of the acidic groups or of the dyes [93] may also be complicating factors. In addition, overdyeing i.e. sorption of dye in excess of the number of charged groups, by analogy with the overdyeing of acid dyes on nylon, may arise as a consequence of the high affinity of the dye [26].
The detailed examination of site mechanisms in acrylic fibres has usually implied at least a partial adherence to a simple *Langmuir* isotherm, but *Guion* et al. [69] have pointed out the need for caution in the interpretation of the data. Thus it was suggested that the differences observed between theory and experiment can be well outside experimental error. It was concluded that this situation could be accounted for by taking into account the sorption of the anions and also the ionization of the weakly acidic groups as well as the strong acidic groups in the fibre.
From the foregoing brief account it is clear that further systematic work is required to clarify the finer details concerning the site mechanisms of dyeing of cationic dyes on acrylic fibres.

4.4. The effect of temperature and carriers on dye uptake

It has been demonstrated as a result of many studies [92, 95–100] that the glass-transition temperature T_g of an acrylic fibre plays a major role in controlling the rate of dye diffusion. At temperatures below the glass-transition temperature effectively little or no dyeing occurs because of the very compact structure of the fibre.
Rosenbaum [95] explained this marked temperature-dependence in terms of the free volume theory and *Aharoni* [101] also concluded that above T_g the free volume would be expected to markedly increase as a result of the greatly increased segmental mobility of the polymer chain molecules. Hence, above T_g dye penetration occurs and from the Arrhenius equation the expected relation between the apparent coefficient D_a and the absolute temperature T [102] is given by

$$D_a = D_o\, e^{-E/RT}$$

$$\text{Thus} \quad \log_{10} D_a = \log_{10} D_o - \frac{0.4343\,E}{R} \cdot \frac{1}{T}$$

where D_0 is a constant, E is the apparent activation energy of diffusion and R is the gas constant.
However the plot of log D versus $1/T$ was shown by *Rosenbaum* not to be linear, as expected, but increasing values of E were obtained with decreasing temperature [95]. The deviation from linearity was described in terms of the free volume theory of polymers. The diffusion coefficient has been shown to depend upon the site content of the acrylic fibre, for the values of D_a were found [103] to decrease with decreasing site content when a series of polymers with varying site contents were dyed at 95 °C.
The significance of these results has been pointed out by *Asquith* et al. [100, 103] who assert that an important factor that must be taken into account is the change in the number of dye sites accessible to dye molecules with increase in temperature in the range 25–100 °C studied by *Rosenbaum*. Thus above T_g all or nearly all of the acidic sites are accessible and the number of sites should correspond to the saturation value S of the fibre. Hence specific values of D_a can be obtained above T_g but below T_g the number of accessible sites is considerably reduced. Thus measurements of the equilibrium adsorption isotherms at various temperatures for a cationic dye on Acrilan were carried out [103] utilizing the *Langmuir* equation in the form

$$\frac{D_\theta}{D_\sigma} = Kn - KD_\theta = K(n - D_\theta)$$

where D_θ, D_σ are the dye concentrations in the fibre and in the bath respectively, K is a constant and n is the number of sites accessible for dyeing. From this equation a plot of D_θ/D_σ against D_θ should yield a linear relation giving an intercept on the D_θ axis on n. Above T_g, n is at the maximum value and should be approximately constant so that $n_{max} = S$, the saturation value of the fibre. For the Acrilan sample used, n was approximately constant above 85 °C and this could be regarded as the dyeing transition temperature. A re-examination of *Rosenbaum*'s experimental results above 85 °C yielded the expected direct relationship [103].

The diffusion of cationic dyes can thus be best explained in terms of segmental mobility and *Rosenbaum* [95, 106] fitted both the diffusion data and the change in the physical properties of the fibres with temperature to the *Williams, Landel* and *Ferry* (WLF) equation [107]

$$\text{Log}\ \frac{D_T}{D_{Tg}} = \log \frac{1}{a_T} = \frac{A(T-T_g)}{B+(T-T_g)}$$

where A and B are constants
T = ambient temperature
T_g = glass-transition temperature.

According to this equation the diffusion of dye is governed by $T - T_g$ only and therefore the rate of diffusion may be increased either by raising T or by decreasing T_g, or both. In this way *Ingamells* et al. [98, 99] have strikingly demonstrated that the action of carriers function by effectively lowering the glass-transition temperature and that this has the same effect on the rate of dye diffusion as an increase in temperature of the dyebath. An important distinction drawn by *Ingamells* [108, 109] is that it can be shown that compounds that are most effective in lowering the glass-transition temperature are least effective in causing fibre swelling. This has ruled out fibre swelling as the most likely cause of increased rate of dye diffusion in acrylic fibres as a result of chemical treatments.

It has been strikingly demonstrated [110] that the solubility parameter concept may be utilized to show that the greater the intensity of the polar interactions between the carrier molecules, the greater are both the reduction in T_g of the fibre and the increase in the diffusion coefficient caused by the carrier. This has been demonstrated not only for aqueous dyebath conditions but also for benzyl alcohol/perchloroethylene systems [98, 110, 111].

An interesting result of viscoelastic studies on Acrilan film in air and in solutions suggests that in fact the position in thermodynamic terms is more complex [100]. Transition temperatures of T_1 = 57 °C and T_2 = 84 °C were reported in water and 56 °C and 110 °C respectively in air. *Gur-Arieh* and *Ingamells* [99] have reported values of 56 °C for Acrilan in water and 90 °C in air. The transition temperature T_2 (84 °C) appears to be the important transition for normal dyeing, but from the dynamic modulus curve it was considered [100] that the T_1 transition, though playing no important role in dyeing, corresponded to the definition of the glass-transition temperature in the true thermodynamic sense.

The use of p-nitrophenol (15 g/l) reduced the activation energy of dyeing from 259.6 to 163.3 kJ.mole^{-1}, and a transition temperature of 57 °C was observed using this compound compared with 83 °C in a conventional dyebath. It was considered [100] that the use of such dyeing assistants could effectively open up the fibre structure at temperatures below T_2 and allow the transition T_1 to come into play. Fibre swelling was shown again to be unimportant, but *p*-nitrophenol may exert an additional influence by acting on the dye molecules in solution, breaking down aggregates and enabling the smaller dye particles to penetrate the relatively low free volume which exists between temperatures of T_1 and T_2 [100]. It is to be hoped that further experimental work will help to clarify this complex situation and shed more light on the effects of temperature and carriers on the fibre structure.

4.5. The relationship between dye sites and saturation

The dyeing of cationic dyes proceeds by the sodium, potassium, hydrogen or other cations present in the fibre being replaced by dye cations [13, 79, 89, 90]. Equilibrium studies have suggested that the dye concentrations in the fibre (C_F) and in the dyebath (C_S) appear to follow a *Langmuir* isotherm with pronounced saturation and high affinity [65, 70–75, 79, 86]. Stoichiometric considerations have established that the maximum number of dye cations absorbed is equal to the number of accessible anionic sites in the fibre [70–72, 90].

From this work, constants, characteristic of dyes and fibres have been introduced. The number of dye sites available per unit weight of the fibre has thus been termed the Fibre Saturation Value [73]. This is determined [112] as that quantity of pure hypothetical dye of molecular weight 400 (calculated as % o.w.f.) which yields 90% dyebath exhaustion when applied for 4 h. at 100 °C, *p*H 4.5, liquor : goods ratio 100 : 1. The fibre saturation value S_F has also been similarly applied [113] where $A = 1.1\ S_F$. Thus the quantities (p) of commercial dyes that may be transformed into molar units of A give the values of the Dye Saturation Factor (f) which decrease for a given dye with increase in diluent concentration. This is an important practical consideration for f may vary for different commercial dyes of the same chemical constitution. The value of A is sensibly independent of liquor range and temperature under normal dyeing conditions [79] but increases slightly with increasing *p*H except for acrylic fibres containing weak acidic sites e.g. carboxyl, where there is a significant increase in the value of A.

The relative saturation S_{rel} defined from

$$S_{rel} = \frac{\Sigma pf}{A}$$

is the ratio of the number of cations in the system to the number of dye sites in the fibre [113]. Clearly cationic retarders with affinities similar to cationic dyes must be included in the term Σpf and this will be discussed at a later stage.

4.6. Relative affinity of cationic dyes

The affinity of cationic dyes for acrylic fibres is important because of its influence upon equilibrium exhaustion, blocking effects in dye mixtures, the use of electrolytes and retarders, and also on the migration and

levelling characteristics of the dyes [86]. Absolute affinities are difficult to determine. Accordingly the concept of Relative Affinities (A_r) has been widely applied [73, 113]. A_r values are comparative values, determined from equilibrium exhaustion of the dye in the presence of a standard dye or cationic retarder for which A_r is assumed to be unity [114, 115].
As *Beckmann* [113] has pointed out, different dye makers have used different rating scales and standards so that the A_r values are not directly comparable. Interrelation between scales is possible however for dyes of identical chemical constitution (i.e. C.I. number) as A_r is not affected by the presence of diluents.
It has been demonstrated that a high A_r value corresponds to low dye migrating power so that such dyes are influenced less by other cationic dyes, cationic retarders or electrolytes. However they are influenced more strongly by anionic retarders than are dyes of lower A_r values [114, 115].

4.7. Causes of unlevelness in acrylic fibre dyeing

The essential stage in the dyeing of acrylic fibres with cationic dyes is salt formation. As this is almost irreversible the wet fastness properties are very high, but the migration and levelling performance of the dyes is poor [116]. Because of this fact recourse has to be made to controlling the rate of adsorption of the dye, for the comparatively rapid rates of diffusion of dyes at around the glass-transition temperature T_g combined with the increased accessibility of the anionic sites can lead to unlevel dyeing if suitable precautions are not observed.
Three fundamental causes of uneven exhaustion have been cited [116], namely:

(i) Differences in the physicochemical structure of the fibre.
(ii) Temperature differences in the dyebath.
(iii) Concentration differences in the dyebath.

By appropriate control procedures the fibre producer endeavours to minimise differences in fibre dyeability, but this is a difficult task because of the complexities of fibre manufacture. From the practical dyeing viewpoint considerable research and development work has been directed to the control of temperature and concentration differences in the dyebath [26, 116–118]. The latter has generally been achieved by:

(i) *p*H control
(ii) addition of electrolyte
and particularly by (iii) the use of retarding agents.

The levelling effects of both *p*H control and additions of electrolyte are limited by the fibre type and the dye selection, so that in practice temperature control [117, 118, 119–121] and the addition of retarders [26, 113, 117, 122, 123] are of the greatest practical benefit. In addition the efficiency of liquor circulation exerts effects on migration and levelling [13].

Because of the very high activation energy of dyeing for cationic dyes (~293 kJ.mole^{-1}) temperature differences within the dyebath can have a very marked influence on the rate of dyeing [95, 114, 115, 124]. A temperature change of only 1°C can increase the rate of dyeing by 30% [97]. For this reason, dyemakers evolved constant temperature dyeing systems in which the material was rapidly raised to the requisite constant temperature for the fibre and dye selection in use and the dyes added at the dyeing temperature [117]. In this manner differences in dyeing rate, as a result of adding the dye at low temperatures and then following a time-temperature profile involving a single or multistage rate of temperature rise, were avoided. Thus, *Herbulot* [118] showed that better levelness could be obtained at a constant temperature as the absorption curve shows a gradual and regular rise. In conventional dyeing machines temperature fluctuations in the material can occur in different parts of the machine as the temperature is raised at a constant rate, since the distribution of heat throughout the machine is not instantaneous.

4.8. Migration of cationic dyes

In a series of levelling trials on C.I. Basic Blue 54 (a high affinity dye) *Zimmerman* and *Cate* [125] demonstrated that the levelness increased rapidly with increasing concentration up to 40% (o.w.f.) sodium sulphate and thereafter increased at a much slower rate. Sodium sulphate has thus been used [73, 126–128] to aid migration particularly at temperatures around 110°C in the dyeing of loose stock or slubbing [128]. However *Cegarra* [13, 129] from a statistical analysis of the effect of temperature (105–120°C), time (30–60 min), *p*H (4–5) and electrolytes (5–15% o.w.f.) on the migration of several dyes on Ultrapan continuous filament has shown that temperature is the most important variable in controlling migration. The time of dyeing had some effect but except with one particular dye, electrolyte had little influence while *p*H had no effect on migration.
With cationic dyes of low substantivity migration does occur [73, 86] and is important, but normally migration is only slight at the temperatures normally employed. As a result careful control of temperature and the use of retarders are normally advocated to control the rate of dyeing in order to obtain level results [13, 73]. In continuous filaments where the fibre substantivity may vary along the fibre length difficulties have sometimes been experienced and it becomes essential to utilize the migration properties of the dyes [13, 73].

4.9. The effect of pH on cationic dye uptake

A detailed study of the equilibrium adsorption of cationic dye by three experimental copolymers has been conducted by *Balmforth, Bowers* and *Guion* [79]. With an acrylonitrile-vinyl acetate copolymer made with a redox catalyst little change was observed in the normal *p*H range employed for dyeing acrylic fibres

(*p*H 4–5.5). However above *p*H 6 a marked increase in adsorption is noted. Thus a change in equilibrium adsorption at finite dyebath concentration would be reflected in a change in the slope of the *Langmuir* isotherm. Little or no change in the intercepts of the *Langmuir* isotherms measured at infinite dyebath concentration at different *p*H values would be expected on the assumption of a considerable difference in affinity between hydrogen ions and dye cations for the polymer.

This however was shown not to be the case, for the *Langmuir* intercepts are *p*H-dependent. *Balmforth* et al. [79] resolved this dichotomy by a refined potentiometric titration technique which demonstrated the presence, and indicated the amount, of at least two types of acid groups in polymers made with redox catalysts, corresponding to weak and strong acid groups respectively. The ionisation constant and the structure of the weak acid groups were conjectured to be similar to that of carboxylic acids. An interesting observation was that a polymer catalysed with azo-bis-isobutyronitrile (AIBN) contained no acidic groups and did not absorb cationic dyes. This was taken as evidence that although non-coulombic attraction between the nitrile groups in the polymer and the dye cations could contribute in a large measure to the high affinity of basic dyes for acrylic polymers [19, 130], this in itself did not appear sufficient for adsorption to take place.

The introduction of only 1% methacrylic acid, or of acrylic acid, by copolymerization [79] resulted in a dramatic increase in dye adsorption, particularly at high *p*H values, although changes are also evident below *p*H 6. The introduction of strong acid groups by copolymerization of sodium styrene sulphonate does not however alter the nature of the response to *p*H changes, but merely causes a general increase in dye adsorption throughout the *p*H range studied.

Commercial acrylic fibres from different origins exhibited very similar behaviour, potentiometric titration indicating the presence of a mixture of weak and strong acid groups in various proportions [79]. The former type dissociate more readily so that the most marked *p*H response was that of Courtelle E (Courtaulds) which appeared to contain a very large number of weak acid groups (154 m.eq/Kg) and no strong acid groups. Thus the dye adsorption dependence on *p*H of the latter is very marked below *p*H 7. However in no sample of polymer or fibre studied was the dye adsorption, even at high *p*H, found to exceed the total number of acid groups present [79]. Accordingly it was concluded that dye adsorption could be adequately described by the *Langmuir* equation, provided suitable modification was made for the effects introduced by the presence of the two types of dye-sites present and also for the desorption of cations initially present in the fibre.

The effect of *p*H is not only greater on equilibrium dye adsorption on fibres which contain weak acidic groups, but is also clearly seen in kinetic studies within the *p*H range 4–5.5 normally used in practice because of the instability of cationic dyes [13]. Thus the rate of dyeing increases more markedly with Courtelle LC, which contains weak acidic groups only, than with Leacril 16, which contains both weak and strong acidic groups. From the foregoing discussion it is clear that attempts to control the rate of dyeing in order to achieve levelness and reproducibility are only successful with those fibres which contain weak acidic groups. However in practice the use of electrolytes, retarders and the control of temperature are widely employed for this purpose [73].

4.10. The effect of electrolytes

The rate of dyeing of cationic dyes is reduced by the addition of electrolytes like sodium sulphate to the dyebath [73, 126, 127, 131]. The more mobile sodium cations are considered to be preferentially absorbed by the fibre and subsequently displaced by the dye cations [13, 73]. The additions of electrolytes also reduce the negative electrokinetic potential of the fibres which in turn decreases the rate of dyeing [70, 73]. Additions of sodium sulphate thus have a levelling effect on dyeing acrylic fibres with cationic dyes, but also affect the dyeing equilibrium [131]. Other compounds such as sodium chlorate have also been suggested [132], but in practice most dye manufacturers recommend the use of sodium sulphate [13]. 10% Sodium sulphate is a moderate retarder [13, 73, 133] and such additions have enabled a reduction of 20–30% in the amount of organic-based retarder required to be achieved [73]. The most lucid account of the retarding effects of different concentrations of selected inorganic cations and anions is to be found in the systematic studies by *Bonche* [134, 135]. The major effects were attributed to the action of the cations in the order potassium > sodium > lithium > aluminium. The smaller size of the hydrated potassium cation resulted in a lower approach distance and a higher diffusion coefficient. The sodium ion with a higher ionic volume and being less electropositive is thus less effective in retarding dye uptake. The retarding effect was independent of the ionic charge on the cation, but was considered to depend primarily on the following parameters, in decreasing order of effectiveness

(i) Mechanical obstruction of the fibre pores.
(ii) Reduction in the zeta potential at the fibre surface in the early stages of dyeing, by adsorption of inorganic cations.
(iii) Ionic interaction with the acidic groups present in the fibre substrate.

The action of the anions is of less importance [133], the retarding effect [135] decreasing in the order

SO_4^{2-} and Cl^- > PO_4^{3-} > SCN^- and I^-.

It is however important to appreciate that the effectiveness of electrolytes in retarding cationic dye uptake decreases with increase in temperature and in addition the retarding effect is greatest with fibres containing weak anionic groups e.g. Courtelle [13]. For these and other reasons considerable research and development efforts have been directed towards the application of organic-based retarders in order to achieve level dyeings on acrylic materials.

Apart from retarding the rate of dyeing, the equilibrium adsorption of dye is reduced because of the competitive effects of the cations and anions of the electrolyte with those of cationic dye. This is also clearly demonstrated in the results of *Balmforth, Bowers* and *Guion* [79].

4.11. The action of retarders

4.11.1. Anionic retarders

Kellett [128, 136] and *Leddy* [137] have discussed the action of anionic retarders for the dyeing of cationic dyes on Orlon 42 and Acrilan 16, and much useful information is summarised elsewhere by *Beckmann* [113]. It was demonstrated that Maxilon (Gy) dyes in the presence of an anionic auxiliary (Irgasol DA) and a nonionic auxiliary (Tinegal NA) could give level dyeings, the principle depending on the ability of the anionic compound, which contained sulphonic groups, to interact with the cationic dyes forming addition compounds which have little or no affinity for the fibre [64, 73, 113, 124, 128, 136–138] viz.

$$Dye^{+} + Retarder^{z-} \rightleftarrows (Dye.Retarder)^{-}$$

Provided the retarder anion contains two or more sulphonic acid groups the 1 : 1 addition compound retains some solubility [73, 75, 139–142], the function of the nonionic auxiliary being to aid keeping the cationic-anionic complex, i.e. the addition compound, in a suitable state of dispersion [128, 137]. The addition compounds formed by anionic retarders based on sodium dinaphthylmethane sulphonates do not enter the fibre so that the rate-controlling reaction is shifted from the fibre or the fibre surface to the dyebath [64]. However *Takaoka* and *Seki* [124] have suggested that the retarding effect increases with an increase in the hydrophobic character of the anionic auxiliaries used in their study (polyoxyethylene alkyl[aryl]sulphates) and Irgasol DA. In addition diffusion within the fibre was still the rate-determining step, since only free dye, and not the anionic retarder-cationic dye complex, diffused.

At temperatures below the boil the complex is very loosely bonded to the fibre, thereby permitting some migration or levelling on the surface of the material. As the temperature rises, this evenly distributed loose complex breaks down, allowing the cationic dyes to accumulate at the fibre surface and diffuse into the fibre [113, 128, 136, 137]. The concentration of free dye cations falls well below the value required for saturation of the fibre surface so that dyeing does not proceed from a saturated surface-layer [113]. In addition the rate of dyeing and equilibrium exhaustion is reduced, the effect being largely dependent upon the dyes used. With dyes of high affinity the equilibrium is in favour of complex formation so that the compatibility values of the dyes are changed, enabling dyes whose rates of dyeing are normally different to be absorbed at about the same rate [73, 113]. In practice to prevent precipitation a surplus of the anionic retarder is used together with nonionic auxiliary [73, 137], and the many other considerations in the selection and use of retarders have been discussed in detail elsewhere [113, 138–142].

4.11.2. Cationic retarders

Cationic retarders have been very widely used to promote level dyeing of acrylic fibres and the pratical details have been discussed in many papers [48, 50, 64, 73, 77, 116, 117, 123, 126–128, 131, 138, 139, 143–150]. Cationic retarders are water-soluble organic compounds which, in water, form colourless cations with an affinity for the fibre [73, 113]. These cations thus compete with the dye cations for the anionic dye sites within the fibre and at the fibre surface. Their action is twofold. Firstly they decrease the rate of exhaustion by reducing the dye concentration gradient effective for diffusion and secondly they increase the total number of cations effective for relative saturation [113]. The amount of retarder used however must be carefully calculated for each dyeing in order to avoid problems due to "oversaturation" or "blocking" and the suppliers of cationic retarders provide the necessary information to simplify the calculations involved.

As *Beckmann* [113] has discussed, the rate of exhaustion can be brought about more cheaply by appropriate temperature control. However the temperature affects only the apparent diffusion rate of dye in the fibre, D_{app}, but the concentration gradient and the relative saturation values are unaffected. With cationic retarders the converse is true, with D_{app} remaining unchanged, while in contrast to the anionic retarder system there is no direct interaction with the dye so that the compatibility values of cationic dyes are unaffected. In pale dyeings adsorption is rapid and cationic retarders are essential to improve levelness, as temperature control is ineffective. As the value of S_{rel} is increased, the migration of cationic dyes is also improved.

In chemical terms, cationic retarders have been based [146] on quaternary ammonium salts with long aliphatic chains and also aromatic groups which determine the affinity [77, 113, 145, 148]. Compounds based on alkylpyridinium salts, imidazole and imidazolium salts, alkyldiamines, alkylpolyamines, sulphonium and phosphonium derivatives have also been reported [144]. Structure-activity relationships have been studied for a number of retarder systems [77, 124, 145, 148]. *Cohen*

and *Endler* [148] in a study of long chain amines and their derivatives for the Orlon/Sevron Green B system (C.I. Basic Green 3, Du Pont) concluded that both unsaturation and the nature of the anion had little effect. The effectiveness of retardation varied inversely with the molecular weight of the quaternizing compound while there was a progressive increase in the induction period of very low dyeing rate taking place with increase in chain length from C_{10} to C_{16}. In another study it was demonstrated [124] that the cationic retarders had higher diffusion coefficients in the fibre than the dyes, with a smaller activation energy of diffusion. The retarders were thus absorbed at lower temperatures (65–70 °C) than the dyes (80–85 °C), the retarding effect depending on the correlation between the relative affinity of the dyes and that of the retarders.

Increase in chain length was shown to be important in the work of *Heimann* and *Feichtmayr* [77] and strikingly demonstrated by *Schiffner* and *Borrmeister* [145] for alkyl pyridinium compounds and alkoxycarbonylmethylpyridinium chlorides. For compounds of chain length C_{8-18}, increase in chain length increased the retarding effect and decreased the exhaustion of the dyebath. Further quantification of this relationship is exemplified by a study of the compatibility behaviour of various cationic retarders to which a C_R value was assigned, on similar principles to the compatibility classification of cationic dyes [149]. The results have clearly demonstrated that as the chain length increases the C_R values increase. However for future work the influence of such factors as conformational mobility, solubility, shielding of charge by substituents and electronegativity of chain substituents on the compatibility behaviour and retarding effect of cationic retarders remain, as yet, unexplored.

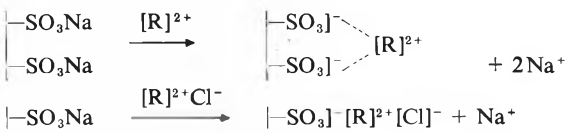
Analytical studies enabling the simultaneous exhaustion of cationic retarders and cationic dyes to be determined have been carried out using a titration-spectrophotometric method [125] and in an elegant fashion using atomic absorption analysis [90]. In the latter paper the ion-exchange mechanism for the dyeing of cationic dyes was corroborated by measuring the dye sorption and correlating the values with the desorption of the cations (41 m.eq/kg Na^+, 5 m.eq/kg K^+, 3 m.eq/kg Ca^{2+}, 1 m.eq/kg $[(CH_3)_2NH_2]^+$) present in the fibre. Apart from the reaction

$$F{-}SO_3Na \xrightarrow{[R]^+} F{-}SO_3[R] + Na^+$$

it was concluded that at 95 °C about 2.5 m.eq/kg of Na^+ desorb very rapidly from Orlon 75 into the bath, possibly via the reaction

$$F{-}SO_3Na \xrightarrow{H_2O} F{-}SO_3H + NaOH$$

The uptake of the cation of N-dodecyl-NN-dimethyl-N-benzyl ammonium chloride [DBBA]Cl, yielded a linear sorption relation against $t^{1/2}$ in the range studied, while the experimentally determined and the calculated sorption values were in excellent agreement. Comparative studies using Indene Yellow and [DDBA]Cl illustrated the more rapid uptake of the retarder [90]. For cationic retarders with divalent cations and with Cl^- as the counterion it was shown [90] that of the two possible reactions



only the former occurred, liberating two sodium ions. It is to be expected that further refinements in such analytical techniques will yield valuable results in this complex field of interrelations.

4.11.3. Cationic polymeric retarders

A recent development is the use of cationic polymer retarders which contain up to several hundred cationic groups per molecule [151–153]. These are strongly adsorbed at the fibre surface forming an electric potential barrier. Diffusion within the fibre does not occur so that S_{rel} is unaffected, leading to little or no improvement in migration [113]. However the dye adsorption and rate of dyeing are dramatically reduced and in addition polymeric retarders do not interfere with crimp development in fabrics containing bicomponent acrylic fibres, so that the fabric aesthetics are not altered [152, 153]. It has been reported that certain types of cationic polymeric retarder can affect the dyeability behaviour and compatibility behaviour of the dye, particularly those of low affinity [113].

4.12. The compatibility of cationic dyes

Compatibility in dye mixtures is extremely important for level dyeing and in the evolution of rapid dyeing processes on acrylic materials [73, 114, 115, 140, 154–156]. Compatible dyes exhaust at the same rate, so that as dyeing proceeds the dyeing shows an increase in depth but not in hue. Many studies have confirmed that the absorption of individual cationic dyes is influenced by the presence of other dyes in the dyebath [73, 140, 154–156]. The poor migration properties of cationic dyes demands that the dyeings should be as level as possible from the start of dyeing, a situation almost impossible to control adequately using an incompatible dye combination [13, 73, 114]. Where compatible dyes are employed experience has shown that shorter dyeing times and improved reproducibility in matching and levelness are obtained while less levelling agent is required [113].

A standard test method has now been instituted to characterize cationic dyes on acrylic fibres according to the Compatibility Value K which ranges from 1–5, the dyes of lower *K* value exhausting more rapidly [112]. Thus equal dyes of equal *K* value are compatible in combination on each acrylic fibre under all practical

exhaust-dyeing conditions, except in the presence of anionic dyes or auxiliaries. They are of lesser importance in determining the selection of dyes for printing processes employing fixation in steam.

The value of *K* is primarily related to affinity so that the effect of cationic retarders and electrolytes is more pronounced with dyes of higher *K* value. The relationship between *K* and the diffusion coefficient is of a lower order so that the *K* value alone does not determine the rate of dyeing [73, 114, 115].

Naturally enough there is some degree of interrelation between compatibility, affinity and the molecular structure of cationic dyes, and efforts continue to be devoted to synthesizing dyes with a defined affinity by altering the nature of the substituent groups. If the incorporation of an additional hydrophilic substituent, or the substitution of a more hydrophilic for a less hydrophilic substituent is carried out the affinity of the dye for water is increased, so that effectively the affinity for the fibre is decreased [157]. Conversely incorporation of hydrophobic substituents increases the affinity for the fibre and lowers the affinity for water. For dyes with similar diffusion coefficients an increase in affinity of the dye for the fibre represents a reduction in *K* value, because the dye of higher affinity occupies more space at the surface and thus is absorbed preferentially. Similarly a reduction in affinity for the fibre results in higher *K* values, but a complex situation may develop where bulky hydrophobic substituents may block the diffusion of dye in the fibre thereby mutually balancing out the effect.

Several examples of dyes synthesized with specific *K* values have been cited [157]. Thus by incorporating sulphonamide or sulphonyl groups dyes of low affinity and high *K* value were prepared. Replacement of the methyl group bound to the thiazole nitrogen by a 2-hydroxypropyl group or a carboxyethyl group gave a similar result for benzthiazole azo dyes. Alkylaryl groups e.g. benzyl groups on the other hand led to higher fibre affinity and lower *K* values. A particularly interesting series illustrating the relationship between chemical constitution and compatibility has been illustrated by *Siepmann* [157] for three blue dyes of *K* values 1.5, 3 and 5 respectively (see Fig. 2).

This has been a fertile area for developments by the dye makers, who have studied this relationship between the chemical constitution of cationic dyes, the rate of diffusion and their affinity for acrylic fibres in depth to produce more satisfactory migrating cationic dyes for rapid dyeing and exhaustion dyeing processes.

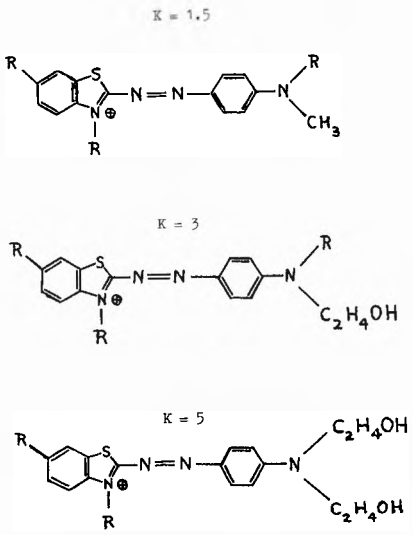


Fig. 2: Effect of substituents on the compatibility of benzthiazole cationic dyes

4.13. Migrating cationic dyes

A major recent development has been the synthesis of migrating cationic dyes which enable acrylic fibres of rapid, normal, and slow adsorptive capacity to be dyed [158–163]. These cationic dyes possess a cation weight of less than 310, a defined parachor value < 750 and a log *P* value < 316. These may be used with electrolytes and specified types of cationic retarder. Particularly suitable dyes [161] have cation weights < 275, parachor values < 860 and log *P* values, calculated without the effect of the charge of the dye cations being taken into account, of < 2.8. Typical examples are illustrated in Fig. 3.

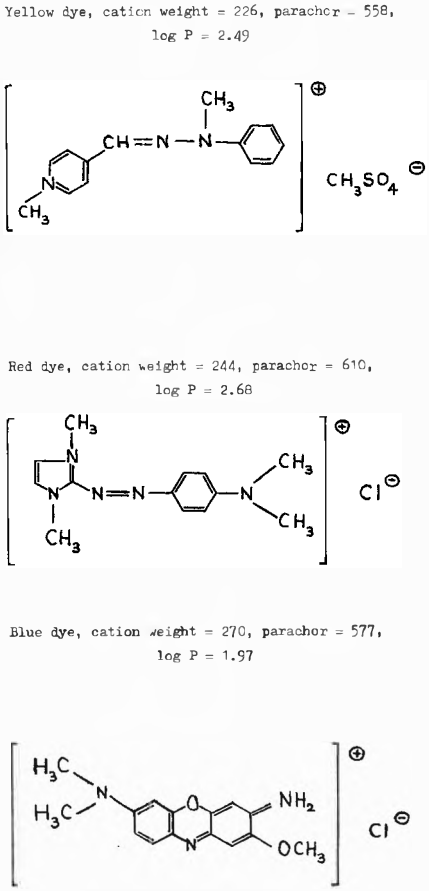


Fig. 3: Examples of migrating cationic dyes

Chlorides, sulphates, onium chlorides or metal halides, for example, zinc chloride salts of azo dyestuffs, such as monoazo dyestuffs or hydrazone dyestuffs, diphenylmethane, methine or azomethine dyestuffs, ketoneimine, cyanine, azine, oxazine or thiazine dyes are mentioned in the patent application [161]. Originally three dyes were available but two further dyes have now been introduced, so that the range consists of a yellow, golden yellow, scarlet, red and a blue. The blue dye has a lower light fastness on Courtelle, possibly because of the presence of the carboxyl end groups in the fibre which are believed to lead to lower light fastness as previously discussed by *Zollinger* [62].

A migrating cationic retarder is preferably used for pale depths, but the range of Maxilon M (Ciba-Geigy) dyes is claimed to be characterized by a high rate of diffusion, low affinity and excellent migration properties at the boil [158–160]. These dyes are thus relatively small molecules compared with conventional cationic dyes and possess good hydrophilic properties.

The rate of dyeing of cationic dyes may be characterized by the values of tan α, the angle of the line relating the amount of dye absorbed versus the square root of the dyeing time at constant temperature [158, 162–164]. As in other dyeing systems the higher the ionic weight of a cationic dye, the slower the diffusion at a given temperature, represented by the value tan α_∞. This is the equilibrium value observed when the accessible surface of the fibre is completely covered by the dye [164]. The mobility of the dyes in the fibre however is another important factor influencing diffusion processes and this has been shown to be dependent upon the specific surface of the fibre, the physical structure e.g. glass-transition temperature and compactness, the chemical composition (i.e. the nature and number of the acidic sites) and the activation energy [158].

In terms of chemical structure the hydrophobicity of the dye generally increases with ionic weight and the compatibility requirements are that

$$\tan \alpha_{\infty 1}(K_D)_1 = \tan \alpha_{\infty 2}(K_D)_2$$

where tan α_∞ is a measure of the rate of diffusion and the constant K_D is a measure of the affinity defined from

$$K_D = \frac{[D_f]\,[Na_{sol}]}{[D_{sol}]\,[Na_f]}$$

and in practice the K values (i.e. the compatibility constants) of the dyes linearly related to the product K_{D1} tan α_∞, K decreasing as K_D tan α_∞ increases [158].

As a result of detailed studies it became apparent [158, 162] that one could synthesize products of high ionic weight and the correct balance of hydrophilicity and hydrophobicity to give a slow rate of exhaustion under isothermal conditions in the critical temperature range at 80–90 °C. However these dyes do not migrate at all so that correction of differences due to the fibre substrate is impossible and ring dyeings are produced in continous dyeing processes. Consequently attention was directed towards the synthesis of dyes of low affinity (i.e. low K_D value) with a high rate of diffusion (i.e. high tan α_∞). The cation weight must therefore be small and consequently quite hydrophilic [158].

Dyes with these properties are migrating cationic dyes and the structures with the smallest ionic weight and the smallest affinity (i.e. the largest hydrophilicity) show the highest ability to migrate (M) viz.

$$M = \frac{100\, D_{M(t)}}{D_{M(\infty)}}$$

Voltz [158] has demonstrated that the behaviour corresponds closely to the equation given by *Gerber* [165] for the rate of migration

$$\text{Tan } \gamma = f(D^{1/2}/K_D)$$
$$= g(\tan \alpha_\infty / K_D)$$

Hence the migration rate increases with increasing coefficient of diffusion D and decreases with increase in affinity K_D. In general the compatibility constant K lies in the range 2.5–3, and if a cationic retarder has to be used it should possess similar properties to the migrating dyes, namely a high rate of diffusion and a low affinity [158, 161]. Migration properties are influenced principally by the temperature, the nature of the fibre and the presence of other cations in the bath. Thus cationic retarders promote more level dyeing and electrolytes in small concentrations improve migration up to a maximum (5% NaCl and 10% Na_2SO_4) but high concentrations diminish migration [158–161].

5. Disperse dyes on acrylic fibres

5.1. Introduction

Some ten years ago, disperse dyes accounted for some 20% of all dyed acrylic fibre [128], but this has now [166] probably declined to a figure as low as 5%. The use of disperse dyes is thus often limited to special purposes such as shading at high temperature, for their deficiencies [128] include

(i) Inadequate wet fastness properties for modern requirements.
(ii) Poor build-up and a lack of reproducibility near the limit of build-up.
(iii) Large variations in yield with liquor to goods ratio.
(iv) A generally duller colour gamut than that obtainable with cationic dyes.

The reasons for these deficiencies are intimately related to the structure of the dyes and the dye-fibre interrelationship and these will now be considered in depth.

5.2. Disperse dyes

A disperse dye has been defined [60] as a "substantially water-insoluble dye having substantivity for one or

more hydrophobic fibres e.g. cellulose acetate, and usually applied from a fine aqueous dispersion".
The discovery, development and application of disperse dyes [61, 167] have centred on the following main types of chemical structure

(i) Nitrodiphenylamine (mainly yellow, orange-yellow)
(ii) Azo (yellow, orange, red, a few violets and blues)
(iii) Anthraquinone (bluish-reds, violets, blues, bluish-greens)
(iv) Styryl(methine) and heterocyclic ring structures such as quinophthalone compounds (greenish-yellows).

Pure disperse dyes are crystalline solids of low molecular weight which melt on heating (150–250 °C) and sublime without decomposition, a factor of essential importance in the development of transfer printing processes [61]. The aqueous solubility is low, generally ranging from 0.2 to 100 mg/l at 80 °C and increases logarithmically with temperature.
Commercial disperse dyes are used in the form of fine dispersions with a particle size of around 2 μ downwards. Power versions are prepared by milling the press-cake generally with an equal weight of a suitable auxiliary product and a small quantity of water [61, 168]. After drying and mixing with suitable diluents e.g. *Glaubers*' salt, wetting agents or anti-dusting formulations, the final product may contain 15–40% of actual colorant. In recent years "liquid" versions of disperse dyes have been increasingly marketed [61, 169] as concentrated, free-flowing aqueous dispersions containing relatively less dispersing agent (1–2 parts per part of dye) than in the power brands (2–4 parts per part of dye). In practice most dyers add more dispersing agent to the dyebath for liquid compared with powder versions of the same dye.
There is no doubt that the success of the disperse dyes as a class of dyes depends in fair measure on the developments in dispersing (or levelling) agents that have taken place [167, 170, 171]. Dispersing agents perform four highly specific functions: namely they

(1) assist in the process of reducing the dye particle size
(2) enable the dye to be prepared in powder form when this is required
(3) facilitate the reverse change from powder to dispersion when the dyebath is prepared
and (4) maintain the dispersion during dyeing.

Modern dispersing agents are high molecular weight compounds and polymeric versions of sodium dinaphthylmethane sulphonate and of lignin sulphonic acids have been used in many dye-fibre systems. *Valko* [170] has suggested that with modern dispersing agents it is unlikely that micelle formation occurs and that it is possible that the dispersing agents are absorbed on to the dye surface with a non-polar backbone adjacent to the dye and pendant solubilizing groups turned outwards from the complex.
The correct dispersing of disperse dyes is of crucial importance to prevent dye specking etc., particularly in yarn and fabric dyeing, and suitable methods have been described in detail elsewhere [172, 173]. Liquid versions of disperse dyes must be carefully stored because agglomeration of the dye particles can occur in warm conditions, or freezing in cold conditions. In all cases homogenization of the liquid dye is essential prior to use to overcome stratification and settling problems on storage [172].

5.3. The mechanism of dyeing disperse dyes on acrylic fibres

Disperse dyeing is generally regarded as a solid solution process similar to that advanced by *Kartaschoff* for secondary cellulose acetate [174]. The work of *Bird* and his coworkers at Leeds [168, 175] has supported the solid solution theory of disperse dyeing but *Giles* [176] and also *Peters* [177] have expressed some reservations because of similarities between the solid solution theory and a special case of *Langmuir* adsorption. Other evidence from the equilibrium uptake of amines used as diazo components in the azoic dyeing of acrylic fibres demonstrated that the components of binary mixtures were adsorbed independently, the distribution of each complying with *Henry's* Law [178].

The progress of dyeing can be depicted [179] as follows in Fig. 4.

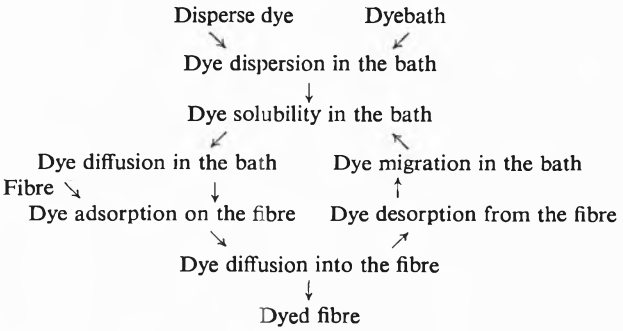


Fig. 4

The main factors affecting the dyeing process are

(1) The dye diffusion in the bath
(2) The dye adsorption of the fibre
(3) The dye diffusion into the fibre

Stage (1) depends on the solubility and the dispersibility of the dye and is independent of the fibre. However both factors are very temperature-dependent. The solubility of the dye is increased with increase in temperature while the dispersibility is often decreased, leading to dye aggregation [168].

5.4. The adsorption of disperse dyes by acrylic fibres

The adsorption of disperse dyes has been shown to be markedly temperature-dependent on Orlon 42 [57] and

Acrilan [45], the exhaustion values increasing to a maximum at about 110 °C for the former. Similar results have been obtained in other studies [58], but even dyeing at 110 °C required the use of selected dyes which combined a comparatively rapid rate of dyeing with high tinctorial power and/or a reasonable saturation value [45, 57, 58].

The saturation values of disperse dyes on acrylic fibres have been shown to be lower than on polyester, nylon, secondary cellulose acetate and cellulose triacetate fibres [45, 57]. This is demonstrated in Table 4 which also emphasizes the fact that saturation values on different acrylic fibres depend essentially on the effects of co-monomers on the fibre structure, the method of fibre extrusion and subsequent processing conditions prior to dyeing. This may partially explain some of the apparent discrepancies in saturation values reported in the literature, although the temperature of dyeing, particularly if just above T_g, must be an additional factor. The values for Duranol Brilliant Blue CB 300 (CI Disperse Blue 1) are somewhat exceptional in that the structure is based essentially on tetraamino anthraquinone. This is more basic in character and behaves as if it were intermediate between the disperse and basic dye classes [58]. The general lack of build-up of disperse dyes however reflects the lack of ionic attraction in the disperse dye-acrylic fibre system which leads to low affinity values.

Table 4: Conditions 100% dye, 98 °C, 48 h; Saturation uptake (g/dye/100 g fibre)

Dye	Acrilan	Orlon 42	Secondary cellulose acetate
Dispersol Fast Yellow G 300 (CI Disperse Yellow 3)	2.6	1.3	7.4
Dispersol Fast Orange B 300 (CI Disperse Orange 13)	6.0	2.8	10.0
Duranol Red X3B 300	7.9	7.6	12.2
Duranol Blue G 300 (CI Disperse Blue 26)	3.2	8.0	10.6
Duranol Brilliant Blue CB 300 (CI Disperse Blue 1)	8.3	8.0	10.6

Hadfield and *Sokol* [58] have also shown that the rate of diffusion of disperse dyes into Acrilan is greater than on Orlon 42, but this will clearly depend upon the size, shape, polarity and basicity of the diffusing disperse dye molecules, so that the degree of levelling is still temperature-dependent and this dependency is more apparent with the slower diffusing dyes. It has been reported [45] that the fastness to washing at 60 °C or below is also good due to the very high activation energy of dyeing, and is similar to polyester and cellulose triacetate. While light fastness values are high for the depth of coloration, cases of anomalous fading have been noted for certain combinations of disperse dyes on Acrilan [45]. Rubbing fastness may often be affected owing to lack of build-up of one or more components if the dye selection is injudicious, while overall there has been a lack of good red disperse dyes on acrylics [128].

The diffusion rates of disperse dyes into cast films of Courtelle polymer have been measured by *Ramachandran* [180, 181]. For Duranol Brilliant Blue CB the results indicated a very marked increase in diffusion rate with increase in temperature, consistent with the opening up of the fibre structure that occurs around the glass transition temperature T_g. For Courtelle, T_g has been measured [92] at 93–94.5 °C and it is in this range that a dramatic increase in the speed of diffusion occurs [97, 180, 181]. The reduced activation energy of diffusion above 90 °C was associated with the changes in the polymer structure occurring around T_g.

Table 5:

Temperature °C	Diffusion coefficient $Dx10^{12}$ cm²/sec	Activation energy ΔE kJ.mole^{-1}
78.5	2.4	
85	17.4	292.2 (at < 90 °C)
90	57.0	201 (at > 90 °C)
95	115.0	
97	200	

These results are in accord with the effect of temperature on dyeing behaviour studied by *Kramrisch* [45] and other workers [57, 58].

The solid solution mechanism has led naturally to the view that the location of dye is not specific and that the dyes may move with comparative freedom within the fibre structure [97]. On this basis it might be presupposed that a dye, if applied in admixture, should be adsorbed independently of the presence of the other dyes i.e. each component dye should achieve its normal saturation value even though the substrate was already saturated with dye.

This has been substantiated in the results of *Hadfield* and *Sokol* [58] who applied a yellow, a red and a blue dye to Acrilan and then repeated the measurements using the dyes in admixture. It is clearly seen in Table 6 that the dyes built up on Acrilan independently of each other, a useful economic advantage in achieving heavier depths without the risk of "over-saturation" leading to deposits of surface dye.

Table 6:

5% Dispersol Fast Yellow GR 300 Powder Fine (CI Disperse Yellow 39)
5% Duranol Red X3B 300 Powder Fine
5% Duranol Blue G 300 Powder Fine
Dyed with 1/1000 Lissapol C at 98 °C for 90 min.

Admixed dye	Yellow	Red	Blue
Yellow	1.58 *	2.19	1.13
Red	1.68	2.23 *	1.17
Blue	1.60	2.08	1.11 *

* These values refer to the individual dyes (5%)

Similar results are evident in the studies by *Reith* and *Andres* [182].

However it may be that where the molecules of two dyes are similar some degree of interaction in admixture may occur, particularly if the dyes are isomorphous i.e. they can replace one another in the crystal lattice of the solid dye. This phenomenon which occurs in some dye-fibre systems is associated with different melting point behaviour in admixture [183]. Non-interacting pairs of dyes form fairly well-defined eutectic points, whereas interacting pairs of dyes show no eutectic, but the melting point changes continuously over the composition range, indicative of isomorphism. With the latter therefore mixed crystals may be formed either in the dyebath, or complexes in solution, in the fibre, or both. The former has been shown to occur with one pair of disperse dyes on polyester and is the most likely explanation as the experimental evidence suggests that dyes are molecularly dispersed in the fibre [184]. As far as is known however this phenomenon has not been noted for the acrylic fibre system.

5.5. Disperse dye-fibre interactions

Feichtmayr and *Wurz* [19] have pointed out the possibility of the polar groups in the dye such as hydroxyl or amino groups interacting with the nitrile groups. However, apart from polar forces, non-polar interactions are operative between all the molecules and may be related to the polarizability, but systematic studies of the nature of the dye-fibre interactions have not been carried out.

In interesting work both the affinities and the heats of dyeing were shown to be increased with acrylic fibres when polar hydroxyl and amino groups as well as non-polar methyl, ethyl or phenyl groups were introduced into the dye molecule [185]. This suggests that both polar and non-polar forces of attraction are involved. There can be little doubt however that the hydrophilic-lipophilic character of the dye molecule is important, while the polarity of the dye may well exert a significant influence on the aqueous solubility. In actual fact, the latter is most likely to be the limiting factor in determining the saturation values when dyeing from aqueous dye liquors. In other work [186], hydrophobic bonding was concluded to be an important factor in a study of the equilibrium adsorption of five disperse dyes on Orlon 42.

6. Conclusions

There is no doubt that the whole spectrum of dye-fibre interrelations in acrylic fibres has posed immense problems for scientists and technologists. The tremendous advances that have been made, and those that continue to be evolved, are the product of much fertile and imaginative research and development work on the part of colour chemists, fibre scientists and textile technologists.

The continued attack on the problems that yet remain should therefore enable the coloration of acrylic fibres to be placed on a more sound theoretical foundation and as a result bring pleasure both to those who delight in aesthetics and to those who desire high standards of performance. In this way the quality of acrylic fibres will be enhanced and their attributes will be appreciated by a wider and more discerning consumer market.

References

1 *P.H. Hobson:* Text. Chem. Colorist *4* (1972) 232.
2 *P.H. Hobson* and *A.L. McPeters:* Kirk-Othmer Encycl. Chem. Technol. 3rd Ed. *1* (1978) 355, ed. *M. Grayson* and *D. Eckroth* (Wiley, New York).
3 *E. Cernia:* Man-Made Fibers Science and Technology Vol. 3, ed. *H.F. Mark, S.M. Atlas* and *E. Cernia* (New York, John Wiley & Sons Inc, 1968) p. 135.
4 *D.R. Baer:* The Chemistry of Synthetic Dyes Vol. IV, ed. *K. Venkataraman* (Academic Press, New York) 1971 Chap. IV p. 161.
5 *C. Moureu:* Paris Soc. Chim. Bull [iii] *9* (1893) 424.
6 *H. Rein:* USP 2,140,921 (Dec. 20, 1938) (to I.G. Farbenindustrie);
H.-J. Manderla: Bayer Farben Revue No. 4 (1963) 24.
7 *R.C. Houtz:* Text. Research J. *20* (1950) 786.
8 Textile Organon XLIX No. 6 June 1978 p. 77.
9 Rules and Regulations under the Textile Fiber Products Identification Act effective Mar. 3 1960, U.S. Federal Trade Commission, Washington D.C. 1960 p. 4.
10 *G.H. Latham:* USP 2,404,714 (July 23, 1946) (to Du Pont).
11 *H.F. Mark* and *A.V. Tobolsky:* Physical Chemistry of High Polymeric Systems, Interscience, New York–London, 1951 p. 141.
12 *C.E. Schildknecht:* Vinyl and Related Polymers, Wiley, New York, 1952 pp. 270, 276.
13 *J. Cegarra:* J.S.D.C. *87* (1971) 149.
14 *C.Y. Liang* and *S. Krimm:* J. Polymer Sci. *31* (1958) 513.
15 *A. Bondi:* Ann. N.Y. Acad. Sci. *53* (4) (1951) 870.
16 *J.S. Rowlinson:* Trans. Faraday Soc. *45* (1949) 974.
17 *A.M. Saum:* J. Polymer Sci. *42* (1960) 57.
18 *I. Davidovits:* Teintex *29* (1964) 254.
19 *F. Feichtmayr* and *A. Würz:* J.S.D.C. *77* (1961) 626.
20 *R. Stéfani, M. Chevreton, J. Terrier* and *Ch. Eyraud:* Compt. rend *248* (1959) 2006.
21 *R. Stéfani, M. Chevreton, M. Garnier* and *Ch. Eyraud:* ibid *251* (1960) 2174.
22 *W. Wegener* and *G. Egbers:* Z. ges. Textilindustrie *68* (1966) 502.
23 *C.W. Lo:* M. Sc. Dissertation, University of Leeds 1978.
24 *G. Hinrichsen* and *H. Orth:* Kolloid-Z *247* (1971) 844.
25 *P.A. Koch:* Z. ges. Textilindustrie *57* No. 21 (1955) 1350.
26 *I. Holme:* Rev. Prog. Coloration *1* (1970) 31.
27 *J.W.S. Hearle* and *R. Greer:* Text. Prog. *2* (No. 4 1970) 88.
28 *C.R. Bohn, J.R. Schaefgan* and *W.O. Statton:* J. Polymer Sci. *55* (1961) 531.
29 *W.R. Krigbaum* and *N. Tokita:* ibid. *43* (1960) 467.
30 *W.B. Achwal:* Colourage *21* (19) (1974) 1.
31 *V.A. Shenai:* Text. Dyer & Printer XI No. 9 (1978) 25.
32 *G.C. Patel:* M. Sc. Dissertation University of Leeds 1978.
33 *J.P. Craig, J.P. Knudsen* and *V.F. Holland:* Text. Research J. *32* (1962) 465.
34 *J.P. Knudson:* ibid. *33* (1963) 13.
35 Monsanto BP 1,193,170 28 May 1970.
36 Monsanto BP 1,017,855 19 Jan. 1966.
37 *P.M. Cross, J.W.S. Hearle, B. Lomas* and *J. Sparrow:* Proc. Third Ann. S.E.M. Symp. Chicago (1970) 81.

38 *R.D. van Veld, G. Morris* and *H.R. Billica:* J. Appl. Polymer Sci. A-1, *12* (1968) 2709.
39 *M. Sotton, A.M. Vialard* and *C. Rabourdin:* Bull. Sci. L'Inst. Text. de France V 2 No. 7 (1973) 173.
40 *M. Sotton* and *A.M. Vialard:* Text. Research J. *41* (1971) 834.
41 *M. Sotton, J. Jacquemart, R. Monrocq:* Bull. Sci. L'Inst. Text. de France V No. 2 8 (1973) 247.
42 *M. Sotton:* Industrie Minérale, No. Special Rheologie III No. 6 (1975) 1.
43 *M. Sotton* and *A.M. Vialard:* Compt. rend. *272C* (1971) 1381.
44 *G.E. Ham:* Text. Research J. *24* (1954) 604.
45 *B. Kramrisch:* J.S.D.C. *73* (1957) 85.
46 *C.C. Wilcock* and *J.L. Ashworth:* Whittaker's dyeing with coal-tar dyestuffs, 6th Ed., Bailliere, Tindall and Cox (London, 1964) p. 285.
47 *W.H. Hindle:* Text. Research J. *27* (1957) 726.
48 *J.F. Laucius, R.A. Clarke* and *J.A. Brooks:* Amer. Dyestuff Rep. *44* (1955) P632.
49 *R.J. Thomas* and *P.L. Meunier:* ibid. *38* (1949) P925.
50 *K. Meldrum* and *J.S. Ward:* J.S.D.C. *74* (1958) 140.
51 *T. Vickerstaff:* The Physical Chemistry of Dyeing, Oliver and Boyd, 2nd Ed. (London, 1954) p. 493.
52 *T.A. Feild:* Amer. Dyestuff Rep. *40* (1951) P737.
53 *T.A. Feild* and *G.H. Fremon:* Text. Research J. *21* (1951) 531.
54 *R.H. Blaker* and *J.F. Laucius:* Amer. Dyestuff Rep. *41* (1952) P39.
55 *W. Flügel, A. Peter* and *H. Egli:* Textil-Rundschau *9* (1954) 509.
56 *C.H.A. Schmitt, C.W. Saalfrank* and *H.R. Walker:* Amer. Dyestuff Rep. *44* (1955) P904.
57 *I.M.S. Walls:* J.S.D.C. *72* (1956) 261.
58 *H.R. Hadfield* and *W.M. Sokol:* ibid. *74* (1958) 629.
59 *R.H. Blaker, S.M. Katz, J.F. Laucius, W.R. Remington* and *H.E. Schroeder:* Disc. Faraday Soc. *16* (1954) 210.
60 Society of Dyers and Colourists: J.S.D.C. *89* (1973) 411.
61 *C.B. Stevens:* The Dyeing of Synthetic-Polymer and Acetate Fibres, ed. *D.M. Nunn*, The Dyers Company Publications Trust, 1979 p. 18.
62 *H. Zollinger:* Amer. Dyestuff Rep. *54* (1965) P634.
63 *P.L. Meunier, J.F. Laucius, J.A. Brooks* and *R.J. Thomas:* ibid. *42* (1953) P470.
64 *H.P. Landerl* and *D.R. Baer:* Amer. Dyestuff Rep. *54* (1965) 222.
65 *S. Rosenbaum:* Text. Research J. *34* (1964) 159.
66 *S. Rosenbaum:* ibid. *33* (1963) 899.
67 *H. Sand:* Kolloid. Z. *218* (1967) 30, 124.
68 *R.J. Harwood, R. McGregor* and *R.H. Peters:* J.S.D.C. *88* (1972) 216.
69 *T.H. Guion, T.M.A. Hossain, R. McGregor* and *J.R. Thagard:* ibid. *89* (1973) 409.
70 *O. Glenz* and *W. Beckmann:* Melliand Textilber. *38* (1957) 296.
71 idem: ibid. *38* (1957) 783.
72 idem: ibid. *38* (1957) 1152.
73 *W. Beckmann:* J.S.D.C. *77* (1961) 616.
74 *G. Weston:* unpublished results, see *T. Vickerstaff:* Hexagon Digest No. 19 (1954) 3.
75 *W. Beckmann:* 3rd Internat. Congress on Surface-active Agents Köln: Universitätsdruckerei Mainz (1960).
76 *V.F. Androsov* and *V.L. Liverant:* Tech. Text. Ind. U.S.S.R. (No. 3, 1966) 98.
77 *S. Heimann* and *F. Feichtmayr:* Canad. Text. J. *83* No. 14 (1966) 42.
78 *R.G.R. Bacon:* Quart. Rev. Chem. Soc. *9* (1955) 287.
79 *D. Balmforth, C.A. Bowers* and *T.H. Guion:* J.S.D.C. *80* (1964) 577.
80 *Y. Tsuda:* J. Appl. Polymer Sci. *5* (1961) 104.
81 *I. Matsubara:* Bull. Chem. Soc. Japan *33* (1960) 1624.
82 *R. Yamadera:* J. Polymer Sci. *50* (1961) S4.
83 *S.R. Sivaraja Iyer:* The Chemistry of Synthetic Dyes, Vol. III, ed. *K. Venkataraman* (Academic Press, New York) 1974 Chap. IV p. 260.
84 *J. Wegmann:* Text. Rundschau *9* (1954) 341.
85 *A. Würz:* Melliand Textilber. *37* (1956) 83.
86 *T. Vogel, J.M.A. DeBruyne* and *C.L. Zimmermann:* Amer. Dyestuff Rep. *47* (1958) P581.
87 *W. Weltzien* and *W. Fester:* Dissertation Aachen (1960).
88 *R. Schiffner:* discussion in Melliand Textilber. *38* (1957) 1156.
89 *W.R. Remington* and *H.E. Schroeder:* Text. Research J. *27* (1957) 177.
90 *W. Biedermann* and *A. Ischi:* J.S.D.C. *95* (1979) 4.
91 *M. Takahashi, Y. Nukushina* and *S. Kosugi:* Text. Research J. *34* (1964) 87.
92 *J. Cegarra, R. Puente* and *J. Valldeperas:* Text. Chem. Colorist *6* (1974) 170.
93 *T.L. Dawson* and *B.P. Roberts:* J.S.D.C. *95* (1979) 47.
94 *R. McGregor* and *P.W. Harris:* J. Appl. Polymer Sci. *14* (1970) 513.
95 *S. Rosenbaum:* J. Polymer Sci. Part A3 (1965) 1949.
96 *W. Ingamells:* The Theory of Coloration of Textiles, ed. *C.L. Bird* and *W.S. Boston:* The Dyers Company Publications Trust (1975) Chap. 6 p. 285.
97 *R.H. Peters:* Textile Chemistry Vol. III, The Physical Chemistry of Dyeing, Amsterdam, Elsevier (1975) p. 550.
98 *W. Ingamells, R.H. Peters* and *S.R. Thornton:* J. Appl. Polymer Sci. *17* (1973) 3733.
99 *Z. Gur-Arieh* and *W. Ingamells:* J.S.D.C. *90* (1974) 12.
100 *R.S. Asquith, H.S. Blair* and *N. Spence:* J.S.D.C. *94* (1978) 49.
101 *S.M. Aharoni:* Proc. Conf. Phase Trans. and Appl. Mat. Sci. (1973) 277.
102 *T. Vickerstaff:* The Physical Chemistry of Dyeing, 1st Edition (London, Oliver and Boyd 1950) p. 146.
103 *R.S. Asquith, H.S. Blair* and *N. Spence:* Text. Research J. *47* (1977) 446.
104 *S. Rosenbaum:* J. Appl. Polymer Sci. *7* (1963) 1225.
105 *J.P. Bell* and *T. Murayama:* J. Appl. Polymer Sci. *12* (1968) 1795.
106 *S. Rosenbaum:* Text. Research J. *34* (1964) 291.
107 *M.L. Williams, R.F. Landel* and *J.D. Ferry:* J. Amer. Chem. Soc. *77* (1955) 3701.
108 *Z. Gur-Arieh, W. Ingamells* and *R.H. Peters:* J. Appl. Polymer Sci., *20* (1976) 41.
109 *W. Ingamells:* Book of Papers, S.D.C. Biennial Symposium University of Sheffield September 1979.
110 *G.S. Dodd* and *W. Ingamells:* J.S.D.C. *93* (1977) 74.
111 idem: ibid. *93* (1977) 79.
112 Basic Dyes on Acrylic Fibres Committee: J.S.D.C. *89* (1973) 292.
113 *W. Beckmann:* Dyeing of Synthetic-Polymer and Acetate Fibres, ed. *D.M. Nunn* Dyers Company Publications Trust 1979 p. 357.
114 *W. Beckmann:* 11th Int. Textile Seminar Kingston Ontario 1968.
115 *W. Beckmann:* Z. Ges. Textilind. *71* (1969) 603.
116 *N.G. Morton* and *M.E. Kracht:* J.S.D.C. *85* (1969) 639.
117 *A.M. Jowett* and *A.S. Cobb:* Rev. Prog. Coloration *3* (1972) 81.
118 *G. Herbulot:* J.S.D.C. *82* (1966) 217.
119 *U. Mayer, M. Brock, H. Fleischer* and *H. Pastor:* Melliand Textilber. *49* (1968) 195.
120 *U. Mayer* and *M. Sülflow:* Melliand Textilber. *49* (1968) 813.
121 *M. Sülflow* and *U. Mayer:* ibid. *49* (1968) 819.
122 *W. Beckmann* and *K. Jakobs:* Bayer Farben Revue No. 16 (1969) 1.
123 *K. Jakobs:* ibid. No. 22 (1972) 12.

124 *A. Takaoka* and *J. Seki:* Sen-i Gakkaishi *21* (1965) 10.
125 *C. L. Zimmermann* and *A. L. Cate:* Text. Chem. Colorist *4* (1972) 150.
126 *R. A. Clarke* and *L. Bidgood* Jr.: Amer. Dyestuff Rep. *44* (1955) P631.
127 *J. P. Neary* and *R. J. Thomas:* ibid. *46* (1957) P625.
128 *H. Kellett:* J.S.D.C. *84* (1968) 257.
129 *J. Cegarra, P. Puente* and *J. Valldeperas:* Boletin de Invest. Textil Cooperation Industrial de Tarrasa (University of Barcelona) No. 64 Oct–Dec 1975 p. 1.
130 *P. V. Moryganov, B. N. Mel'nikov* and *O. B. Lyakisheva:* Tekhnol. tekstil. Prom. No. 22 (1962) 114.
131 *H. P. Landerl, J. J. Iannarone* and *J. J. Wilson:* S.V.F. Fachorgan *12* (1957) 668.
132 *A. Würz:* Melliand Textilber. *38* (1957) 817.
133 *J. P. Neary* and *R. J. Thomas:* Amer. Dyestuff Rep. *47* (1958) P325.
134 *M. Bonche:* Teintex *33* (1968) 519.
135 *M. Bonche:* Teintex *33* (1968) 585.
136 *H. Kellett:* Text. Manuf. *84* (1958) 313.
137 *J. A. Leddy:* Amer. Dyestuff Rep. *49* (1960) P272.
138 *R. Défago:* Ciba Review 1962 No. 5 40.
139 *W. Beckmann:* Bayer Farben Revue *9* (1964) 13.
140 *W. L. Anderson, C. J. Bent* and *R. H. Ricketts:* J.S.D.C. *88* (1972) 250.
141 *G. Siegrist:* Text. Rundschau *17* (1962) 143.
142 *G. Thiel:* Amer. Dyestuff Rep. *55* (1966) P505.
143 *P. Galafassi* and *H. Scheidegger:* Teintex No. 8–9 (1976) 399.
144 *R. Rokohl:* Tenside *2* (1965) 76.
145 *R. Schiffner* and *B. Borrmeister:* Faserforschung und Textiltech. *16* (1965) 264.
146 *D. Blackburn:* Int. Dyer *153* No. 8 (1975) 418.
147 *W. Beckmann:* Melliand Textilber. *39* (1958) 1121.
148 *S. Cohen* and *A. S. Endler:* Amer. Dyestuff Rep. *47* (1958) 325.
149 Metropolitan Section A.A.T.C.C.: Text. Chem. Colorist *8* (1976) 34/165.
150 *W. Beckmann:* Reyon Zellwolle Chemiefasern (1958) 452.
151 Canadian P. 793,184, 27 Aug. 1968 (Bayer).
152 *M. E. Dullaghan* and *A. J. Ultee:* Text. Research J. *43* (1973) 10.
153 Midwest Section A.A.T.C.C. Text. Chem. Colorist *8* (1976) 22/6.
154 *U. Mayer:* Melliand Textilber. *47* (1966) 653.
155 *U. Mayer:* Melliand Textilber. *47* (1966) 772.
156 *W. Beckmann, F. Hoffmann* and *H. G. Otten:* J.S.D.C. *88* (1972) 354.
157 *E. J. Siepmann:* Text. Chem. Colorist *7* (1975) 28/46.
158 *J. T. Voltz:* Text. Chem. Colorist *9* (1977) 114/23.
159 *J. A. Koller* and *M. Motter:* Amer. Dyestuff Rep. *66* (Mar 1977) 34.
160 *W. Beal:* Int. Dyer 157 No. 6 (1977) 261.
161 Ciba Geigy A.G. British Patent Application No. 44138/75 27 Oct 1975.
162 *W. Biedermann, P. Galafassi, P. Moser* and *H. Scheidegger:* Textilver. 12 (1977) 122.
163 *P. Galafassi, W. Biedermann, U. Horn, P. Moser* and *H. Scheidegger:* Textilver. *12* (1977) 250.
164 *U. Mayer:* Amer. Dyestuff Rep. *56* (1967) P869.
165 *H. Gerber* and *K. Grieder:* paper presented at SVF-Arbeitstagung March 1975.
166 *I. B. Beattie, R. J. Dudley* and *K. W. Smalldon:* J.S.D.C. *95* (1979) 295.
167 *R. K. Fourness:* J.S.D.C. *72* (1956) 513.
168 *C. L. Bird:* ibid. *70* (1954) 68.
169 *D. Blackburn:* The Dyeing of Synthetic-Polymer and Acetate Fibres, ed. *D. M. Nunn,* The Dyers Company Publications Trust, 1979, p. 76.
170 *E. I. Valko:* Rev. Prog. Coloration *3* (1972) 50.
171 *R. K. Fourness:* J.S.D.C. *90* (1974) 15.
172 *I. Holme:* ibid. *94* (1978) 375.
173 B.A.S.F. Manual: Dyeing and Finishing of Polyamide Fibres and their blends with other fibres, 1972, p. 37.
174 *V. Kartaschoff* and *G. Farine:* Helv. Chim. Acta *11* (1928) 813.
175 *C. L. Bird* and *F. Manchester:* J.S.D.C. *71* (1955) 604.
176 *C. H. Giles:* The Theory of Coloration of Textiles, ed. *C. L. Bird* and *S. M. Boston,* Dyers Company Publications Trust, 1975, p. 73.
177 *L. Peters:* ibid. p. 187.
178 *A. A. Kharkharov* and *G. A. Arestova:* Teknol. Tekstil. Prom. *44* (No. 1 1965) 92.
179 *J. Carbonell:* Amer. Dyestuff Rep. *51* (1962) 83.
180 *C. R. Ramachandran:* Ph. D. Thesis U. M. I. S. T. 1963.
181 *R. McGregor, R. H. Peters* and *C. R. Ramachandran:* J.S.D.C. *84* (1968) 9.
182 *J. R. Reith* and *R. J. Andres:* Amer. Dyestuff Rep. *42* (1953) 35.
183 *C. L. Bird* and *P. Rhyner:* J.S.D.C. *77* (1961) 12.
184 *A. Johnson, R. H. Peters* and *A. S. Ramadan:* ibid. *80* (1965) 129.
185 *M. Hotai* and *S. Okada:* Sen-i Gakkaishi *23* (1967) 321.
186 *A. Takaoka, A. Katayama, N. Kuroki* and *K. Konishi:* ibid. *21* (1965) 158.