THE PREPARATION, PROPERTIES
AND DYEING BEHAVIOUR OF
DIFFERENTIAL-DYEING CELLULOSE

by

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Thesis submitted in partial
fulfilment of the requirements
for the degree of Doctor of Philosophy (C.N.A.A.)

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and in collaboration with
the British Technology Group

Submitted October, 1987.

ABSTRACT

Title: The preparation, properties and dyeing behaviour of differential-dyeing cellulose.

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Treatment of cotton fibre or yarn with colourless reactive dye analogues containing quaternary ammonium groups introduced positive sites into cotton which enhanced its affinity for anionic dyes. Yarns pre-treated with such cationic reagents, or spun from treated fibres, showed preferential dye uptake when dyed together with untreated cotton.

Since the degree of differential dye uptake depended on the level of pre-treatment a range of yarns of differing dye capacities could be produced enabling a variety of tone-on-tone effects to be obtained.

Treated yarns showed differential-dyeing behaviour with all the normal cellulosic dyes and also with acid dyes, which showed a 1:1 stoichiometry between the sulphonic acid groups on the dye and cationic sites in the fibre. Some control could be exercised over the high diffusion rates of dyes by the selection of suitable counter-ions or use of anionic levelling agents.

The contrast between treated and untreated yarns generally increased with decreasing concentration of added electrolyte, increasing temperature and liquor ratio and decreasing affinity of the dye for untreated cellulose. Mercerising, and bleaching of treated cotton with sodium hypochlorite, had no effect on its dyeability.

Treatment of cotton with cationic reagents considerably improved the wash fastness properties of direct dyes, although those of reactive dyes were slightly reduced. Light fastness ratings on treated cotton were slightly lowered, particularly with reactive dyes.

Cotton fibre and yarn has also been treated with analogous reactive anionic reagents to produce basic-dyeable cotton and combinations of anionic and cationic yarns cross-dyed two colours from one dyebath containing anionic and cationic dyes in a one-step process, with minimal cross-staining.

Both cationic and anionic differential-dyeing varieties of cellulose triacetate and viscose rayon have also been prepared from celluloses pre-treated with cationic and anionic reagents respectively. Such reagents have also found application in the printing of cotton fabrics.

To David and 'Nina'!

"I stand in tongue-tied awe of
the cellulose molecule"

Charles F. Cross
1855-1935

ACKNOWLEDGEMENTS

The work described in this thesis was carried out in the laboratories of the Department of Physical Sciences, Trent Polytechnic, Nottingham between September 1983 and September 1986.

First and foremost I should like to thank Dr G.A.F. Roberts for his excellent supervision, constant encouragment and good humour during the course of this work. Thanks are also due particularly to Dr P.R. Huddleston, Mr J. Miller and Mr T. Flynn for giving of their time and expertise in the course of many helpful discussions.

I should also like to thank especially Mrs F.A. Wood for her technical expertise and assistance, and am indebted to all the technical staff of the Department of Physical Sciences, notably Mr M.L. Wood and Mr G. Patel, and to members of the Department of Fashion and Textiles for their advice and technical assistance, namely Mrs S. Hudson, Mr J.S. Bellamy, Mr A.G. Symonds and Mr J. Meehan.

I should also like to acknowledge the friendly and efficient service of both Dryden and Clifton libraries which was - and still is - much appreciated. Thanks are also due to Mrs F.A. Wood and Mr P. Lane for the preparation of the manuscript and the photographic work.

Lastly, but certainly not least, I should like to offer my personal thanks to Dr K. Hills for his support and encouragement during the project and to the British Technology Group for the award of a research grant.

Part of this thesis has been published in the International Dyer and Textile Printer and a copy of this article is included in Appendix VII.

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CHAPTER 1

INTRODUCTION

Just over 80 years ago, in 1903, the following notice appeared in the Society of Dyers and Colourists January edition:

> "The Publication Committee have decided to offer money, prizes or medals for the solution of problems in connection with processes, materials etc. used in dyeing and printing; and, in order that the selection made may be as practically useful as possible, they invite suggestions from members of the Society based upon difficulties or defects which they have experienced in the works"[1].

Funds were duly placed at the disposal of the Council of the Society for distribution in the form of prizes for the solution of those technical problems submitted. These they hoped would "form the nucleus of a comprehensive prize scheme which would prove of value to the progress of the dyeing and allied industries, and would stimulate research".

Accordingly, in March 1905, the first set of problems were published but it was not until 1906, as problem No. 2 of the second series, that a prize of £10 was announced for:

> "A practical method of so treating or preparing cotton yarn as to cause it to resist direct dyeing cotton colours. (The object being the production of a pattern or mixed effect in the piece dyeing of all-cotton goods.)"[2]

This then would appear to be the impetus behind the first concerted attempts by members of the Society to produce what would later be referred to as "immunised" or "passivated" cotton and much later as "differential-dyeing" cotton. In fact, the first work on the subject had been carried out some five years earlier by Cross and Bevan[3] who treated bleached cotton with boiling acetic anhydride in the presence of anhydrous sodium acetate. However, the fibres they obtained in these early experiments were weak and brittle and thus not suitable for textile purposes.

The first direct attempts at a solution to the problem appeared in the J.S.D.C. in 1907[4,5] and 1908[6] and two prizes were duly awarded. Not surprisingly, one of them was to Cross and Briggs, who submitted a modified version of Cross and Bevan's earlier process. The other recipient was J.B. Fothergill who submitted a process involving mordanting the fibre with tannate of tin. Nevertheless, it is interesting to note that at the time the awards were made it was pointed out in the umpires report that, whilst both papers were valuable contributions to the subject, neither had provided a complete solution to the original problem. (They obviously had their reservations!)

Thus a train of thought and endeavour was initiated in relation to a problem which still exists to the present day - a problem to which the only true solution must be the successful realisation of a commercially viable process for the production of "differential-dyeing" cotton.

1.1 Cotton and the chemistry of cellulose

Cellulose is the worlds most abundant naturally occurring organic polymer - without it life as we know it could not exist. In nature it is produced, consumed and destroyed in tremendous quantities every day. Its part in the carbon dioxide cycle is unmatched whilst its stabilising influence on the level of carbon dioxide in the atmosphere is of the same magnitude as that of the oceans[7]. Recent reports based on spectroscopic evidence even suggest its existence in interstellar space[8].

Whilst cellulose had been used by man over the centuries for such necessities as fire, food, clothing and shelter, its chemical value has only been utilised since the classic work of Payen in 1838[9]. He was the first to recognise that the cell walls of all land plants are constructed from the same substance. This substance he called cellulose after the Latin word cellula, the diminutive of cella, meaning chamber. Besides being an essential constituent of plants, cellulose also has great industrial importance since it is the raw material of a large part of the textile industry, the paper industry and several others.

Cellulose for paper is derived almost entirely from wood and a significant proportion of that required for textiles comes from the same source. Wood fibres themselves are too short for spinning directly into textile yarns; the cellulose they contain is dissolved in a suitable solvent and regenerated in order to render it usable. Longer cellulosic fibres can be extracted from certain plants by relatively simple purification treatments. These include flax (from which linen is obtained), hemp and jute, which are used mainly for industrial textiles, china grass (to produce ramie) and most importantly of all, cotton.

1.1.1 Production of cotton fibre

Cotton has been produced, processed and consumed since about 3000 B.C. Today it is a major world fibre and cellulose resource and is grown in over 68 countries, the main producing areas being concentrated in North America, USSR, Asia and Oceania. Recent figures indicate that whilst synthetic fibres, mainly polyester, acrylics and nylon, now comprise 33% of the total world production of textile fibres, and cellulose based man-made fibres are 13%, cotton is 48%[10].

The cotton plant is a member of the Malvaceae or mallow family. The particular species from which cotton fibre is obtained is called Gossypium, different varieties being cultivated according to geographical location[11]. Cottons of commercial importance can be divided into 3 main types: the highest quality fine cottons such as the Egyptian, Sudanese and Sea Island varieties with fibres having staple lengths (ie average fibre lengths) of 25-60 mm; coarser species with shorter staple lengths (about 13-33 mm) such as American upland cottons; and species of still shorter staple length (about 9-25 mm) commonly produced in India and other parts of Asia[12].

The flowers appear in June and the cotton is usually ripe for gathering between August and October. As the flower withers it is succeeded by a closed pod. This contains seeds which are surrounded by young, actively growing hairs whose function is to protect the young unripe seed and to assist in its dispersal when it matures. When the seeds are nearly ripe the pod bursts open and the cotton hairs project forming a white fluffy mass or "boll". Further exposure to the sun completes the ripening process, gradually drying up the contents of the cells.

The proper drying up of the cell in the sun is a very important factor in producing one of the essential properties of cotton, namely its characteristic twist. At the same time mineral salts and proteins are deposited in the central cavity as the cell sap evaporates and in fact these are amongst the impurities which have to be removed when the cotton is later scoured and bleached. Finally the fibres are ready for harvesting and after the crop has been gathered the fibres are removed from the seed by a process known as ginning[11].

1.1.2 Structure of cotton fibre

Each fibre thus consists of a single elongated vegetable cell with many convolutions throughout its length. It is composed of 3 main parts: primary wall, secondary wall and lumen, as shown in Figure 1[13].

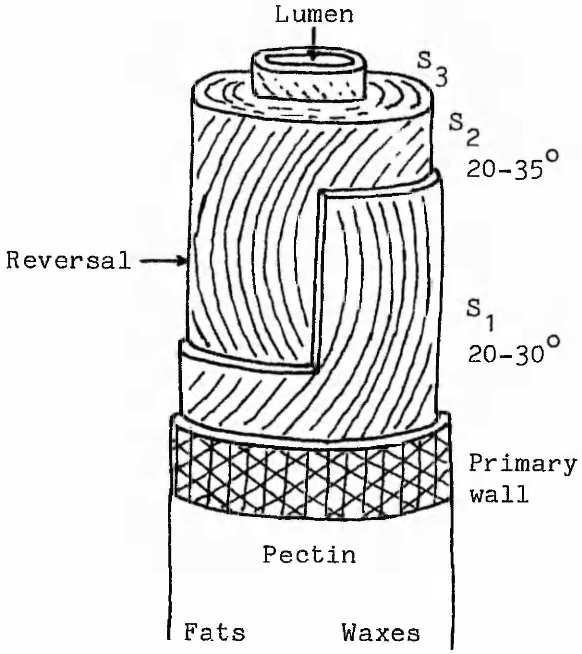


Figure 1. Idealised morphology of cotton fibre.

The primary wall consists of a network of cellulose fibrils arranged in a criss-cross pattern and covered with an outer layer, or cuticle, of pectin, protein, mineral matter and wax. The secondary wall constitutes the bulk of a mature fibre and consists almost entirely of fibrils of cellulose arranged spirally around the fibre axis, the direction of the spiral reversing many times along a single fibril.

The scanning electron microscope has revealed that these fibrils are in fact bundles of smaller microfibrils and it is believed that these microfibrils actually consist of still smaller 'elementary' fibrils that are 0.004 x 0.006 μm in cross-section. The secondary wall is thus laid down in successive layers, visible as rings corresponding with daily growth, the spiral angle of the fibrils varying from one layer to the next, from about 20-35 degrees[14].

Thus the cotton fibre consists of an assembly of fibrils in which the cellulose is accessible to most (but not all) chemical reagents only at fibrillar surfaces by way of a system of voids and channels[15,16]. The lumen is what remains of the central canal from which the layers of cellulose were laid down in the secondary wall, while the fibre was growing, and consists mainly of residual protein.

The composition of a typical mature cotton fibre is given in Table 1; as can be seen a 'typical' cotton consists of 94% cellulose the other components being protein, pectin substances, ash, wax, water-soluble organic acids and sugars[17].

Table 1. Composition of typical mature cotton fibre - on a dry weight basis. Moisture constitutes about 8%.

Constituent	% composition
Cellulose	94.0
Protein %N x 6.25	1.3
Pectin substances	0.9
Ash	1.2
Wax	0.6
Malic, citric acid and other organic acids	0.8
Total sugars	0.3
Other	0.9

1.1.3 Structure of cellulose

Cellulose is a polysaccharide with an empirical formula of $(C_6H_{10}O_5)_n$. It is a condensation polymer of β-D-glucopyranose with 1,4-glycosidic bonds and in chemical nomenclature is thus referred to as poly[(1-4)-anhydro-β-D-glucose]. Its structural formula is given below in Figure 2, where n = degree of polymerisation.

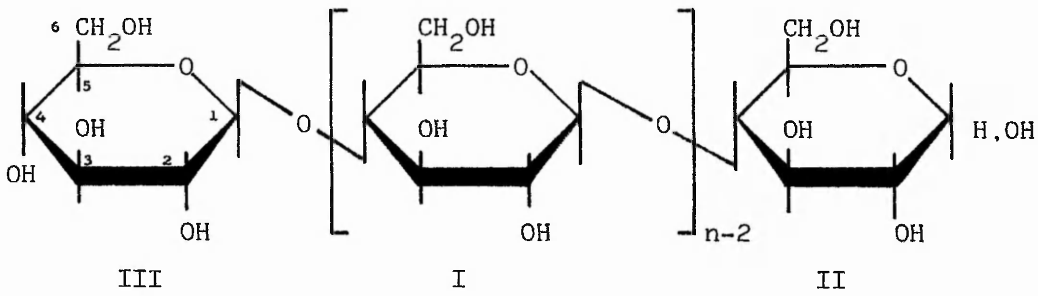


Figure 2.

The essential features of the polymer chain are thus the main sequence of repeat units I, the reducing and non-reducing end groups II and III, and the β-glycosidic linkages[18]. These *beta* linkages are particularly important because they result in a unique structural arrangement of the glucose units within the cellulose.

The two forms of D-glucose are illustrated below in Figure 3, the only difference between the two structures being in the distribution of the C(1)-hydroxyl group above and below the plane of the pyranose ring. Examination of the structure of β-D-glucose reveals that for a linkage between the 1:4 positions, each alternative unit must be turned through an angle of 180 degrees in order that the C(1) and C(4) hydroxyl groups can be brought to the same side of the plane of the molecular configuration, and therefore adjacent to each other.

α-D-glucose β-D-glucose

Figure 3.

Theoretical considerations demonstrate that it is only in the case of the *beta* linkage that it is possible for the polymer to be orientated in a straight line and therefore to be potentially fibre-forming. Starch, for example, is a polymer of α-D-glucose molecules in which this alternate rotation of the molecule is not required for condensation leading to linkages in the 1:4 positions, and is not fibre-forming.

The degree of polymerisation of cellulose varies with its source but it is generally agreed that the number of glucose units in an average molecule of native cellulose is of the order of 10,000, which corresponds to a molecular weight of 1,590,000[19]. It is a highly crystalline material and exists in at least five polymorphic forms[20], of which only cellulose I and cellulose II are important from the textile point of view.

Cellulose I is the form found in nature whilst cellulose II is the thermodynamically stable form produced when cellulose is regenerated from solution or is subjected in the solid state to the process of mercerisation; the main differences between the two forms being the arrangement of chains making up the unit cell of each and in the extent of the hydrogen bonding which exists between the chains, cellulose II having a rather more complex hydrogen bonded system than cellulose I[21].

In the native form cotton is considered to consist of essentially crystalline fibrils built up from a number of identical unit cells of cellulose I[22]. These combine together to form fibres which may be interspersed with less well ordered non-crystalline regions. These disordered regions consist of parts that are either truly random, ie. amorphous, or of varying levels of higher structural order.

The crystalline regions form the bulk of the fibrils whilst the disordered regions are confined to the surface of the fibrils and to very short regions along their length. It is the relative proportion of crystalline to amorphous material which determines the response of the fibre to coloration processes[23,24] since the diffusion and sorption of dyes and other reagents depends upon the extent to which the amorphous regions in the fibre are accessible. This is because it is only in these less ordered regions that the movement of dyes or reagents inward to, and out from, the site of reaction can occur[25].

Penetration of dye molecules, etc. within the crystalline fibril is not normally possible although in some instances adsorption may occur on the accessible surfaces of crystallites, depending upon the structural packing of the chain molecules[23,24]. The degree of penetration and accessibility of the fibre may, however, be altered by the ability of penetrant molecules such as water or organic solvents to swell or plasticise the fibre structure[22,23,25].

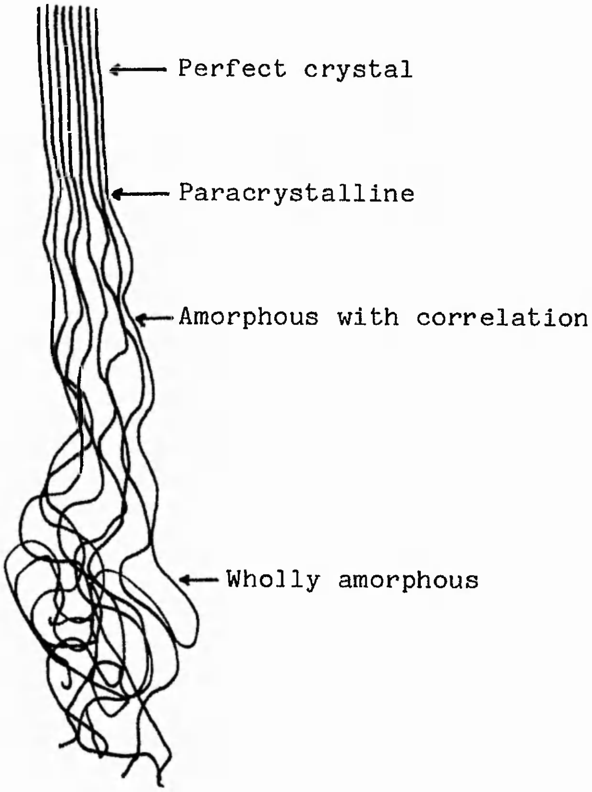


Figure 4. Range in degrees of order in the packing of chain molecules[26].
Diagram of crystalline and amorphous packing.

1.2 Dyes used with cellulose

1.2.1 Direct dyes

Up until 1884 cotton had to be dyed by lengthy and complicated procedures which were not only troublesome but also expensive. In the wake of the Industrial Revolution an urgent need arose for a quick and cheap method of dyeing the mass-produced cloth. It was therefore a very welcome event when Böttiger discovered Congo Red, the first direct dye, so called because it could be applied directly to cotton without the need for a mordanting pretreatment[27].

It was not long before an adequate range of similar dyes became available and, although of indifferent wet fastness, their cheapness and ease of application meant that their use spread rapidly. Today they are used mainly on cellulosic materials that will not be washed frequently in their end use, such as furnishing fabrics, some curtaining material, and for the dyeing of paper.

The direct dyes are generally large planar molecules and are strongly substantive towards cellulosic fibres. They are anionic and water-soluble, their solubility normally being due to the presence of one or more sulphonic acid groups (as the sodium salt). They are divided into 3 groups depending upon their migration properties and substantivity towards cellulose in the absence of salt - Class A dyes have the lowest substantivity and Class C the highest. Dyeing is normally carried out at or near the boil in the presence of sodium chloride or sodium sulphate.

Most of the direct dyes are sulphonated azo compounds. The Colour Index (3rd edn.) contains about 900 azo direct dyes of which approximately 45% are disazo and 25% trisazo. A typical disazo dye, C.I. Direct Yellow 12 is shown below in Figure 5:

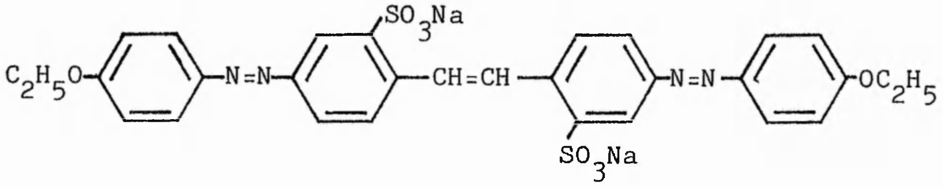


Figure 5. C.I. Direct Yellow 12; C.I. 24895.

Within this group there are many premetallised direct dyes, water-soluble copper complexes of O,O'-dihydroxyazo dyes with improved light and wash fastness properties. Triazone structures which combine yellow and blue chromogens are also used in the manufacture of green dyes which are much brighter than conventional polyazo dyes.

C.I. Direct Yellow 12 is also an example of another important class of direct dyes derived from stilbene. Other direct dyes include those based on copper phthalocyanine and a few which are dioxazine, quinoline and triazole derivatives.

1.2.2 Vat dyes

The vat dyes are found amongst the oldest naturally occurring colouring matters used for textiles. Indigo has been known in India since about 2,500 B.C., whilst Tyrian Purple was the badge of the patrician Roman. It is said to have been discovered by a shepherd whose dog broke a shellfish in his mouth with the result that his mouth turned purple[28]. Unfortunately, reproducible shades could not be obtained from these natural products of varying composition however, since the successful large scale industrial production of indigo in 1900, the synthesis of vat dyes has been an extremely active field of research and many new members have been added to this class.

The vat dyes are all insoluble in water but form alkali-soluble "leuco" compounds when treated with reducing agents such as sodium dithionite (or in some cases sodium formaldehyde sulphoxylate) and sodium hydroxide - a process known as vatting. These leuco compounds are substantive towards cellulose and are thus adsorbed by the fibres. They can then be reoxidised back to the insoluble coloured pigment within the fibre by exposure to air or by the use of certain oxidising agents such as alkaline sodium perborate or alkaline sodium hypochlorite, depending on the particular vat dye in use.

The reversible alkaline reduction of Indigo to Leuco indigo is shown below in Figure 6.

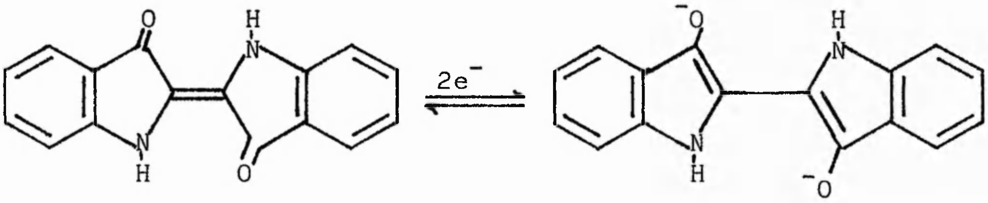


Figure 6.

Chemically the vat dyes can be divided into two main classes; the indigoids, usually derivatives of Indigotin or Thioindigo, and those derived mainly from anthraquinone and from higher condensed aromatic ring systems with a closed system of conjugated double bonds. They may be homogeneous dyes or mixtures and generally contain two, four or six reducible carbonyl groups.

The indanthrones, for example, are one of the most important groups of vat dyes based on the anthraquinone structure. They are derivatives of Indanthrone (C.I. Vat Blue 4), discovered by Bohn in 1901[29], and can be made in a greater range of shades, and possess better fastness properties, than dyes obtained from indigo.

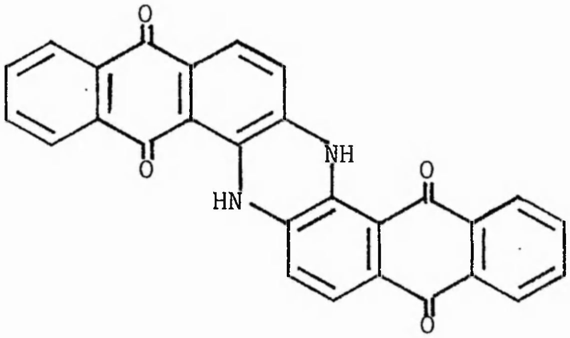
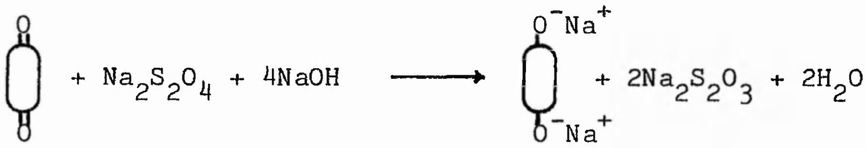


Figure 7. Indanthrone

In the above case two or four of the carbonyl groups are reduced to hydroxyl groups during vatting, giving leuco compounds which are soluble in alkali and substantive to cellulose.



where  represents the indanthrone ring system.

As a class the vat dyes have very good-excellent wet fastness properties and light fastness and a good shade range, apart from reds, scarlets and maroons. They are used extensively for furnishings, towellings, sheetings and canvas awnings.

1.2.3 Sulphur dyes

The first sulphur dye was Cachou de Laval, a brownish-khaki colour discovered in 1873 but which was never commercially successful. More important were the Vidal Blacks, prepared by Vidal in 1893 by fusing p-phenylenediamine or p-aminophenol with sodium sulphate and sulphur and then oxidising with potassium dichromate. Many new dyes followed, prepared by the action of sulphur and alkalis on a variety of phenols, amines, nitro-compounds and quinoneimines in the presence of heat but, in every case, very little was known about the chemical constitution of the dyes produced.

Since then it has been established that all dyes of this class are characterised by the presence of sulphur-sulphur linkages within their molecules and slowly some of the structures of these very complex molecules are being elucidated. C.I. Sulphur Yellow 4, for example, is composed of units of the following structure[30]:

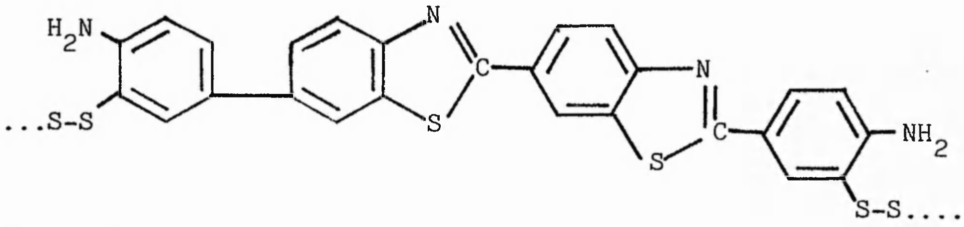


Figure 8.

They are usually insoluble in water and, like vat dyes, first have to be reduced to the water-soluble leuco form which shows substantivity for cellulose. Sodium sulphate, frequently with the addition of sodium carbonate, is most commonly used as the reducing agent. After dyeing they are readily oxidised back to the original insoluble form giving colours with very good wet-fastness.

Sulphur dyes are widely used for blacks, blues and browns in medium or heavy depths, especially where all round fastness and cheapness is required, eg. overalls, work clothes, etc. In terms of quantity they are the largest colorant class, with 29% of the world dye market for use on cellulosic fibres[31].

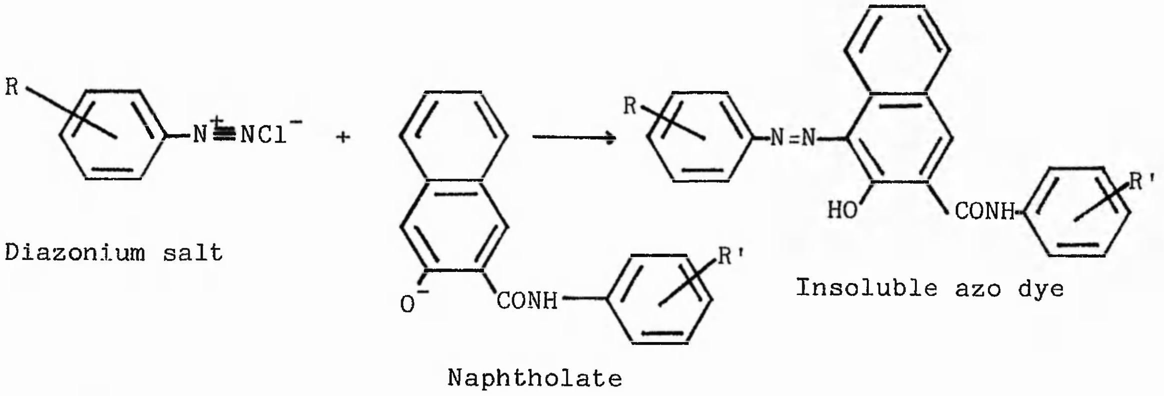
1.2.4 Azoic dyes

The first recommendation for the production of insoluble azo dyes on cotton was made in 1880 by Thomas and Robert Holliday[32]. Their patent described coupling diazotised 1- or 2-naphthylamine with 2-naphthol to produce reds or bordeaux. Para Red was another important early dye of this class, first synthesised by Meldola in 1885 by coupling diazotised p-nitroaniline with 2-naphthol.

The general procedure for dyeing with azoic dyes includes firstly impregnating the material with a solution of an Azoic Coupling Component in sodium hydroxide, normally with the addition of salt. These are mainly derivatives of 2-naphthol (three quarters of those marketed being anilides of 2-hydroxy-3-naphthoic acid) and are substantive towards cellulose; they are often simply referred to as naphthols.

After removal of excess liquor the dyeing is developed in a solution of diazonium compound. Azoic Diazo Components are sold commercially in two forms, Bases and stabilised Diazo Salts, hence depending on the form in use the developing solution is prepared either by diazotisation of a base (using hydrochloric acid and sodium nitrite) or simply by dissolving a diazo salt.

The dyeing process thus consists essentially of the coupling of these two relatively colourless soluble components within the fibre to produce a larger water-insoluble coloured molecule. The reaction taking place may be given by:



Although in theory there are some 1700 potential azoic combinations from the available components (34 naphthols and about 50 bases) not all are of commercial value. A good range of yellows, oranges, and reds exist although blues, browns and greens are limited. Generally azoic dyes are used for furnishings, etc. wherever good to excellent wash fastness, reasonable light fastness combined with cheapness are required.

1.2.5 Reactive dyes

As long ago as 1895 Cross and Bevan[3] recognised the advantages to be gained, in terms of improved wet fastness properties, by creating a chemical bond between the dye and the fibre. However, it was not until 1953 that the breakthrough took place, when Rattee and Stephen of ICI discovered that dyes containing the dichlorotriazinyl group could be made to form a covalent bond with cellulose[33].

The dichlorotriazinyl group has two electron-deficient carbon atoms and is therefore susceptible to nucleophilic substitution reactions with the partially ionised hydroxyl groups of the cellulose.

At the same time triazinyl dyes also undergo hydrolysis in the presence of water. These two competing reactions are illustrated in Figure 9.

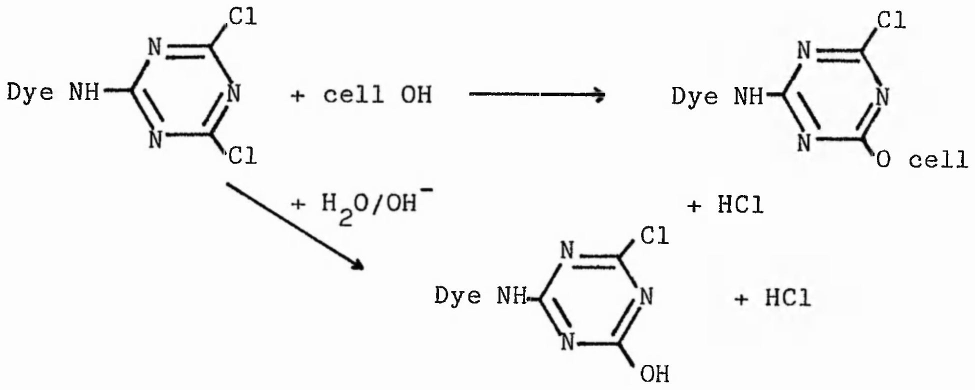


Figure 9.

Below is an example of one of the first three commercially successful dichlorotriazinyl dyes for cellulose, marketed in 1956.

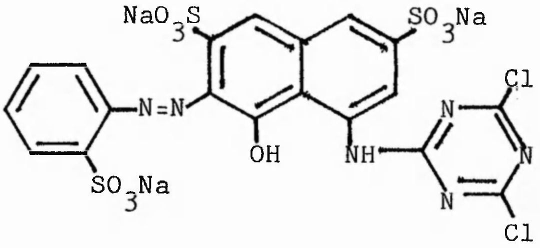
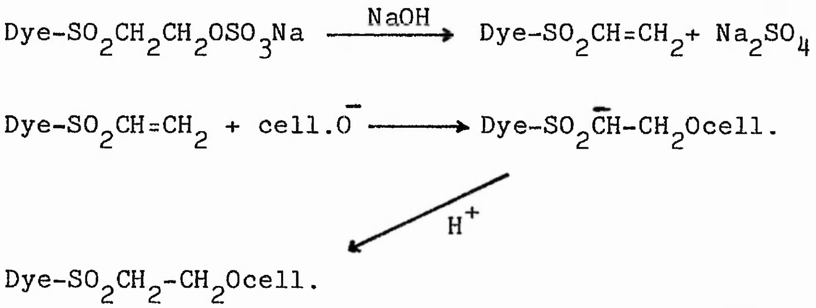


Figure 10. Procion Brilliant Red 2BS (ICI: C.I. Reactive Red 1).

Since then many other dyes have been introduced which react by a similar mechanism based on the presence of labile halogeno substituents in a hetero aromatic system, eg. the monochlorotriazinyl dyes, and others based on the pyrimidine, pyrazine, quinoxaline, thiazole and pyridazone reactive systems[34].

The vinyl sulphone dyes also represent another important class of reactive dyes. They react by way of addition of the nucleophilic cellulosate anion to an unsaturated carbon-carbon double bond of the reactive system formed in the dyebath by the elimination of a leaving group, usually sulphuric acid.



$$\text{Dye-SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na} \xrightarrow{\text{NaOH}} \text{Dye-SO}_2\text{CH=CH}_2 + \text{Na}_2\text{SO}_4$$

$$\text{Dye-SO}_2\text{CH=CH}_2 + \text{cell.O}^- \longrightarrow \text{Dye-SO}_2\bar{\text{C}}\text{H-CH}_2\text{Ocell.}$$

$$\xrightarrow{\text{H}^+} \text{Dye-SO}_2\text{CH}_2\text{-CH}_2\text{Ocell.}$$

An example of a typical vinyl sulphone dye is given below.

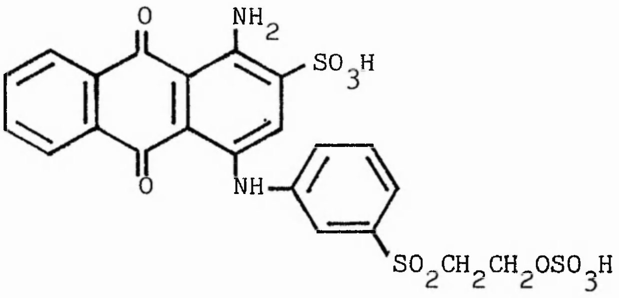


Figure 11. Remazol Brilliant Blue R (C.I. Reactive Blue 19; C.I. 61200).

The reactive dyes are thus water-soluble, anionic dyes characterised by their ability to react chemically with the fibre under alkaline conditions. They have lower substantivity for cellulose than direct dyes and hence higher concentrations of electrolyte (either sodium chloride or sodium sulphate) are required to promote adequate exhaustion, prior to the addition of alkali to bring about fixation.

Different types of reactive dyes have different reactivities, some reacting at room temperature whilst others require temperatures of 80-100°C. Once reaction is complete, hydrolysed dye adsorbed by the fibre is removed by thorough soaping. This leaves the dye chemically bound to the fibre giving very high wash fastness.

Reactive dyes are thus particularly suited for use where good wash fastness without maximum light fastness is required, for example in garments and fashion articles. They have a full range of shades, most of the colours being brighter than those given by direct dyes.

1.3 The theory of cellulose dyeing

The origin of the very strong substantivity which many dyes have for cellulose has been the subject of much investigation, particularly since there appear to be few reactive groups in the fibre[35]. The earliest theories[36], advanced by Hellot and others from the mid-eighteenth century onwards, offered a purely mechanical explanation whereby the fibre pores were swollen sufficiently by the hot dyebath to admit dye particles which entered and were later trapped inside the fibre on cooling. In fact, recently, similar ideas have again begun to come to the fore.

There is also much evidence, however, in support of the view that various forces of attraction operate between the dye and the fibre and that consequently the substantivity exhibited by a particular dye is closely related to it's molecular structure. Direct dyes which are substantive to cellulose tend to be large, linear, coplanar molecules which are capable of closely approaching the cellulose molecule and aligning more or less parallel to the fibre axis.

This explains the outstanding importance of J acid (Figure 12) as a middle component of direct dyes, for it is the only aminonaphthol to give linear azo dyes, deviations from linearity generally being accompanied by a loss in substantivity.

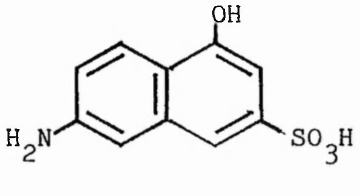


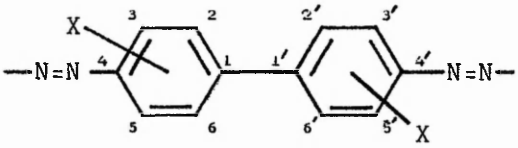
Figure 12. J acid. (6-amino-1-naphthol-3-sulphonic acid)

Several authors also advanced the hypothesis that hydrogen bonds could form between the dye and the fibre molecules[37]. However, it has since been suggested that hydrogen bonds are not formed because the cellulose hydroxyl groups are liable to be too firmly attached to water to allow bonding to the polar groups of a dye by this mechanism.

This conclusion was supported by monolayer studies, carried out by Allingham and co-workers[38], in which a single layer of water molecules was found to exist between each dye and cellobiose molecule effectively preventing hydrogen bonds forming between them.

The linear relationship which exists between the affinity of anionic dyes for cellulose and the (log) length of the conjugate chain in their molecules also suggests that the source of affinity lies in either or both of dye-fibre or dye-dye van der Waals forces rather than in hydrogen-bonding groups, since many of the dyes do not differ in their content of the latter,yet differ markedly in affinity[39,40].

Although the first direct dye was prepared by Bottiger, Hodgson[41] was possibly the first to clearly state that for a dye to be substantive towards cellulose the various benzene and naphthalene nuclei of which it is composed must be capable of lying in one plane. Working with disubstituted benzidine derivatives it was discovered that only those derivatives which contained substituents in the 3,3' positions yielded substantive dyes.



X = CH_3, OCH_3, NO_2,
OH, Cl.

Figure 13. Main structural feature of disubstituted benzidine derivatives.

Generally speaking, derivatives with substituents in the 2,2' positions, or even unsymmetrically substituted derivatives, had too low an affinity to be practically useful on cellulose owing to the fact that steric interactions between the two substituents did not allow free rotation of the two benzene nuclei about the common bond thus preventing them from being coplanar.

Schirm[42] on the other hand suggested that, in addition to being linear, a dye which is substantive towards cellulose must also contain a long conjugated chain of double bonds. Vickerstaff[37], however, considered the conjugation theory was more than likely another way of expressing Hodgson's coplanarity theory since resonance, for example between two benzene nuclei, (an important property of conjugated chains) forces the rings to assume a coplanar configuration by virtue of the fact that one of the resonance forms is the quinonoid structure (Figure 14).

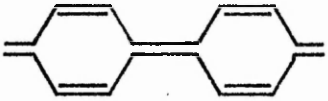


Figure 14.

Further understanding of the importance of van der Waals forces in the dyeing of cellulose was again derived from monolayer experiments[43]. The evidence pointed to a definite attraction between cellulose and direct dyes, supporting the hypothesis that the dye molecules are orientated flat, face to face with, and parallel to, the cellulose chains on the water surface. A similar suggestion was made by Morton[44] to account for the dichroic effects shown by dyed cellulose.

Moreover a significant degree of planarity is also known to be of importance in determining the affinities of leuco vat dyes. Daruwalla et al.[45] synthesised a series of identical pairs of vat dyes, the only difference between them being that one of each pair was planar and the other was non-planar, and found that the affinities of the non-planar derivatives were all less than 5% of their planar analogues.

The marked need for a planar molecular configuration may thus be taken as an indication that close proximity between dye molecules and the polymer chain is an essential factor in the dye binding mechanism. This in turn suggests that van der Waals forces in the form of dipole interactions, either of a permanent character between dipoles in the molecule, or of the perturbation type (ie. dispersion forces) are likely to be of great importance in cellulose dyeing.

Examination of some of the more important groups in direct dyes known to confer increased affinity reveals the presence of several dipolar groups, such as the benzoylamino and ureido groups and the imido system and, in the case of fibre-reactive dyes for cellulose containing a wide variety of heterocyclic substituents, it is clear that the more dipolar the character of the heterocycle the higher the affinity of the dye[46].

The possibility of a type of acid-base bond between cellulosic hydroxy groups and the free hydrogen atoms on amino groups in dyes has also been reported[43]. The hypothesis is supported by the finding that C.I. Direct Blue 1 forms a complex with cellulose in Cadoxen solution whereas C.I. Direct Blue 10 (which is very similar in structure but has -OH and no $-NH_2$ groups) does not. The complex is also very weak and, in common with other ionic bonds, has no influence on the surface viscosity of a monolayer of cellulose whilst the presence of hydrogen bonds would be expected to considerably increase the viscosity of the monolayer.

It has also been suggested that a form of hydrophobic bonding may exist between the hydrophobic portions of a dye molecule and the CH groups in the cellulose molecule[47]. However, the lack of influence of paraffinic weighting groups in dye molecules, as compared with conjugated or dipolar substituents, argues against hydrophobic interactions, as normally understood, playing any significant role in dye binding[46].

The possibility of an attraction between dipoles on the cellulose ether groups and ionic groups in the dye molecules has also been advanced as a potential contribution to the attractive forces operating between dye and fibre[48] although no extensive research has been carried out to investigate this.

The evidence thus points to the simultaneous operation of a number of weak forces between a dye and a cellulosic substrate all of which assist the initial concentration of dye at the fibre-solution interface. Once the dye has entered the fibre there is now a growing body of evidence which suggests that the next step in the dyeing mechanism is self-association into quite large molecular aggregates.

This would explain why dye molecules held by ion exchange forces at a non-porous surface are almost instantly removed by cold water yet when they are held by similar forces in a fibre they are far more resistant to removal. Moreover electron micrographs have been obtained[49] clearly showing aggregates of several direct dyes within the cellulose structure and the results have been correlated with light fastness tests.

Dyes with low fastness on cellulose showed no particles whereas those with high fastness formed clearly visible particles (order of magnitude 1 μm). In fact the growth of aggregates of water-insoluble dye on soaping is a phenomenon known from other investigations to be an essential part of the dyeing process with both vat and azoic dyes.

In addition, a new method for measuring the state of association of dyes in cellulosic substrates (using the adsorption of p-nitrophenol from aqueous solution onto the dye)[50] has shown that direct dyes of low fastness are, in fact, present as multilayers (superimposed monolayers up to ten or twenty layers deep) whereas, for example, a monoazo acid dye at a weak depth was found to be adsorbed on cellulose as a monolayer or as only a few superimposed monolayers.

It would appear then that the affinity of a dye for a fibre may be expected to rise with ease of dye association, which could explain the linear relationship between the length of conjugate chain in the molecules of certain series of vat and sulphonated azo dyes and their affinity for cellulose[39,40].

It also seems fairly certain that even at high temperatures the association of dyes in solution is greatly increased by the fact that the structure of cellulose is such, that dyeing takes place, in effect, in a mass of submicroscopic pores.

Since cellulose acquires a negative surface charge when immersed in water, due to the ionisation of hydroxyl groups, the dyeing of cellulose is usually carried out by employing dyebaths of high ionic strength. This offsets the electrical effect by screening of the surface charge and compression of the electrical double layer, thus allowing anionic dyes to enter the fibre. (Most dyes for cellulose are anionic - at least in their application stage). In the case of cellulose the presence in the dyebath of an excess of inorganic salts is likely to further enhance the association of dyes in solution.

Recently a new hypothesis of the mechanism of cellulose dyeing has been put forward which claims to explain all the facts better than any former suggestion[51]. It recalls very early theories which linked substantivity with colloidal character by suggesting that colloidal particles of dye are embedded in the fibre.

The difference in substantivity between a direct dye and a monoazo dye is explained simply by the difference in their respective association ability. Both dyes are believed to be accepted on areas of internal surface of the same magnitude, but the larger direct dye molecule has the much greater power of self association and so builds up multilayers.

The need for length and planarity in a dye molecule for cellulose is explained by the fact that both properties allow the molecule to readily penetrate the intermicellar spaces in the fibre and once there to form large aggregates. The explanation of aggregation is that the water of solvation carried by the dye is preferentially adsorbed on the walls of the pores, allowing the dye molecules to combine together more readily.

Inorganic salts greatly assist aggregation, in fact, the order in which the alkali metal chlorides assist the adsorption of C.I. Direct Blue 1 by cellulose[52] is almost the same as their order in promoting aggregation of the same dye in aqueous solution[53].

There are therefore two different hypotheses to account for the substantivity of direct dyes for cellulose, one based on the operation of one or more of a variety of chemical attractions between the dye and the fibre, and the other on a purely mechanical effect arising from the pore structure of cellulose.

CHAPTER 2

HISTORICAL REVIEW

2.1 Differential-dyeing cotton: Introduction

With the discovery of the new regenerated cellulose fibres, viscose rayon and acetate rayon, in the later part of the 19th century it soon became apparent that, whilst uniform, lustrous and silk-like artificial fibres could be obtained, at the same time certain desirable properties of the original cotton fibre, such as its porosity, its ability to swell and to resist, without loss of strength, hot aqueous solutions were considerably diminished[54].

These fibres were produced by drastic chemical treatments requiring dissolution of the various salts and esters of cellulose in suitable solvents and resulting, therefore, in irreversible changes in the structure of the original cotton fibres and, consequently, in the dyeing properties of the resultant yarns.

Viscose rayon, for example, shows an increased affinity for direct dyes whereas the acetylated derivatives of cellulose exhibit a very characteristic "resist" effect since, owing to their essentially hydrophobic character, they possess no affinity for the direct cotton colours whilst still being capable of adsorbing readily basic dyestuffs, diazotisable amino bases and, as subsequently found, disperse dyes.

It was soon realised, however, that a commercially viable process for the treatment of cotton, which would confer upon it the special dyeing properties of the new acetylated cellulose without alteration of its physical structure, would be of marked importance to the textile industry for the production of two-colour and white and coloured effects in the piece dyeing of all-cotton goods.

Fabric woven from treated cotton (capable of being dyed only with basic dyes) and untreated cotton could thus be dyed two colours from one dyebath containing, for example, a basic and a direct dye. Similarly three shades of one colour could be obtained from one dyebath by combining mercerised, untreated and treated cotton in one fabric (called a "tone-on-tone" effect).

Such a product could thus prove of considerable advantage to producers of coloured cotton goods who are continually affected by the vagaries of fashion. A large quantity of fabric with a popular weave could thus be made up and, after testing the market to determine the most popular colours, dyed quickly without having to revert to the package dyer and the weaver. Alternatively, customers purchasing in bulk could select their own particular colour schemes and the yarn could then be quickly dyed to their individual specifications.

Interest in the concept of this new differential-dyeing cotton and its commercial possibilities quickly grew spurred on by the setting of a prize problem, in the J.S.D.C. of March 1906, "to so treat or prepare cotton yarn as to cause it to resist direct cotton colours".

The following is a critical account of the various attempts of research workers to produce such a cotton and includes mention of, not only those efforts submitted as a direct result of the competition, but also the many and various attempts which have been recorded in the literature in the ensuing years leading up to the commencement of the present work.

It should be noted that, in much of the later work (although not all), the problem has in fact been approached from an entirely different viewpoint - that of treating the cellulose so as to enhance its dye uptake capabilities with respect to untreated cellulose, rather than preparing a cotton which was resistant to the normal cotton dyestuffs.

For clarity, the literature relating to cotton has therefore been divided into two main sections - the first devoted to those treatments or modifications of cotton designed so as to cause it to resist direct dyes, and the second to those where enhancement of the dye uptake capabilities of the yarn was the main intention.

In both cases, however, the ultimate objective remained the same, that is, the preparation of two-colour, white-and-coloured, and tone-on-tone patterned effects from one dyebath in the piece dyeing of all-cotton goods.

2.2 Chemical modification of cellulose to resist direct dyes

2.2.1 Early treatments of cotton

The earliest methods of treating cotton so as to cause it to resist direct dyes relied upon bringing about a physical reserve by precipitating on the fibre certain substances which did not absorb dye so that the colour could not actually penetrate into the fibrous substrate. One such example was the tannin-tin mordant which was first introduced by Mercier and Chaumartin of Lyons for silk in 1897 and adapted by Fothergill[5] for use with cotton.

Submitted to the aforementioned competition under the nom de plume "Vogue la Galere" (which translates as "Come what may!"), the method involved soaking the cotton in a 3% solution of tannic acid, hydro-extracting and fixing in a 2% solution of tin II chloride at 30°C; any tenderisation of the cotton being largely prevented by a subsequent treatment with a weak alkaline solution of soap or sodium carbonate[55].

Haller[56] later proved by microscopical measurements that the tannin was actually deposited in the "micellar spaces" of the cotton thus revealing the physical nature of the reserving properties produced by the treatment.

On awarding Fothergill the Bronze Medal of the Society for his contribution to the competition the adjudicators did, however, point out at the time that, whilst the process was practicable in that it was inexpensive and no special apparatus was required, at the same time the resulting yarn could be expected to find only limited demand on account of the considerable discoloration and harsh handle resulting from such a heavy deposit of tannin.

Other attempts to obtain such results involved the impregnation of the goods with suitable drying oils or, alternatively, the production on the fibre of certain higher metallic oxides[54]. However the uncertainty of the results obtained, and the fact that both fibre and dyestuff were liable to attack by the reagents used, meant that these processes were uneconomic and of low efficiency and thus they too were never adopted on a commercial scale.

2.2.2 The preparation of non-ionic derivatives

2.2.2.1 Acetylation of cellulose

The first work on this subject was due to Cross and Bevan[3] who, in 1901, described the preparation of a low acetylated cellulose fibre in which the original physical form of the cellulose was reserved. The method involved treating bleached cotton with boiling acetic anhydride at 118°C in the presence of anhydrous sodium acetate and ensured that the fibrous nature of the cellulose was retained by excluding glacial acetic acid (a solvent for the acetate) from the acetylation mixture, thus preventing the product from passing into solution during the course of the reaction. The reaction taking place may be represented by the following equation, although it's mechanism is more complex and is discussed in more detail later:

$$\text{Cell.(OH)}_3 + (\text{CH}_3\text{CO})_2\text{O} \longrightarrow \text{Cell.OCOCH}_3 + \text{CH}_3\text{COOH}$$

The resultant fibres were insoluble in all the organic solvents suitable for the highly acetylated celluloses and insoluble also in the usual solvents for cellulose eg. ammonium nitrate and zinc chloride solutions. Unfortunately, however, these fibrous acetates were of no practical use since the yarns had lost all tensile strength and were weak and brittle, due most probably to the high reaction temperature. The treatment also resulted in fibres with considerably reduced hygroscopic capacity compared with the original fibres.

Another early attempt to produce a cotton which did not dye readily with direct dyes, whilst retaining its normal physical characteristics, was that of Meister, Lucius and Bruning[54] (now Hoechst A.G.). They recommended a treatment of cellulose with glacial acetic acid and, though a decided difference in depth of shade was noticeable when a hank of the treated cotton was dyed with a hank of ordinary cotton, at the same time the results obtained were far from satisfactory.

Other processes for the acetylation of cellulose, which preserved its fibrous structure, involved carrying out the reaction in the presence of sulphuric acid and in a non-solvent medium such as tetrachloromethane, ether or benzene which was miscible with acetic anhydride[58-60].

However, these techniques generally required the action of sulphuric acid at relatively high temperatures of 70-80°C for several hours which, Cross and Briggs[6] claimed, produced structural modifications which so weakened the fibre as to make it unsuitable for textile purposes. In addition the cost of the ether or benzene, together with the large proportion of acetic anhydride used (five to six times the weight of the cellulose), would mean that, even if suitable, the product would have been too costly.

Cross and Briggs, however, had come to realise that, in order to obtain a perfect resistance to the substantive dyes, it was not necessary to prepare an acetate with the maximum limit of esterification and that lower acetates might be obtained which showed a full resistance to these dyestuffs.

These lower acetates were insoluble in the acetylating mixture and thus non-solvents, such as benzene, were not necessary. Furthermore, large excesses of reagents were not required for their preparation and milder conditions could be employed, resulting in less degradation of the resultant fibres.

The original process of Cross and Bevan was therefore modified accordingly, with a view also to conducting the acetylation at lower temperatures, and the work was subsequently submitted to the Society of Dyers and Colourists as a solution to their technical problem No. 2 of 1906 ("to so treat or prepare cotton as to cause it to resist direct cotton colours"). The treatment, which they claimed had no apparent effect on structure and which reduced the consumption of acetic anhydride to only 100-150% of the weight of the cellulose, consisted of steeping the cotton in a mixture of acetic anhydride, acetyl chloride, glacial acetic acid and zinc oxide, squeezing so as to retain a certain definite percentage of the liquid, and then allowing it to react in a closed vessel at 35°C for 36-48 hours[6].

Although it was awarded the prize of £10 for the best entry to the competition, the umpires report did, however, point out at the time that the high cost of the reagents and the special apparatus required would render the process uneconomical from a commercial standpoint. This, together with the fact that unevenly acetylated fibres were obtained owing to a lack of control during the reaction, resulted in the process not achieving any technical or commercial importance.

Numerous other similar processes were patented all of which relied upon carrying out the reaction outside of the acetylation mixture, or in an insufficiency of acetic anhydride, so as to prevent the higher acetylation of the cotton and thus the dissolution of the resultant ester.

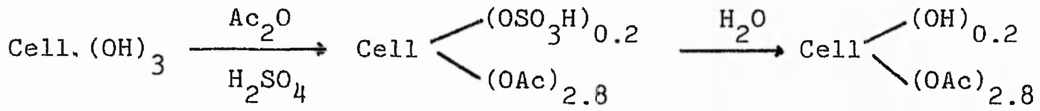
In one process, for example, cellulose was impregnated with the vapour of acetic anhydride boiling under reduced pressure[61]. Unfortunately, the acetylation was carried out in the absence of catalysts in which case the reaction took place very slowly in spite of the high reaction temperatures and tendering of the fibres could not be avoided[62].

Hess and Ljubitsch[63] discovered, however, that by omitting the acid catalyst and using acetic anhydride in the presence of pyridine, degradation of the fibres could be avoided. Unfortunately, even at temperatures of 55°C, the acetylation still proceeded rather too slowly for the process to be practicable. Nevertheless, since then, mixtures of acetic anhydride and pyridine have been used to bring about partial fibrous acetylation in laboratory investigations of the properties of cellulose (eg. reactivity)[64].

Less degradation was also claimed to occur if the acetylation was carried out in toluene with a mixture of sulphur dioxide and a small amount of perchloric acid as catalyst[65]. In fact Kreuger and Tschirch showed that perchloric acid alone had a greater catalytic effect on acetylation than sulphuric acid, and could be used, in the presence of acetic anhydride and benzene, to prepare a true cellulose triacetate (degree of substitution [D.S.] = 3.0) free from combined perchloric acid [66]:

$$\text{Cell.(OH)}_3 \xrightarrow[\text{HClO}_4]{\text{Ac}_2\text{O}} \text{Cell.(OAc)}_3 \qquad \text{D.S.} = 3.0$$

Sulphuric acid, on the other hand, combines with cellulose in the course of the acetylation to give a cellulose acetate sulphate triester which may be isolated as such or the combined sulphate may be removed, without loss of acetyl, giving a high-acetyl cellulose acetate (D.S. = 2.8)[67]:



$$\text{Cell.(OH)}_3 \xrightarrow[H_2SO_4]{Ac_2O} \text{Cell}\left\langle\begin{matrix}(OSO_3H)_{0.2}\\(OAc)_{2.8}\end{matrix}\right. \xrightarrow{H_2O} \text{Cell}\left\langle\begin{matrix}(OH)_{0.2}\\(OAc)_{2.8}\end{matrix}\right.$$

D.S. = 2.8

Rheiner and his colleagues at Sandoz also prepared fibrous acetates, in this case the mono- and diacetates, by choosing an acetylating mixture of moderate activity which reacted so slowly that even acetylation to the monoacetate took 20 hours or longer. Descriptions of the various processes may be found in the patent literature[68].

During the acetylation the affinity for direct dyes decreased rapidly at first and, as the process continued, became gradually less until the monoacetate stage was reached when the fibres were very highly swollen and the affinity for direct dyes practically nil. Drying of the fibres then completed the immunisation process to produce what was called "Passive Cotton", which was incapable of swelling again to the same extent, or "reactivating", even in boiling water, and was thus resistant not only to direct dyes but also to vat and sulphur dyes which could not penetrate into the fibre.

Stronger swelling agents such as solutions of aliphatic carboxylic acids and particularly aqueous solutions of formic, acetic or butyric acids were, however, capable of reactivating the low acetylated fibres and thus restoring their dyeing properties. In fact, after drying, cotton colours were said to be, not only faster on low acetylated fibres dyed in the swollen state than they were on ordinary cotton, but also faster than disperse dyes were on low acetylated fibres[69].

An even more effective method of preventing subsequent swelling, than that of drying, was to steam under high pressure, whereby treated yarns were rendered immune to direct dyes even before they were esterified entirely to the monoacetate stage[70].

One such preparation of passive cotton consisted essentially of acetylating well-scoured cotton yarn in a mixture of acetic anhydride, glacial acetic acid and zinc chloride for 20 hours at 25°C. After acetylation the original physical structure of the cotton was unchanged and the fibres were found to possess the same strength and elasticity as untreated cotton but a somewhat firmer handle.

The regularity of the treatment was demonstrated when cross-sections of these low acetylated fibres, dyed with disperse (acetate) dyes, were shown to have dyed evenly throughout, whereas previous fibrous esters had shown an ester layer as a dyed outer ring surrounding unchanged cellulose[71]. Hess[72], however, showed that Rheiner's product could not be regarded as a homogeneous monoacetate.

Cotton yarn prepared according to the above specifications was sold commercially as "Cotopa" (a contraction of cotton-passivated) up until the late 1960's. The Cotopas (which consisted of Cotopa 30 - the monoacetate - containing 30% acetic acid, and Cotopa 60 - the triacetate - containing 60% acetic acid) were generally much more resistant to heat and oxidation than cotton, silk or acetate rayon and also showed interesting electrical properties, eg. the d.c. insulation resistance of Cotopa 30 was 25,000 that of ordinary scoured cotton[73].

They also showed considerable advantages over acetate rayon for use as immunised yarns[74]; not only were they physically and chemically more stable, they were also much less lustrous and they could be dealt with on ordinary cotton machinery whereas rayon required special winding machines and special looms. A lustrous form of the product, known as "Crestol", could also be obtained by a similar treatment of mercerised cotton.

Cotopa thus found many applications as a dye resist yarn particularly for the production of stripe and check effects in piece-dyed cottons for use in shirtings and pyjama cloths, candlewick bedspreads, towelling, furnishings etc. It was also widely used in the lace trade for producing dye resist effects in cotton lace before the large scale change over to the use of nylon[75].

Other commercial process for the partial acetylation of cellulose, retaining the original fibrous structure, were developed at the Southern Regional Research Laboratory in New Orleans by Goldthwait and co-workers from around 1964[76]. Both batchwise and continuous methods were adopted, generally employing glacial acetic acid and acetic anhydride as the acetylating mixture with small amounts of perchloric acid as catalyst[77].

Partially acetylated cottons were thus prepared containing D.S.'s of 1.1 and 2.6 and both were shown to be resistant to direct dyes but readily dyed by disperse colours. However, in this case, the outstanding properties of the treated material as regards heat and rot resistance seemed to be the main points of interest, rather than its ability to resist direct dyes and so act as a differential-dyeing cotton.

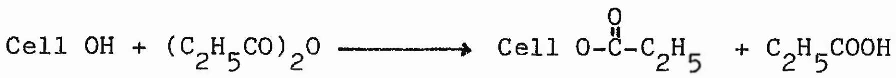
Partially acetylated cotton was expected to find considerable use, for example, as an outdoor fabric for the manufacture of tents, tarpaulins and awnings. Unfortunately, resistance to sunlight was only slightly improved over that of unmodified cotton, and the acetylated fabric did not succeed in penetrating this market.

Much more recently, however, interest in the dyeing characteristics of acetylated cotton has been revived by the discovery that the modern contact printing paper used in printing polyester, and employing disperse dyes, can be used on lightly-acetylated cotton[78].

2.2.2.2 Esterification with other aliphatic acids

The products obtained by the fibrous esterification of cellulose using other aliphatic acids have not generated as much commercial interest as the cellulose acetates with regard to their potential for the preparation of differential-dyeing yarns.

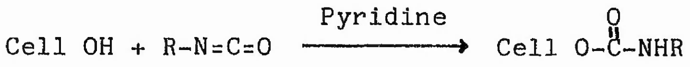
Whilst the formates are rather unstable, the preparation of the propionates and the butyrates is generally accompanied by degradation of the fibre. Malm and Clarke[79] prepared them by reaction of the two acid anhydrides with cellulose for about 100 hours at the boiling point in the absence of a catalyst but, although the fibrous structure was retained, the fibres were weak and friable. In the case of the propionate the amount of combined propionic acid was 8.1% corresponding to $C_{24}H_{39}O_{20}(COC_2H_5)$ or a D.S. = 0.25:



$$\text{Cell OH} + (C_2H_5CO)_2O \longrightarrow \text{Cell O-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}C_2H_5 + C_2H_5COOH$$

The esterification of cellulose with halogenated fatty acids, by Knoll and co-workers in 1906, was also reported to reduce the affinity of cellulose for direct dyes[80]. However, whilst the formation of the straight or mixed cellulose fatty acid esters, such as stearate and palmitate, were important from the point of view of preparing perfectly stable esters of high molecular weight, at the same time they did not offer anything new as far as their dyeing properties were concerned and the difficulties involved in their preparation increased as the molecular weight increased[81].

Cellulose alkyl urethanes with hydrophobic properties and resistance to dyestuffs have been made from various isocyanates. In one method, for example, the fibrous structure of the cellulose was retained by allowing the isocyanate to act upon cellulose in the presence of anhydrous pyridine[82]. In general the reaction may be given as:

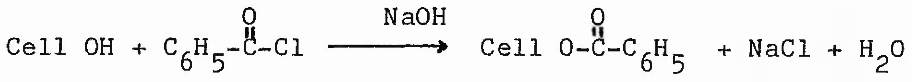


$$\text{Cell OH} + \text{R-N=C=O} \xrightarrow{\text{Pyridine}} \text{Cell O-}\overset{O}{\overset{\|}{C}}\text{-NHR}$$

More recently developments have been directed towards stabilising the treated fabrics[83], particularly with respect to the mechanical effects produced by various forms of calendering[84]. Organic di-isocyanates are used eg. hexamethylene di-isocyanate, either from xylene solution or aqueous dispersion, followed by heating at 150°C[85].

2.2.2.3 Esterification with aromatic acids

Early investigators made use of the Schotten-Baumann reaction to prepare the benzoic acid ester of cellulose by treating cellulose with benzoyl chloride in the presence of aqueous sodium hydroxide[86]. Cross and Bevan[87], for example, obtained a fibrous mono-benzoate by careful adjustment of the alkali concentration and removal of cellulose and the higher benzoates by means of suitable solvents:



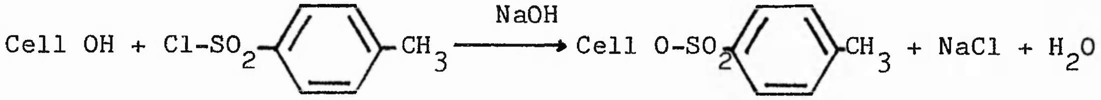
$$\text{Cell OH} + C_6H_5\text{-}\overset{\overset{O}{\|}}{C}\text{-Cl} \xrightarrow{NaOH} \text{Cell O-}\overset{\overset{O}{\|}}{C}\text{-}C_6H_5 + NaCl + H_2O$$

Employing a similar method L. Cassella and Co. obtained a patent[88] in 1922 claiming the action of aromatic acid chlorides, such as benzoyl and phthaloyl chlorides on cotton in the presence of alkali and a non-solvent eg. benzene. A pretreatment with caustic alkali in the presence of soap or Turkey Red oil followed by steeping in an aromatic acid chloride in benzene was later said to give improved results. These methods were developed commercially on the Continent, the product being sold under the name of "Reserve Cotton", which was stated to be a benzoyl derivative[57].

Although these esters resisted cotton dyes they were apt to be unstable, being readily saponified by alkali. Esters of sulphonic acid chlorides were, however, found to be much more stable and in December 1923 a patent was granted to Textilwork Horn A.G. which proved to be the basis of a commercially successful process[89].

Claims were made in the patent not only for o- and p-toluene sulphonyl chlorides but also for the benzene, xylene and naphthalene analogues together with their chloro, bromo, and nitro derivatives. In practice p-toluene sulphonyl chloride, occurring as it does as a by-product in the manufacture of saccharin, was found to be a cheap and effective agent and was used in the bulk manufacture of what later became known as "Immunised Cotton" on acount of its immunity to direct dyes. (This particular name had, in fact, been used some years earlier to describe cotton and wool blends treated so as to resist dyes).[54].

The process consisted essentially of immersing bleached cotton in a warm concentrated alcoholic solution of sodium hydroxide for an hour to form alkali cellulose. After centrifuging, the alkali cellulose was then placed in a solution of p-toluene sulphonyl chloride in tetrachloromethane at 15-20°C. The temperature rose with the course of the reaction and was then allowed to fall, after which it was raised to near the boiling point; the material was then extracted, soaped, washed and dried. Toluene could also be used as a solvent for the sulphonyl chloride. The reaction taking place may be given as:



The treatment, which resulted in about 50% of the cellulose being converted to the p-toluene sulphonyl ester, caused considerable shrinkage of the cotton with almost complete disappearance of the lumen or central canal. The weight of the cotton could be increased up to 40% without appreciable reduction in the tensile strength although the handle was somewhat harsh. The resultant fibres resisted direct dyes, even in the wet state, whereas their affinity for basic dyes was increased. The poor light fastness of the basic colours on esterified cotton, however, militated seriously against their wide employment.

In contrast to the results obtained with passive cotton, a microscopical examination of the immunised cotton fibres revealed that only the outer layers of the fibre had been esterified[71]. Cross-sections of the fibre dyed with disperse dyes showed a dark ring, indicating the outer layer of esterified material, surrounding a central core of unmodified cotton. This outer layer could be removed with pyridine leaving the unesterified centre as a somewhat thinner fibre, or, alternatively the cellulose could be removed in cuprammonia, the swelling pressure of the cellulose bursting the outer esterified layer which, after the cellulose had dissolved, remained as a fairly wide spiral tape.

Chippendale[71] attributed the reserving properties of these immunised yarns entirely to the presence of this outer esterified layer and the fact that during esterification all the molecular interspaces probably became closed thus preventing the colloidal particles of the direct dyes from penetrating the fibres.

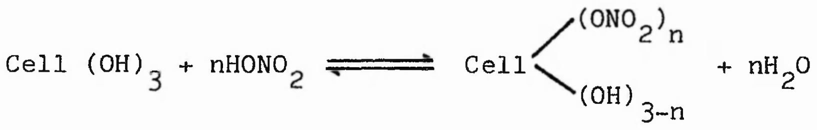
Immunised cotton was thus the first form of esterified cotton to be manufactured on a commercial scale. Four factories were concerned with its bulk production; three in Europe, including one in the north of England,and one in the United States. However by 1930 it was considered an obsolescent product and, save for a few special purposes, it had largely been replaced by passive cotton.

2.2.3 The preparation of anionic derivatives

2.2.3.1 Esterification with inorganic acids

By 1908, as a result of the work of Witz[90] and others,it was widely known that cotton could be treated with oxidising agents to obtain a fibre which showed an increased affinity for basic dyes and a reduced affinity for the direct dyes. This was attributed to the formation of ionisable carboxylic acid groups within the fibre, however, the overall effect was small and never approached a full resist. Also in many cases it is not clear whether or not the treated material retained its original fibrous structure.

However, in the course of a study of the behaviour of fibrous cellulose nitrates towards a variety of dyes under various conditions, Cross and Briggs[6] found that these derivatives, although not ionic, in fact showed a total resistance to the direct dyestuffs, which they ascribed to the influence of the electronegative nitrate groups which had been incorporated into the fibre.

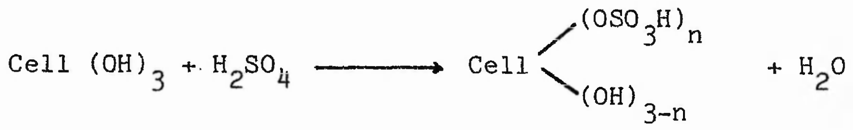


$$\text{Cell}\,(OH)_3 + nHONO_2 \rightleftharpoons \text{Cell}\begin{cases}(ONO_2)_n \\ (OH)_{3-n}\end{cases} + nH_2O$$

Schneider[4] also prepared a fibrous cellulose nitrate derivative, containing 12-13% nitrogen, which did not take up direct dyes but showed an affinity for basic colours. The treatment was carried out by steeping the yarn in a mixture of sulphuric and nitric acids at 10°C for one hour, hydroextracting the product, washing it with a large volume of cold water and then finally boiling it in a solution of sodium carbonate to remove the last trace of acid which, if left in the yarn, could seriously impair the stability of the final product.

However, the fact that cellulose nitrates with high nitrogen contents are very unstable and that all cellulose nitrates are inflammable, generally precluded their use in textile applications. Attention was therefore turned towards the preparation of similar cellulose derivatives of other inorganic acids which would contain acidic groups but which would be free from the drawback of inflammability.

Caille[91], for example, prepared sulphuric esters of cellulose which were anionic and showed affinity for basic dyes which increased with the sulphate content, whilst affinity for the acid and direct dyes diminished. They were prepared by treating cotton with 15 times its weight of a mixture of equal proportions of sulphuric and glacial acetic acids at 45°C for 30 minutes and resulted in the fibrous structure of the cellulose being retained[92]. The reaction may be given as:



$$\text{Cell}\,(\text{OH})_3 + H_2SO_4 \longrightarrow \text{Cell}\begin{cases}(\text{OSO}_3\text{H})_n \\ (\text{OH})_{3-n}\end{cases} + H_2O$$

However, it is unlikely that the above sulphation could have proceeded without some degradation of the cellulose occurring since most sulphation methods employing sulphuric acid degrade cellulose to a certain extent, the exact degree being dependant on the time and temperature of the reaction[93].

Chlorosulphonic acid could also be used to prepare cellulose sulphates containing 2.5 sulphuric acid radicals per glucose residue[94]. By immersing the cellulose in a mixture of the acid and a large excess of pyridine under cooling and subsequent heating to 80°C the fibrous structure of the material was said to have been retained to a large extent. Hydrochloric acid formed in the reaction was neutralised by combination with pyridine.

$$\text{Cell OH} + \text{ClSO}_2\text{OH} \xrightarrow{\text{Pyridine}} \text{Cell OSO}_2\text{OH} + \text{HCl}$$

Further details of the preparation of cellulose esters containing inorganic acidic groups, by treatment of cellulose with acid chlorides including thionyl chloride, sulphuryl chloride, phosphoryl chloride, and pyrosulphuryl chloride, dissolved in an inert solvent, are given in the literature[81,95].

Phosphoric acid can also be used to prepare cellulose phosphates which, in fact, have proved useful as cation exchange materials, on account of the anionic phosphate groups which are incorporated into the fibre on esterification[96]. A description of the dye-resistant properties of various cellulose phosphates will be given in the section on the cross-linking of cellulose (2.2.4.2).

2.2.3.2 Esterification with organic dicarboxylic acids

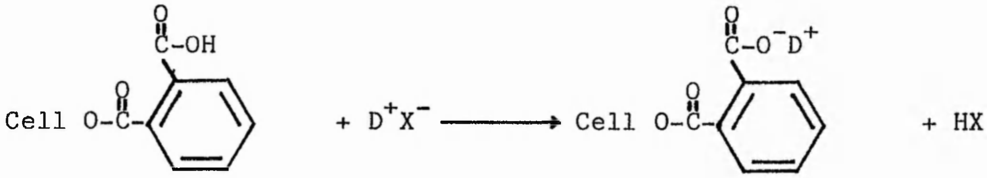
The possibilities of reaction inherent in organic dibasic acids attracted early research workers, however, their attempts to introduce charged groups into cellulose by reaction with dicarboxylic acids, such as oxalic acid, did not meet with much success. Frank and Caro[97] prepared several derivatives in which one carboxyl reacted with the acid whilst the other was esterified with an alkyl group but attempts to prepare the free ester by elimination of the alkyl radical were not successful.

Later, however, cellulose esters of dicarboxylic acids in which one of the carboxyl groups remained unesterified were prepared by reaction of cellulose with several acid anhydrides, including phthalic, succinic and glutaric anhydrides, in the presence of pyridine, although in these cases the fibrous structure of the cotton was not retained[98].

Recently, Lupton and Loughlin[99] described an alternative process whereby cellulose could be esterified with anhydrides, with retention of the original fibrous structure thus rendering it immune to direct dyes. Bleached cotton was treated locally with a 4% solution of phthalic anhydride in dimethyl formamide or dimethyl sulphoxide, cured at 155°C for 2.5 minutes, scoured and then dyed with 1% o.w.f. of a direct dye.

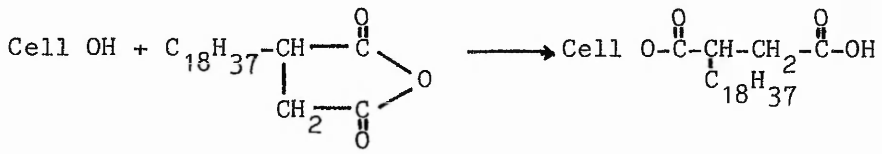
Alternatively bleached cotton was treated locally with a 4% solution of phthalic anhydride, acetic acid (10%) and non-ionic detergent (0.01%) in hot water at 80°C. The treated fabric was then cured at 170-180°C for 2.5 minutes, scoured and dyed with a direct dye.

In both cases the treated portions of the fabric were thus found to be completely resistant to most direct dyes, with very little weakening of the fabric as a result of the treatment and, in addition, showed great affinity for basic dyes, the free carboxyl groups incorporated into the fibre being capable of forming salts with the bases of cationic dyes.



Attractive dyeings of immunised fabric have reportedly been produced using direct and basic dyes in the same dyebath. However, it is not clear whether any cross-staining occurred, as is often the case with cross-dyeing systems, particularly when direct dyes are employed.

Similar, though invariably inferior, effects (ie. less immunisation against direct dyes and poorer affinity for basic dyes) were also obtained when other, more exotic, anhydrides were applied to cotton - with one exception. Interestingly, when the technique was carried out using n-octadecyl succinic anhydride, cotton did not become immunised against direct dyes but an affinity for basic dyes was imparted as well as a degree of water repellency. The reaction taking place may be given as:



The aqueous phthalic acid system could also be used to treat yarn used as a filling, in combination with an untreated cotton warp, to produce chambray and other speciality fabrics showing differential-dyeing characteristics[99]. Similarly, treated and untreated yarns could be woven into a fabric and dyed two colours from one dyebath.

In this way, as the authors point out, the product could prove a boon to the producers of coloured cotton goods since large quantities of fabric with a popular weave could be held in reserve until a popular colour scheme was decided upon and then quickly dyed and marketed without having to revert to the package dyer or the weaver.

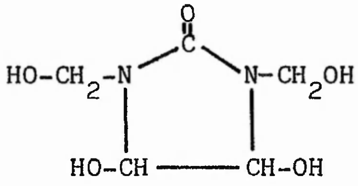
The number of basic dyes available for use would, however, be restricted by the poor light and wet fastness properties generally exhibited by this class of dye on the esterified cotton. Dramatic improvements in these properties were claimed for selected dyes aftertreated with phosphomolybdic tungstic acid, although such treatments would obviously add to the cost of the process.

A further disadvantage associated with the use of cellulose acid dicarboxylates is that, whilst they are insoluble in water they dissolve in dilute alkali to form salts[100]. This would further serve to limit the applications to which the end-product could be put, particularly since most cotton dyes are applied under alkaline conditions and, as a consequence, it is unlikely that dicarboxylated cotton could achieve any technical importance from a commercial standpoint.

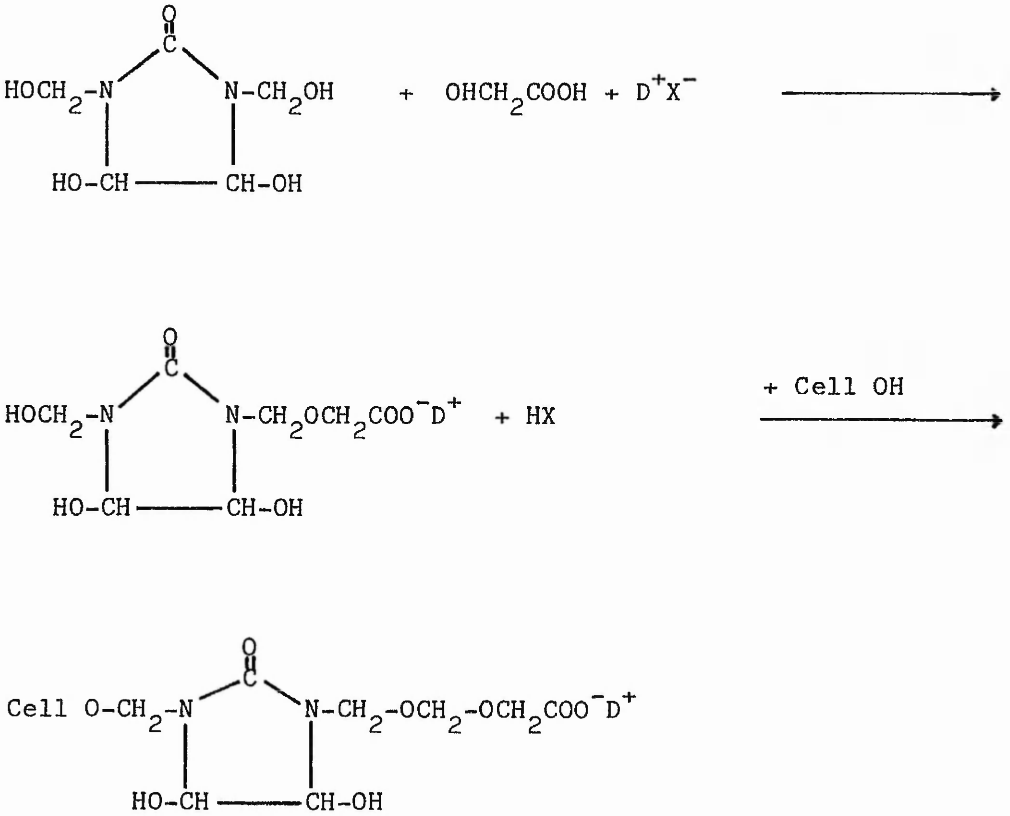
2.2.4 The cross-linking of cellulose

2.2.4.1 Application of polyfunctional cross-linking agents

Normally applied as an aftertreatment to impart a crease-resist finish to cotton, polyfunctional cross-linking agents such as dimethylol dihydroxyethyleneurea (DMDHEU), below, and methylolmelamine react with cellulose as well as forming an inert polymeric filling of the amorphous regions.



This causes the fibres to become more rigid and therefore they resist the formation of lasting creases. The availability of the amorphous regions of the cellulose, in which dyeing takes place, is also considerably reduced and hence the fibre becomes resistant to cotton dyes whilst, at the same time, a means is provided of grafting a reactive acid moiety, such as glycollic acid, onto the fabric in order to retain a basic dye.



Harper and co-workers[101] have developed several such techniques to obtain bi-coloured fabrics and although this actually involves the production of fabrics coloured differently on the two sides, in theory, at least, there does not appear to be any reson why these techniques could not be modified for appication to yarn so that a differential-dyeing cotton fabric might be obtained.

In one example cotton fabric was coated with a formulation containing 11% DMDHEU, 1% magnesium chloride hexahydrate, 2% citric acid, 1% C.I. Basic Yellow 11 and 0.7% HEC (hydroxyethyl cellulose) thickener after which the fabric was dried. The fabric was then either coated on the reverse with a second formulation containing a differently coloured dye or it was cured at 120°C for 5 minutes and then dyed with a conventional cotton dye. In both cases a bi-coloured fabric was produced.

These bi-coloured fabrics were durable to repeated laundering and crocking values were excellent. However, although the basic dyes gave brilliant colours on cotton, their light fastness was very poor. No mention was made of the losses in fabric strength which are generally associated with the use of methylolated cross-linking agents on cotton, hydrolysis of the fabric normally being required to restore fabric strength after curing.

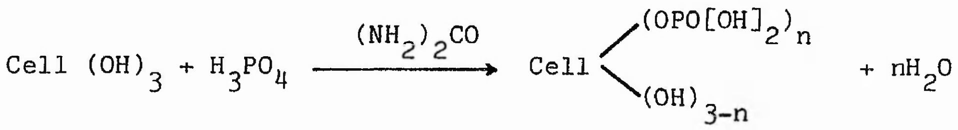
Further examples were also given of techniques involving dyeable polymers which could be used to produce bi-coloured cotton fabrics. Polymers, such as Vinyl Latex 660*1, supplied a surface which was dyeable with a non-cotton dye (in this case a disperse dye was used) whilst the cross-linking agent made the same surface resistant to cotton dyes.

A similar principle was used to produce cross-dyeable cotton. Either the warp or the filling yarns could be treated with a formulation consisting of 4% polyvinyl alcohol, 12% polyacrylate E-358, 3% DMDHEU and 0.2% zinc nitrate hexahydrate catalyst. In either case, curing of the cross-linking agent was preferred after weaving. Fabric woven from combinations of treated and untreated yarn was then dyed, firstly with disperse, basic or acid metallised dyes, depending on the polymer used, and secondly with a reactive dye for the untreated cotton, to produce a cross-dyed all-cotton fabric.

Once again the light fastness properties of basic and disperse dyes on polymer treated cotton yarn left much to be desired, although when acid-metallised dyes were used the light fastness was satisfactory. In order to obtain a commercially viable product on all counts, the authors suggest it may therefore be necessary to develop special polymers which would, ideally, be capable of accepting a wide variety of different dye classes and have excellent durability on cotton so that the colour was retained.

2.2.4.2 Phosphorylation of cellulose

Phosphorylation can also be used as a means of cross-linking cotton and is usually carried out by treating the fibre with a phosphoric acid-urea mixture[102]:



$$\mathrm{Cell\,(OH)_3 + H_3PO_4 \xrightarrow{(NH_2)_2CO} Cell}\left\langle\begin{matrix}(\mathrm{OPO[OH]_2})_n\\ (\mathrm{OH})_{3-n}\end{matrix}\right. + n\mathrm{H_2O}$$

Reid and Mazzeno[103], however, have investigated the phosphorylation of cotton with a number of other agents.

Gallagher[104] discovered that phosphorylated cotton could be prepared by a pad-cure procedure using alkali metal phosphates or condensed phosphate salts. The products were found to be insoluble in cupriethylenediamine, indicating that the cellulose had been cross-linked, but no mention was made of the dye-resistant properties of the modified cotton.

More recently Blanchard and co-workers[105] have studied the phosphorylation of cotton using a number of mono- and dibasic alkali metal phosphates and ammonium phosphates specifically in order to determine the dye-resist characteristics of the yarns produced.

Phosphorylation of cotton was thus shown to be an effective method for producing dye-resistant yarns and fabrics. Yarns treated with phosphorylating agent could be woven with untreated yarns to produce a fabric which, after curing at 170°C for 2.5-10 minutes, exhibited a chambray effect on dyeing with reactive, vat or other cotton dyes, such as directs. (Chambray is a cotton fabric which contains a coloured warp and an undyed filling. Usually the yarns are dyed on the warp beam, sized and then woven with a white filling to obtain the desired effect).

In addition, frosted and shade differential pile fabrics could be produced by preferentially treating the pile of the fabric with various amounts of phosphorylating agent. Good resistance to most dye classes was thus shown by the phosphorylated cotton without the severe strength losses normally associated with cross-linked cotton, and there was no need to hydrolyse the fabric to restore fabric strength after curing, as was the case with the methylolated cross-linking agents used previously to obtain cross-dyeable cotton fabrics[101].

Phosphorylated cotton did, however, show good affinity for acid metallised dyes whereas acid dyes that were not metallised showed no affinity for the treated cotton. This was attributed to the ability of the phosphate to complex with the chromium ion of the acid metallised dye molecule.

However, microscopic examination of cross-sections of dyed fibres revealed that there was little penetration of dye into the fibre and that most of the dye was concentrated at the fibre surface; consequently colour fastness to washing for all the phosphorylated samples was not good.

2.2.4.3 Pyrolytic cross-linking of cellulose

Laser treatment of cotton has also been shown to produce a resist effect where direct dyes are concerned, whilst the usual lack of affinity for acid, basic and disperse dyes remained unaltered[106]. This resistance to direct dyes was attributed to pyrolytic cross-linking of the cellulose molecule, which would again tend to reduce the accessibility of the lower ordered regions of the fibre where dyeing is known to take place[107].

By applying subcutting doses of radiation of increasing energy to a strip of cotton fabric and then dyeing the treated fabric, a pattern of white stripes (the laser-treated areas) was obtained on a normally dyed backgroud, the presence of which became more pronounced as the energy dose increased.

In this way, the author suggests, a differential-dyeing fabric might be produced, for example, by tracing a pattern on a fabric using a laser under computer control. The fabric could then be dyed to develop the pattern. Random dye effects in yarns could also be produced by exposing a moving line of thread to laser pulses of varying duration. Dyeing yarns or fabrics made from them would again develop the pattern.

No information was given, however, regarding the tensile strengths of the laser-treated yarns and fabrics - a factor which could be of importance since severe strength losses are often associated with cross-linked cotton.

2.3 Chemical modification of cellulose to confer affinity for acid dyes

2.3.1 Early treatments of cotton

The early treatments of cotton which conferred affinity for acid dyes, and thus imparted to the fibres similar dyeing properties to those of wool and silk, were originally undertaken with a view to eliminating the difficulties encountered when trying to obtain solid shades on mixed fabrics consisting of wool and cotton blends. Such fibres, which dyed similarly to the animal fibres, were called "animalised" and the procedures by which they were obtained "animalization" processes.

Generally these processes consisted of the introduction of nitrogen-containing organic substances into the body of the fibres, or onto their surface, resulting in a substantial basification of the fibres, and enabling them to be dyed by acid dyestuffs.

Knecht[108] mentions several methods, for example, impregnation with albumen, with or without subsequent steaming, which was originally employed by calico printers to prevent bleeding of direct dyes, but with little success. Similarly cotton could be animalised by impregnation with a solution of casein or by treatment with tannic acid, followed by fixing in gelatine or lanuginic acid although, again, neither of these methods gave good results.

In the method devised by Knecht[108], cotton, in the form of calico, was padded with a solution of formaldehyde and "lanuginic acid". The latter was prepared by dissolving wool in a boiling solution of barium hydrate from which the barium was then precipitated by carbonic acid. After drying and steaming under pressure, the treated cotton could be dyed directly with acid dyes although the shades obtained were not as fast as on wool.

Further techniques involved dyeing the cotton with an acid dye after mordanting with sodium stannate or alternatively in a bath containing Glauber's salt (hydrated sodium sulphate) and alum, but again the shades obtained were not fast[109].

Other early attempts to introduce basic nitrogen into cellulose were by reaction with ammonia. In 1861 both Thenard and Schutzenberger claimed to have produced an amidated cellulose by treatment with ammonia in an autoclave. Leo Vignon[110] also described how he had prepared an amidated cellulose containing as much as 3% of nitrogen, and with affinity for acid colours, by treatment of cotton with ammoniacal calcium chloride and aqueous ammonia for some hours at 100-200°C. However, these results were not reproducible and it is possible that the products were merely cellulose in which the air spaces were filled with ammonia, especially as ammonia in gaseous form is known to be retained by cotton fibre in large amounts[111].

Many other early methods for the fixation of acid dyes on cellulose fibres have been patented, and are described by Diserens[112], although none have proved of commercial importance.

Fornelli[109], in his review of the animalization of cellulosic fibres, refers mainly to methods which involve regenerated fibres and are therefore not relevant to a discussion of differential-dyeing cotton since the original fibrous form of the cellulose must necessarily be destroyed. Further details of these methods will, however, be given in section 2.4.1.

A method which involves increasing the affinity of cotton for direct dyes, rather than actually conferring substantivity for acid dyes is based on the technique of mercerisation discovered by Mercer[113] in 1844, and successfully developed by Lowe[114] forty-five years later.

Treatment of cotton with concentrated (20-25%) sodium hydroxide was found to increase the capacity of the fibre for anionic dyestuffs as well as increasing it's tensile strength, properties which have since been attributed to the formation of cellulose II, in which there is a somewhat less closely packed arrangement of glucose units within the structural cell that exists in native cellulose, ie, cellulose I.

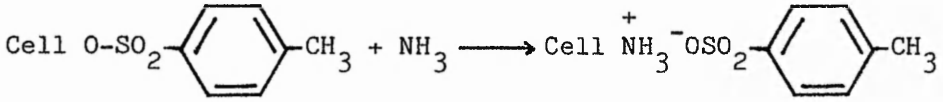
The process is now used extensively for the treatment of cotton and as recently as 1979 there were reports of localised caustic mercerisation being used as a tecnique to create fashionable fabrics by producing tone-on-tone effects with fibre-reactive dyes[115].

2.3.2 Aminisation - the preparation of ionisable derivatives

Since previous attempts to produce amino-cellulose by a direct method had failed, Karrer and Wehrli[116] approached the problem by an indirect route making use of the fact that, whereas esters of carboxylic acids are decomposed by ammonia and amines into acid amides and alcohols, the esters of mono- and disulphonic acids form amines as the ammonium salt of the sulphonic acid:

$$R^1O\text{-}SO_2\text{-}R^2 + NR^3 \longrightarrow R^1\text{-}N^+R_3\,^-SO_3\text{-}R^2$$

A satisfactory ester, cellulose toluene sulphonate (known as immunised cotton) had just been produced on a commercial scale and was found to react readily with ammonia, primary and secondary aliphatic amines, and hydrazine; the reaction with ammonia, for example, was found to be complete after one hour at 100°C. The immunised cotton before treatment contained 1.9% of sulphur which was reduced to 1.3%; there was a total loss in weight of 7.6% and about 0.8% of nitrogen, equivalent to one amino group every ten or so glucose residues, had entered into combination with the cellulose.



However, even this small amount of combined nitrogen was sufficient to impart characteristic dyeing properties to the fibre. The original immunised cotton had resisted direct dyes but showed an increased affinity for the basic colours, but in the case of the aminised product this affinity was less and could even be destroyed by prolonged treatment with ammonia. On the other hand, tests carried out with acid dyes revealed that aminised cotton had excellent affinity for these colours and that the dyeings were of good fastness.

Karrer and Wehrli explained this effect on the assumption that the tosyl groups were replaced by amino groups to form amino-cellulose in much the same way as the toluene sulphonyl ester of 2,4-dinitrophenol was converted into 2,4-dinitroaniline, as was shown by Ullman[117]. In support of this view they cited the affinity of aminised cotton for acids, which were taken up in amounts which were directly proportional to the amine content, as determined by nitrogen values; this they explained in terms of the formation of salts[116].

Dyeing of amino-cellulose in the presence of acid resulted, therefore, in protonation of the amine groups, previously incorporated into the fibre, to produce quaternary ammonium groups which could act as cationic sites for acid (anionic) dyes, for which they showed a strong affinity.

$$\text{Cell NH}_2 \xrightleftharpoons{\text{HCl}} \text{Cell }\overset{+}{\text{N}}\text{H}_3\text{Cl}^- \xrightarrow{\text{D}^-\text{X}^+} \text{Cell }\overset{+}{\text{N}}\text{H}_3\text{D}^- + \text{X}^+\text{Cl}^-$$

Ammonia-treated immunised cotton was given the trade name Amine Yarn. Various other types of amine yarn prepared from heterocyclic bases such as pyridine, quinoline and piperidine are also referred to in the patent literature[118,119], but will be discussed further in section 2.3.3. In the long term, however, the poor economics of the process impeded it's practical development on a commercial scale and interest therefore turned towards other ways of producing a fibrous cotton with affinity for acid dyes.

Hartmann[120], for example, reported the preparation of aminoalkyl celluloses by reaction of the corresponding aminoalkyl halides with cellulose in an alkaline medium. A typical method involved treating cotton fabric with an aqueous solution of 2-chloroethylamine hydrochloride, drying it, and then placing it in 50% sodium hydroxide solution at 100°C for one minute. Although the method was quick and convenient and good dyeings with acid wool dyes could be obtained, at the same time only about 0.2% of nitrogen could be introduced into the fabric by this technique. The reaction may be given as:

$$\text{Cell OH} + \text{ClCH}_2\text{CH}_2\overset{+}{\text{N}}\text{H}_3\text{Cl}^- \xrightarrow{\text{NaOH}} \text{Cell OCH}_2\text{CH}_2\text{NH}_2 + \text{NaCl} + \text{H}_2\text{O}$$

Similarly low levels of substitution were also obtained by Stahn[121] who aminised cotton by treating it with epichlorohydrin in the presence of ethanolamine and sodium hydroxide. The resulting fabric contining about 0.2% nitrogen and dyed with an acid dye. Ammonium hydroxide, melamine, or other amino compounds could be used in place of the ethanolamine.

Aminisation of cotton fabric has also been discussed by Guthrie[122], who found that cotton immersed in a 25% sodium hydroxide solution containing 10% 2-aminoethylsulphuric acid, heated for 40 minutes in a drying oven at 100°C and then washed free of sodium hydroxide, dyed dark with an acid wool dye and also showed increased affinity for direct dyes.

$$\text{Cell OH} + \text{HO-SO}_2\text{-OCH}_2\text{CH}_2\text{NH}_2 \longrightarrow \text{Cell OCH}_2\text{CH}_2\text{NH}_2 + \text{H}_2\text{SO}_4$$

The aminised fabric also dyed well with chrome dyes and by controlling the acidity of the dyebath with formic acid a match in shade between wool fabric and aminised yarn could be obtained. That amine groups had been introduced into the fibre, presumably as aminoethoxyl groups replacing some of the hydroxyl groups of the cellulose, was shown by the capacity of the aminised fabric to take up hydrochloric acid in amounts commensurate with its amine content, measured by total nitrogen values. The amine groups also underwent many of the reactions which are characteristic of aliphatic amines.

Aminisation of cellulose could also be carried out using a number of other sulphato compounds related to 2-aminoethylsulphuric acid, although lower degrees of substitution were obtained in these cases[123]. Even using 2-aminoethylsulphuric acid, the extent of substitution could only be varied up to about one aminoethoxyl group per six glucose units (1.4%), due to the fact that highly aminised cellulose was water-soluble[124].

This was a comparatively low figure compared to that obtained with, for example, partially acetylated cotton, however, these free amino groups, even in very low concentrations were capable of altering the dyeing properties of cotton considerably, whilst retaining the original fibrous structure.

Aminised cotton was thus observed to have a noticeably better affinity for direct, vat, sulphur and developed dyes than either mercerised or untreated cotton and, with the exception of the vat colours, these dyes were slightly more fast to light on aminised cotton. Many of the dyes, particularly the direct dyes, were also faster to washing on aminised cotton than on untreated yarn. Dyeing of the treated yarn with cotton colours was also found to require a shorter time and lower temperatures than usual, and less or no salt was required to exhaust the dyebath.

This method of aminisation was thus claimed to have several advantages over previous techniques; the process could be applied to both yarn and fabric, 2-aminoethylsulphuric acid was a much cheaper and thus more economical reagent and, apart from its greater effectiveness, it was also non-volatile and stable in sodium hydroxide solution at room temperature. Due to the ether linkage it formed with cellulose, it could also be expected to be more stable to hydrolytic agents than the esterified derivatives of cellulose which had earlier been used to modify the dyeing behaviour of cotton.

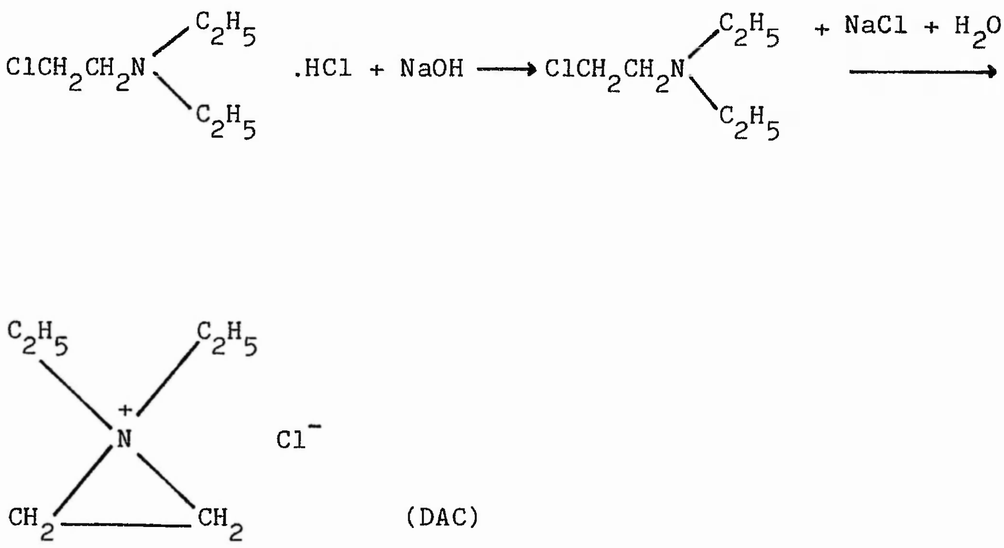
Aminised cotton was also observed to take up acid and chrome dyes in a manner similar to that of wool, unfortunately, however, whilst their light fastness on the two substrates was about equal, the wash fastness of the acid dyes on aminised cotton was less than that obtained on wool.

This, combined with the fact that very careful control of the dyebath pH was required in order to obtain level dyeings, particularly with direct dyes due to their very strong affinity for the aminised cotton under acidic conditions, meant that the process never achieved any commercial importance for the preparation of differential-dyeing cotton although, more recently, the corresponding N,N-diethyl derivative has been studied with this application in mind[125].

The preparation of diethylaminoethylcellulose (DEAE-cellulose) was first reported by Hartmann[120] who used cotton as the source of cellulose. DEAE-cotton has since been prepared by a variety of procedures although all have involved wet-cure processes requiring multistep batch operations[126,127].

Recently, however, an improved pad-cure process was developed which was a one step operation, amenable to continuous processing, and at room temperature resulted in four times the fixed N content obtainable in a wet-cure process using the same concentration of sodium hydroxide and reagent[128].

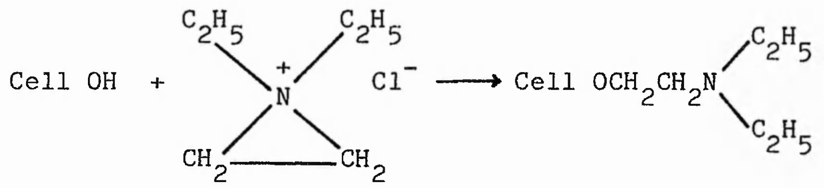
Roberts and co-workers[125] have since discovered that DEAE substituents can be introduced into cotton under mild conditions using a similar pad-cure treatment but in the absence of strong caustic. The padding solution was prepared by dissolving 2-chloroethyldiethylamine hydrochloride in water and then adding sufficient 1M sodium hydroxide to just neutralise the hydrochloride. Water was then added to adjust the reagent to the desired molarity and the mixture was stirred mechanically for 5-15 minutes until the insoluble 2-chloroethyldiethylamine (free base) was converted into the soluble N,N-diethylaziridinium chloride (DAC):



$$ClCH_2CH_2N(C_2H_5)_2 .HCl + NaOH \longrightarrow ClCH_2CH_2N(C_2H_5)_2 + NaCl + H_2O \longrightarrow$$

(DAC)

0.1% of a wetting agent was then added to the reagent solution which was shown to be stable at neutral pH for at least 24 hours. Cotton, in the form of fabric, yarn or raw fibre, was then treated by padding in a DAC solution to a wet-pickup of approximately 100-115%, and then cured at 125-150°C for five minutes. The reaction taking place may be given as:



DEAE-cotton

The treated DEAE-cottons were shown to dye deeply with a variety of acid dyes but, unfortunately, the colour fastness properties of the treated cottons were, generally, not good although they varied from one dye to another. However, the extent of fading was said to be reduced very substantially by a cross-linking treatment with DMDHEU, without causing any change in shade or colour, although obviously this would add to the overall cost of the treatment.

DEAE-cotton was also shown to have a greater affinity for optical brighteners (many of which are also anionic in character) than did unmodified cotton.

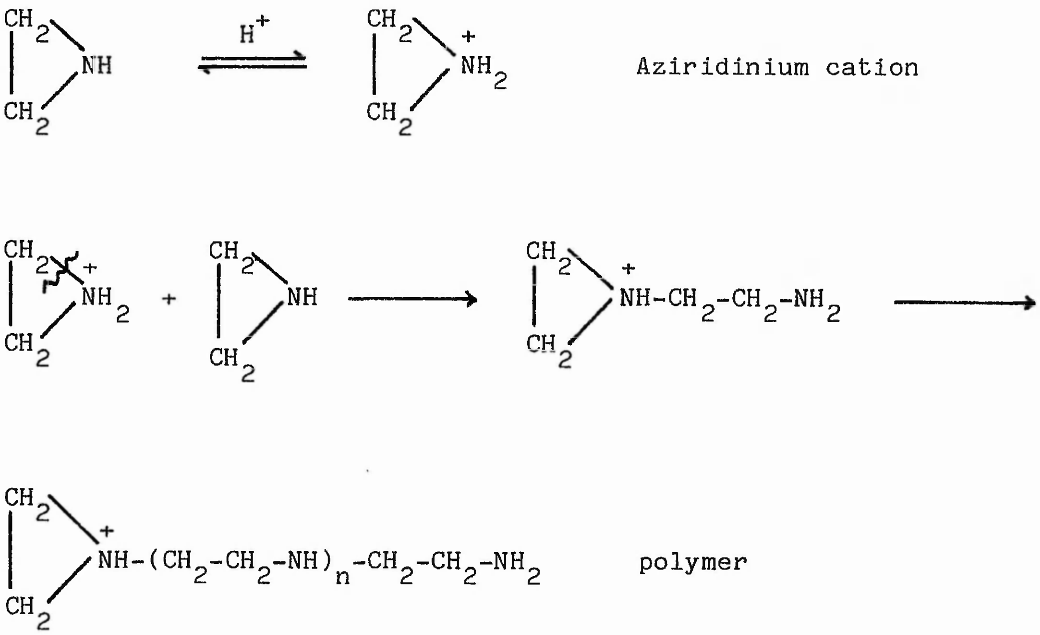
Tone-on-tone effects could be produced by dyeing all-cotton blend fabrics woven from DEAE yarns and unmodified yarns. By using fabrics of different construction it was suggested that a variety of interesting and attractive designs might be obtained. However, when trying to obtain a particular degree of contrast, the fact that staining of the unmodified cotton was observed to be slightly greater in the blend fabric than in a separate sample of unmodified cotton should be taken into account. Processing of the treated yarns and fibres was essentially the same as that of untreated fibres, and could therefore be carried out on conventional textile equipment.

Considerable work was also done on reacting cotton with the vapour of ethylenimine at temperatures ranging from 60-100°C[129]. The resulting cotton contained nitrogen and dyed well with acid dyes although much of the ethylenimine was merely polymerised in, or on, the fibre, since it could be removed by boiling with dilute sodium hydroxide solution or by extracting with dilute acid. However some nitrogen remained in the cotton after these extractions indicating that some of the ethylenimine may have combined with the cellulose.

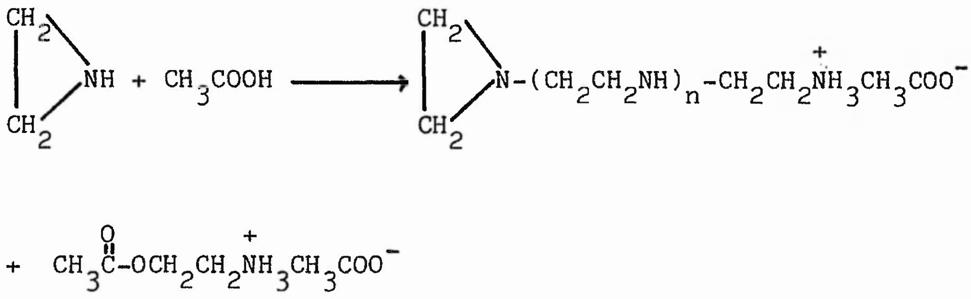
Drake and co-workers[130] also reacted ethylenimine with cotton fabric but again only a small quantity of nitrogen was shown to have actually reacted with the fibre. By treatment of aminised cotton fabric with ethylenimine it was, however, suggested that the ethylenimine may react with the amino groups of the aminoethylcellulose to form poly(ethyleneamino)aminoethyl groups within the fibre[131].

Cooper and Smith[132] later described carrying out a reaction with cotton in a benzene solution of the imine at elevated temperature and pressure. In this way a graft polymerisation of the imine onto the cellulose chain was said to have occurred although the authors believed that the graft polymer side chain contained no more than six monomer units.

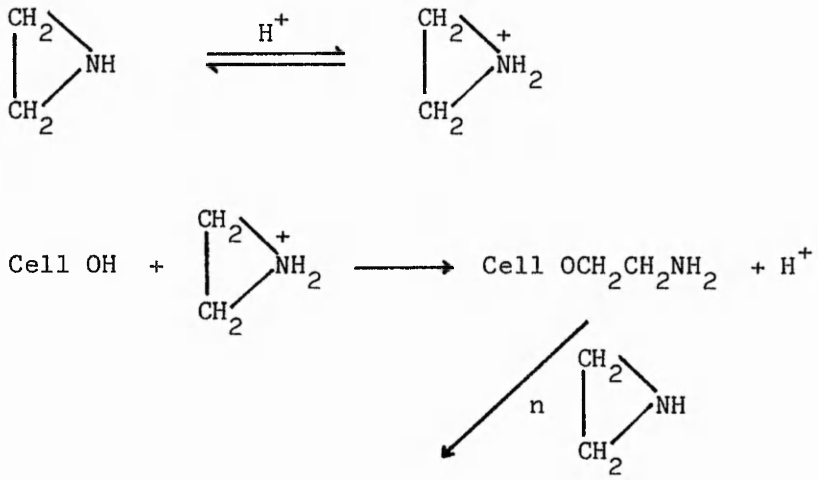
Previous studies on the polymerisation of ethylenimine had shown that the rate of the reaction was increased by the presence of traces of water and still further by organic acids, the acid serving to catalyse opening of the imine ring[133]. The course of the polymerisation is given below:



Glacial acetic acid, for example, was shown to cause polymerisation of the imine giving water-soluble quaternary salts of acetic acid[134]:



Segal and Eggerton[135] subsequently reported that the reaction of cellulose with ethylenimine in benzene could also be catalysed by the presence of acetic acid with little, if any, change in the tensile strength of the yarn after treatment. A possible course for the polymerisation of the imine with cellulose or aminoethylcellulose in the presence of acetic acid may be given as:



$$\text{Cell O}(CH_2CH_2NH)_nCH_2CH_2NH_2 \;+\; H^+$$

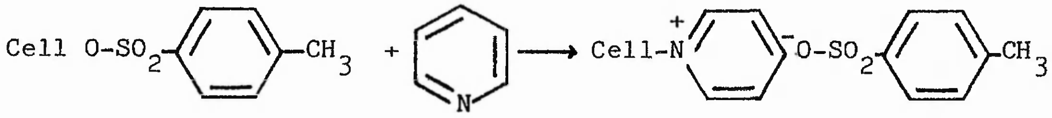
Thus cotton yarn, refluxed in the presence of ethylenimine and acetic acid for 4 hours at atmospheric pressure, was found to contain a significant amount of fixed nitrogen, whereas similar experiments carried out in the absence of acetic acid showed little evidence of reaction. Some polymer was formed but was removed by washing with water. Even after a 2 hour boil in 2% sodium hydroxide the nitrogen content of the treated cotton remained at about 1.5%.

The I.R. spectrum of the product strongly resembled that of aminoethylcellulose. The treated cellulose also dyed strongly with acid wool dyes and generally displayed many of the other properties associated with aminoethylcellulose such as complexing with metal ions and showing moderate ion-exchange capacity.

2.3.3 Preparation of cationic derivatives

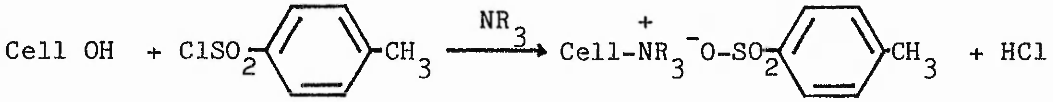
One of the earliest examples of the introduction of permanently charged sites into cotton fibres by means of the preparation of cationic derivatives of cellulose (as opposed to merely impregnating the material with various quaternary ammonium, sulphonium and phosphonium compounds[136]) was mentioned by Karrer and Kwong[137] who reacted cellulose toluene sulphonate with pyridine to produce a pyridinated cotton which did not take up acids in proportion to the amino content, as the aminised product had done, but nevertheless showed a strong affinity for the acid dyestuffs.

By reacting cellulose toluene sulphonate with a tertiary amine permanent quaternary nitrogen groups, which could act as cationic sites for acid dyes, even in the absence of acid, were thus incorporated into the fibre.

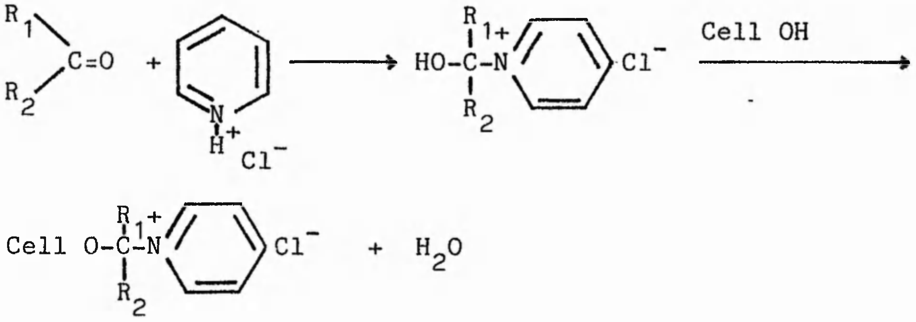


Amine yarns containing permanent quaternary cationic sites were also prepared from other tertiary heterocyclic amino bases such as quinoline and piperidine[118,119].

A simplification of the original process describes the preparation of quaternary ammonium compounds of cellulose directly by the action of sulphonic acid chlorides on cellulose in the presence of tertiary amines[138]. Generally the reaction can be given as:



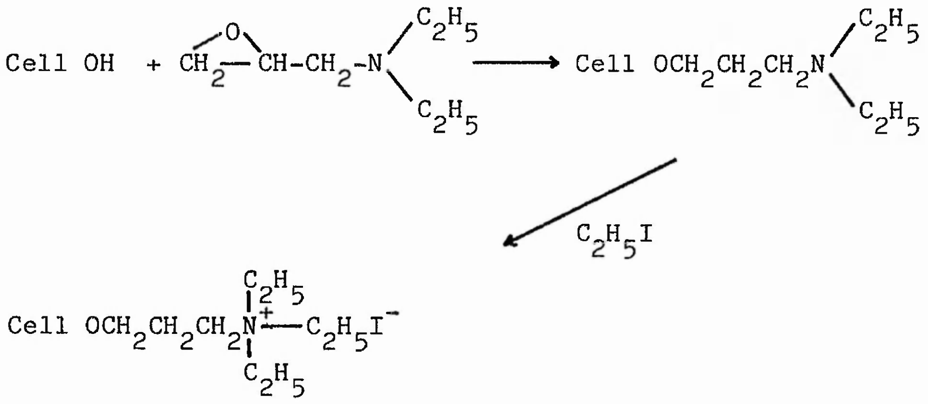
Treatment of cellulose with ketones or aldehydes and pyridine bases was also said to impart dyeing properties similar to those of the amine yarns, no doubt as a result of quaternary cationic sites being incorporated into the fibre[139]. In one example formaldehyde was mixed with pyridine and pyridine hydrochloride and allowed to react with cellulose for three to four hours at 90-100°C. Generally the reaction taking place may be given as:



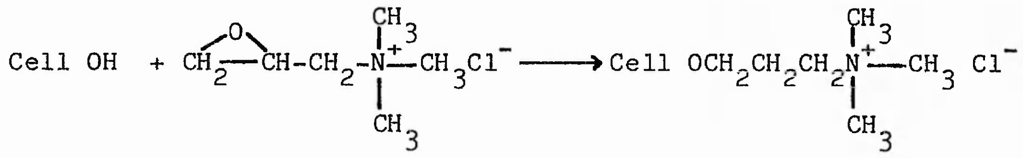
Another patent describes reacting cellulose with carboxylic methylolamides containing at least one halogen atom by heating at 110°C for 4 hours, and then treating with an organic base such as pyridine[140].

Cellulosic material, treated in such a way as to incorporate cationic quaternary sites into the fibre, exhibited, not only a newly acquired affinity for acid dyes, but also much improved affinity for direct dyes compared to that obtained with similar dyes on untreated cellulose.

Other quaternary ammonium derivatives of cellulose were prepared by reaction of cellulose with epoxypropyldiethylamine, under alkaline conditions, followed by quaternisation with, for example, ethyl iodide[141].



Alternatively, fixed cationic sites may be introduced into cellulose by treatment of the fibres with reactive quaternary compounds, etherification of cellulose occurring via the reactive epoxy group. Cellulosic fibres modified by reaction with, for example, glycidyltrimethylammonium chloride, below, showed considerable affinity for acid dyes whereas for unmodified cotton little, if any, affinity was shown[142-144].



Epoxy compounds, capable of reacting with cellulose under alkaline conditions, had been widely used in textile printing and resin finishing. This, combined with the limited effectiveness of the non-reactive quaternary compounds used for fixing substantive dyes onto cellulosic substrates, prompted the introduction of aqueous solutions of glycidyltrimethylammonium chloride onto the market as Glytac (Protex).

The dyeing of Glytac-treated cellulose with direct and reactive dyes has been outlined by Rupin and co-workers[145,146]. Considerable improvements in wet fastness were claimed for both direct and reactive dyes on Glytac-treated cellulose, over similar dyeings aftertreated with conventional non-reactive compounds.

The best wet fastness levels were given by reactive dyes on cellulose pretreated with a reactive quaternary compound, since both components which contribute to the dye-reagent complex were also able to form covalent bonds with the substrate. In this way electrostatic bonds between the sulphonic acid groups of the dye and the quaternary nitrogen centres in the fibres were reinforced by covalent linkages to cellulose.

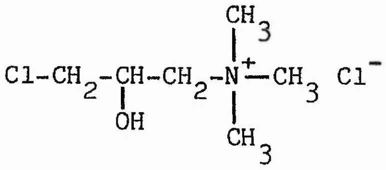
An improved colour yield was also obtained for several reactive dyes on Glytac-treated cellulose, and attributed by Rupin to the fixation of hydrolysed dye, by electrostatic attraction, to the cationic sites in the fibre. Fastness to washing was said to be unchanged although two of the dyes showed a marked drop in fastness to perspiration and sea water.

Later work by Van Rensburg[147], however, demonstrated that some of the claims for the effectiveness and versatility of Glytac were greatly exaggerated. With direct dyes, for example, he obtained little or no improvement in fastness to alkaline perspiration or ISO 3 washing.

Moderate increases in the exhaustion of three acid dyes were confirmed, but again the fastness to alkaline perspiration was very poor and in ISO 3 washing tests all the acid dyes were completely stripped from the fabrics, presumably by a process of anion exchange.

With reactive dyes the fixation of dye by a cold pad-batch application to Glytac-treated cotton was shown to have actually decreased by 20% relative to control dyeings.

Recent developments again concerned with enhancing the dyeability of cellulose, as distinct from actually producing a differential-dyeing cotton fabric, have employed the epichlorohydrin precursor of Glytac[148,149] (Figure 15). When treated with alkali the epoxy compound is formed and reacts with cellulose.



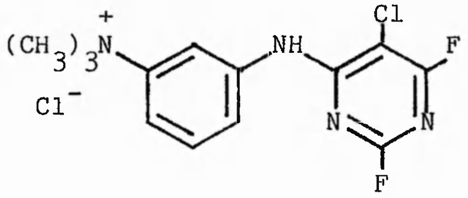
$Cl\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}CH_3\ Cl^-$

Figure 15. Epichlorohydrin percursor of Glytac.

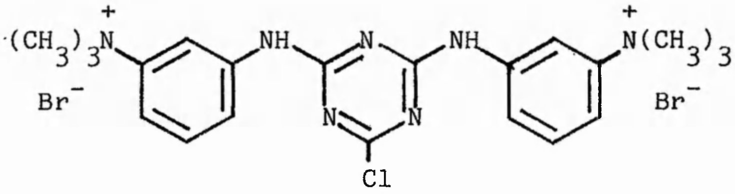
Care must be taken during the alkaline cure necessary for epoxy fixation since discoloration of the fibre can occur during this stage of the process. Difficulties have also arisen as a result of the thermal instability which is a characteristic of Glytac and its precursor. Loss of trimethylamine, released during application, destroys the effectiveness of the reagent and simultaneously gives rise to objectionable odour in the treated fabric.

Selected direct dyes can be applied to the quaternised cellulose without salt, yielding satisfactory fastness to ISO 3 washing[149]. Reactive dyes show high exhaustion in the absence of salt and reportedly become bound to the modified substrate from either neutral or alkaline dyebaths[148].

Since the commencement of this project further work has emerged relating to quaternary reagents of a different class, namely, mono-reactive halogenoheterocyclic compounds, including both mono- and bis-quaternary derivatives[150-152]. Examples of these compounds are shown below (Figure 16).



mono-quaternary derivative



bis-quaternary derivative

Figure 16.

Treatment of cellulose using reactive halogenoheterocyclic quaternary reagents of this class as fixing agents also considerably improved the colour yield and wet fastness properties of dyeings produced with anionic dyes on cellulosic substrates.

These reagents also reacted more rapidly with cellulose so that they could be applied under particularly mild conditions of temperature and pH and also with shorter reaction times than when using fixing agents containing the epoxy group as reactive radical.

They also showed better thermal stability than the epoxypropyl type, however, both classes mentioned, namely mono-reactive halogenoheterocyclic and epoxypropyl, shared the disadvantage of having relatively low substantivity for cellulose; they must be applied by a semi- or fully-continuous process before dyeing[148].

In 1983, Evans, Shore and Stead, however, reported that bis-reactive, bis-quaternary reagents based on the halogenoheterocyclic class of compounds, mentioned earlier, were found to offer more scope for achieving high substantivity for cellulose under batchwise conditions of application[153,148] (Figure 17).

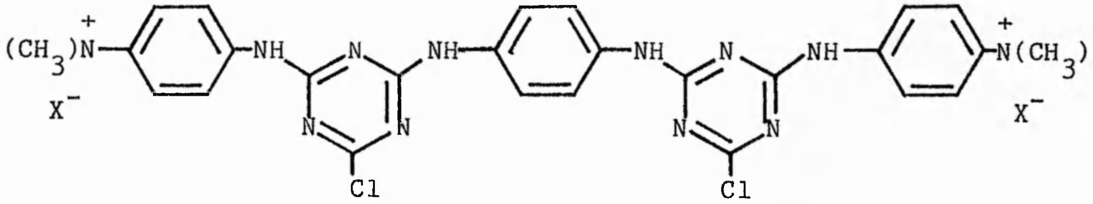


Figure 17.

Quaternisation could be intergrated with batchwise dyeing, offering substantial savings in process costs.

However, once again, the main objective of pretreatement was to enhance the fixation of anionic dyestuffs onto the cotton in the form of fabric, no mention being made of the possible treatment of yarn, from which a differential-dyeing fabric could be woven using treated and untreated fibres.

Reactive dyes were of particular importance in this respect because they offered significantly better wet fastness on quaternised cellulose than any other dye class, due to the fact that both parts of the dye-reagent complex were capable of reacting with the fibre.

The build-up of di-sulphonated reactive dyes was observed to be exceptionally good on quaternised cellulose; deep colours, economically unattainable on untreated cotton, could be achieved without difficulty. This was seen by the authors as where quaternisation of cellulose offered most advantages since other features of the process (reduced chemical usage and ease of washing-off) also would attain maximum impact when dyeing to full depths.

In conclusion, the authors[148] stated that the ideal quaternising pretreatment to enhance the dyeability of cellulose with anionic dyes had not yet emerged. Less reactive quaternary agents, such as the epoxypropyl type, required severe conditions of pretreatment and stability was lacking, whilst low-substantivity quaternary agents of the haloheterocyclic class required application by a relatively costly semi- or fully-continuous process and also showed migration problems in drying, a fault which only became fully evident on subsequent dyeing.

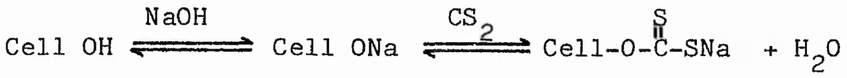
Finally, although many of these drawbacks were overcome using readily reactive and highly substantive agents, such as the bis-quaternary, bis-reactive derivatives, it then became difficult to avoid preferential reaction of the agent in the surface regions of the fibre. Ring dyeing of the modified substrate therefore occurred resulting in marked, and mostly undesirable differences in hue and brightness compared with conventional dyeings.

2.4 Other differential-dyeing fibres

2.4.1 Regenerated cellulosics

There are two main methods for the formation of regenerated cellulose fibres - the viscose process and the cuprammonium process[22,23,154,155]. The viscose process is by far the most important method, both for the production of regular and modified viscose fibres, and also from the point of view of the preparation of differential-dyeing cellulosic fibres. A brief description of the process is therefore warranted.

Viscose, or sodium cellulose xanthate, is the sodium salt of the O-ester of unsymmetrical dithiocarbonic acid. It is made by the action of carbon disulphide on alkali cellulose[156]:



$$\text{Cell OH} \xrightleftharpoons{\text{NaOH}} \text{Cell ONa} \xrightleftharpoons{\text{CS}_2} \text{Cell-O-}\overset{\overset{\text{S}}{\|}}{\text{C}}\text{-SNa} + \text{H}_2\text{O}$$

The substance forms a viscous solution which, after ripening for one to three days to bring it to the correct condition for regeneration, is spun by being pumped through spinnerets into a coagulating bath usually consisting of dilute sulphuric acid, sodium sulphate and zinc sulphate.

The resultant silk-like fibres are composed of chains of cellulose II molecules in which the degree of polymerisation, or DP, has been reduced to about 250-300. (The average DP of purified native cellulose is typically 1000-2000). Chemically similar to cotton, viscose fibres do not contain any specific dyesites and are dyed with direct, reactive, vat or azoic colours.

Various types of viscose fibres are now available commercially with wide differences in structure, cross-section, physical properties and dyeability. These modifications improve the physical properties of the fibre and are brought about by reducing the rate of regeneration of the cellulose so that stretching of the filaments can be employed to produce a higher degree of orientation and crystallinity[157-159,154,155].

Generally known as the high wet modulus (HWM) fibres, this term now embraces the high tenacity viscose fibres and the polynosic fibres. A number of methods are available for reducing the regeneration rate[157,158]:

1. Use of a viscose dope with a high carbon disulphide content;
2. Incorporation of additives or modifiers (eg. various amines or poly[ethylene glycol]) in the viscose dope or in the coagulation bath;
3. Lowering the coagulation bath temperature;
4. Using low concentrations of sulphuric acid and high concentrations of zinc sulphate in the coagulation bath;
5. Spinning at lower speeds.

The difference in structure between conventional viscose fibres and HWM fibres inevitably gives rise to differences in dyeing behaviour, however, the actual differences occurring are markedly dependant upon the individual dyes applied. The rate of uptake of direct dyes, for example, compared with that for viscose rayon or cotton, can be higher or lower depending on the individual dye and the conditions of application[160].

Other modifications of viscose rayon principally concerned with conferring affinity for acid dyes and so providing solid shades on wool/viscose blends have a long history. Originally carried out to impart "wool-dyeing" properties to cellulosic fibres, the process was known as animalization.

Fornelli[109], in his very comprehensive review of the various methods of animalizing cellulosic fibres, divides them into those which involved incorporating animalizing substances into the viscose dope before regeneration, for example, proteins from various sources, amines, polyamides, polyalkylene imines and amino-formaldehyde polymers, and those which were applied to the fibres after regeneration, including quaternary ammonium, sulphonium and phosphonium compounds and amino-formaldehyde resins. In this latter class may be mentioned "Rayolanda", an acid-dyeing fibre made by Courtaulds in the 1939-1949 period[161].

None of these methods, however, produced a fully satisfactory product, one of the major drawbacks being the fact that, on some of these fibres the dyeings produced exhibited very poor light and/or wet fastness properties. Hence for the dyeing of blends, for example, the dyeing performance of the modified viscose fibres was often not sufficiently near to that of wool.

In many cases the stability of the additives to wool-dyeing conditions was also insufficient, the dyeability of the fibre decreasing as dyeing progressed. This last feature made dyeing processes difficult to control and was a distinct disadvantage in the case of "Rayolanda"[161].

The incorporation of poly(vinylpyrrolidone)[162] into viscose dope before extrusion has also been reported to confer substantivity for acid dyes. Moreover further research by Courtaulds in this field led to a method for modifying viscose fibres which involved the use of a cellulose derivative containing basic groups - the aminoethyl ether of cellulose[183] (cf. the aminised cellulose derivative prepared by Hartmann and Guthrie).

Using viscose fibres modified in this way a near approach to a "wool-dyeing" fibre was obtained, although certain practical application difficulties persisted[161]. Also, to impart this level of dyeability, a high content of the basic substituent was necessary, at a substantial cost, making it unlikely that the modified fibres could be of interest commercially.

Of greater significance, however, was the use of viscose fibres modified with the same basic substituent but having a much lower degree of substitution. Economically more viable, they were found to still have markedly different direct-dyeing properties, such that, when dyed with direct dyes in the presence of unmodified viscose, tone-on-tone effects were produced. A specific level of substitution was therefore adopted for bulk development and subsequently led to the introduction of deep-dyeing (DD) varieties of Sarille, Evlan and Vincel (Courtaulds).

Ward and Hill[161] have shown that these deep-dyeing fibres absorb direct dyes much more rapidly and give much higher exhaustion than normal viscose rayon, particularly in the absence of salt. This is because positive charges, associated with the basic groups, have been introduced into the fibre which attract direct dye anions, whereas normal viscose fibres carry either no charge or a negative charge and therefore tend to repel direct dyes, unless the ionic strength of the solution is increased by the addition of electrolyte.

Maximum contrast is achieved under acid conditions (usually acetic acid), in the absence of salt, the positive charge on the DD fibres building up to a higher level and therefore attracting more dye, whilst more subdued contrasts can be obtained by the use of electrolyte and the omission of acid.

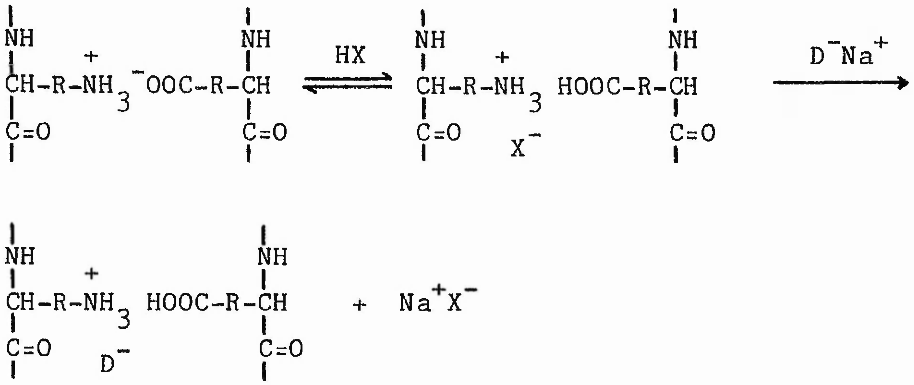
When reactive dyes are applied under normal conditions, ie. in the presence of alkali and salt, the positive charge on the DD fibres is suppressed and solid dyeings result. Dyeing with vat and sulphur dyes, which also need alkali for their application, also leads to more or less solid shades. However, colour-and-white effects can be obtained with reactive dyes applied under acid conditions or with direct dyes at pale depths (0.05% based on the weight of the fabric).

Fastness properties were generally satisfactory although, in the case of directs, certain dyes did show a slight decrease in light fastness. Care was also advised, and weak solutions recommended, when using oxidising agents such as hydrogen peroxide or sodium chlorite, eg. when bleaching or stripping since, at the strengths required for cotton bleaching, DD fibres suffered irreversible loss in dyeability.

Dye selection was important, as with all differential-dyeing systems, nevertheless a wide range of multicoloured effects could be obtained on 100% viscose rayon fabrics, the physical properties of the DD fibres remaining the same as those of the parent fibres. However, in spite of many attractive properties, commercial production of differential-dyeing viscose has now virtually ceased because the modified fibres were expensive and of limited appeal.

2.4.2 Wool

Wool is the major protein fibre. Chemically it is built up from approximately twenty different amino acids and, from the point of view of dyeing, it's most important feature is the presence of salt linkages between adjacent polymer chains. These are formed between amino acid residues containing free amino groups and those containing free carboxyl groups. On treatment with acid the carboxylate ions are protonated allowing the quaternary nitrogens to provide dyesites for anionic (acid) dyes which can displace the small counterion X-.



$$\underset{\underset{|}{C=O}}{\overset{\overset{|}{NH}}{CH}}-R-\overset{+}{N}H_3\ {}^{-}OOC-R-\underset{\underset{|}{C=O}}{\overset{\overset{|}{NH}}{CH}} \overset{HX}{\rightleftharpoons} \underset{\underset{|}{C=O}}{\overset{\overset{|}{NH}}{CH}}-R-\overset{+}{N}H_3\ \underset{X^-}{}\ HOOC-R-\underset{\underset{|}{C=O}}{\overset{\overset{|}{NH}}{CH}} \xrightarrow{D^-Na^+}$$

$$\underset{\underset{|}{C=O}}{\overset{\overset{|}{NH}}{CH}}-R-\overset{+}{N}H_3\ \underset{D^-}{}\ HOOC-R-\underset{\underset{|}{C=O}}{\overset{\overset{|}{NH}}{CH}} + Na^+X^-$$

The dyeability of wool is thus dependant on the number and reactivity of the N and C terminal amino acids and acidic and basic side-chains in the polypeptide chain[164] and on the accessibility of these groups[165]. Accessibility is influenced by the epicuticle, a membrane which covers the outer fibre sheath and which is more hydrophobic and resistant to degradation than the rest of the fibre.

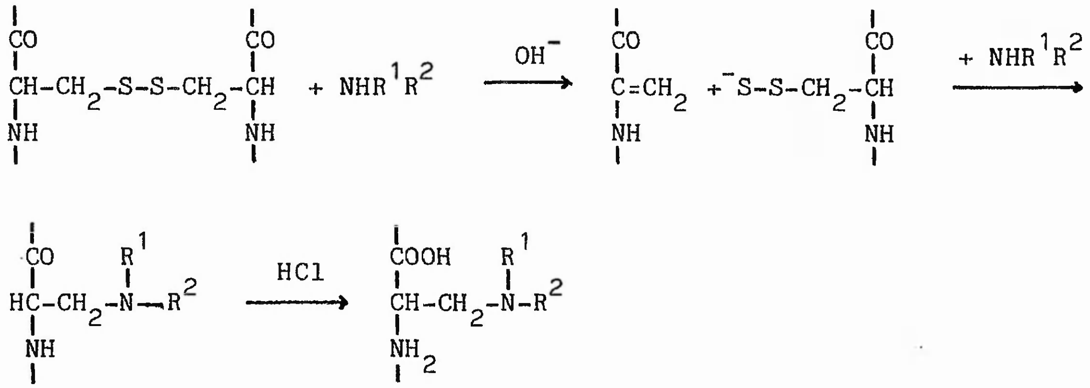
If the epicuticle is damaged, for example by shrink resist treatments, the rates of diffusion of dyes into the fibre will increase, rendering the wool more accessible to dyes so that differential effects can be obtained when mixtures of treated and untreated wool are dyed together[22].

Many immunization treatments of wool, such as in tannic acid solution and by acetylation, have been described for the purpose of changing its affinity for dyestuffs[166]. Dye resist techniques involving blocking of reactive groups and silent electrical discharge processes alter the dyeability of wool enabling tonal effects to be obtained[167].

The use of tetrakis (hydroxymethyl)phosphonium chloride (Cl-P-$[CH_2OH]_4$) in conjunction with an amine (eg. melamine) gives shrink resist, flame retardant fabrics with such an increase in affinity for acid dyes that low temperature dyeing techniques can be employed[168].

Chrome mordanting of wool has also been used to obtain multi-tonal effects in the Multikrome process[169], designs prepared using chromed and unchromed fibres giving different colours because a mordant dye changes colour on reaction with chromium. This technique is used in the piece-dyeing of carpets, the best contrast and fastnes between chromed and unchromed yarns being obtained at the boil, when maximum migration of the mordant dye to the chromed yarns occurs.

The reaction of wool with alkyl amines has also been proposed as a possible technique for producing differential-dyeing wool since the treated fibres showed far greater substantivity for anionic dyes than exhibited by untreated wool. The reaction between the amine and wool is considered to be:



$$\text{CO-CH(NH)-CH}_2\text{-S-S-CH}_2\text{-CH(NH)-CO} + NHR^1R^2 \xrightarrow{OH^-} \text{CO-C(NH)=CH}_2 + {}^-\text{S-S-CH}_2\text{-CH(NH)-CO} + NHR^1R^2 \longrightarrow$$

$$\text{CO-HC(NH)-CH}_2\text{-N}(R^1)\text{-}R^2 \xrightarrow{HCl} \text{COOH-CH(NH}_2\text{)-CH}_2\text{-N}(R^1)\text{-}R^2$$

Differential-dyeing effects are reported when treated and untreated wool are dyed in the same bath with acid, basic, reactive and metal-complex acid dyes, and it is thought that the technique could also be applied to silk, skin and human hair[170].

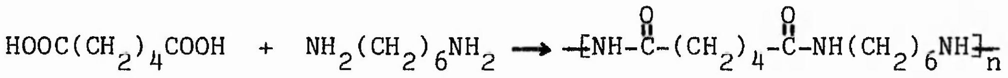
Laser irradiation has also been shown to modify the dyeing behaviour of wool. After laser treatment the affinity of wool for both cationic and disperse dyes was shown to increase relative to untreated material, possibly as a result of a more "open" structure being produced, whilst the affinity for acid dyes remained unchanged[106].

Apart from chemical modification after growth, modification of fibre properties during growth by dietary additives to produce purpose-grown wools is now seriously being studied[171] and may eventually lead to a differential-dyeing wool fibre[22]. Progress, however, will no doubt be slow because of the length of time required for experimentation.

2.4.3 Synthetic polymer fibres

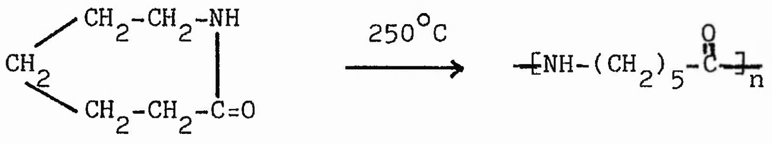
2.4.3.1 Polyamide

There are two main types of polyamide; nylon 6.6, prepared from adipic acid and hexamethylene diamine, and nylon 6 from caprolactam:



$$HOOC(CH_2)_4COOH + NH_2(CH_2)_6NH_2 \longrightarrow \left[NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH(CH_2)_6NH \right]_n$$

Nylon 6.6



Nylon 6

Both types of polyamide contain terminal amine groups which can be readily protonated in the presence of acid enabling the quaternary nitrogens produced to act as dye sites for anionic dyes, including acid, reactive and metal-complex dyes, in a manner similar to wool. Nylon, however, has far fewer sites - only about 5% of the concentration present in wool - so that dye adsorption is limited, although it can also be dyed with non-ionic disperse dyes.

Differential-dyeing polyamide yarns are obtained from modified nylon fibres with inherently different levels of substantivity for either acid or basic dyes[172]. This is conveniently achieved by varying the amine end group contents of the yarns to vary the substantivity for acid dyes, and by the introduction of acidic groups to impart substantivity for basic dyes[173].

Generally, acid-dyeable nylons are commercially available at four levels of adsorption: ultra-deep-, deep-, regular- and light-dyeing fibres. Basic-dyeable nylon yarns are also available[172,174].

Increased substantivity for acid dyes may be conferred on nylon by the introduction of phenyl phosphinic or phosphoric acid derivatives and N-(2-aminoethyl)piperazine[175], p-toluenesulphonic acid derivatives[176], and tributyl phosphate and hexamethylenediamine[177]. Numerous related amines and phosphorus derivatives have also been used[177].

The introduction of amine groups to produce deep- and ultra-deep-dyeing nylon yarns is shown below in equations (i) and (ii) respectively:

(i) $\mathrm{NH_2{-}{-}{-}NH_2 + HOOC{-}Ny{-}NH_2 \longrightarrow NH_2{-}{-}{-}NHCO{-}Ny{-}NH_2}$

diamine nylon molecule deep-dyeing nylon

(ii) $\mathrm{NH_2{-}{-}{-}NH{-}{-}{-}NH_2 + HOOC{-}Ny{-}NH_2 \longrightarrow NH_2{-}{-}{-}NH{-}{-}{-}NHCO{-}Ny{-}NH_2}$

triamine nylon molecule ultra-deep-dyeing nylon

Other methods of obtaining pale and deep effects of the same colour are by using different amounts of delustrant, eg. titanium dioxide, and by combining normal nylon fibres with hollow-filament nylon fibres (the hollow fibres appearing paler than the normal fibres)[178].

The treatment of locallised portions of nylon 6.6 using relatively high subcutting doses of laser radiation has also been shown to increase the substantivity of the fibre for acid dyes in the treated areas, whereas at lower doses the complete reverse (ie. a resist effect) was observed[106].

The resist effect was attributed to the thermally-induced oxidation of amine end groups. Higher energy doses, it was suggested, may counterbalance the destruction of amine end groups by the formation of new ones via hydrolysis of amide bonds and cyclization of adipoyl groups (an initial stage in gelation)[179,180]. Hydrolysis was considered unimportant in this case since there was no increased adsorption of cationic dye. This indicated no significant increase in carboxyl groups, which would be expected to be produced as a result of hydrolysis.

For some differential-dyeing yarns the amine end group contents have been measured[181]; values of 41, 89 and 95 m eqv. of HCl/Kg of fibre being obtained for Monsanto's regular-, deep-dyeing and ultra-deep-dyeing respectively.

The difference in dyeability between the deep-dyeing and ultra-deep-dyeing fibres has been shown, however, to be too great to be explained merely by the difference in amine end group content and it has been suggested that non-ionic forces may be responsible for the additional dye uptake[181].

Many dyes are also adsorbed to an extent which is in excess of the end group content. Such behaviour is typical of those dyes which have a low degree of sulphonation and a high molecular weight and whose adsorption by nylon fibres is thus significantly dependant on non-ionic interactions[162].

A reduction in the acid dye adsorption can, on the other hand, be achieved by increasing the amide content of the yarn or by introducing other basic groups, eg. imine groups, into the fibres:

$$\mathrm{HOOC\ \text{-}Ny\text{-}NH_2} \quad + \quad \mathrm{HOOC\text{---}NHR} \longrightarrow \mathrm{HOOC\text{-}Ny\text{-}NHCO\text{---}NHR}$$

nylon molecule   aminocarboxylic acid   light-dyeing nylon

Substantivity for basic dyes can be imparted to nylon by introducing acid groups such as carboxylic or sulphonic acid (typically sulpho-isophthalic acid) into the polymer whilst at the same time the adsorption of acid dyes is decreased[139]:

$$\mathrm{HOOC\text{-}Ny\text{-}NH_2} \quad + \quad \mathrm{HOOC\text{---}SO_3H} \longrightarrow \mathrm{HOOC\text{-}Ny\text{-}NHCO\text{---}SO_3H}$$

nylon molecule	carboxylic acid containing sulphonic acid groups	basic-dyeable nylon

Blocking of the amine end groups by increasing the carboxyl group content does not confer complete reservation of acid dyes, partly because of the non-ionic interactions which exist between the dye and fibre and partly owing to the incomplete ionisation of the carboxyl groups. However, the addition of sulphonic acid groups, which are fully ionised, strongly suppresses the adsorption of acid dyes over a wide pH range by conferring a large negative potential to the fibre[172,182].

Acetylation has also been shown to reduce the adsorption of acid dyes by nylon by reducing the concentration of amine end groups and increasing the hydrophobic nature of the polyamide[181].

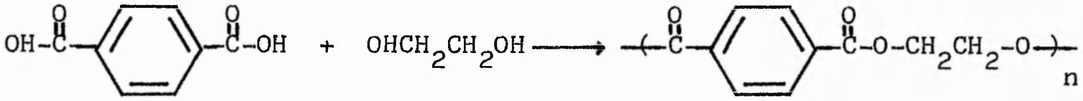
Differential-dyeing nylon can thus be dyed with anionic dyes including acid, direct, reactive and metal-complex as well as disperse dyes, although with the latter equal substantivity for all nylon 6.6 fibres is shown. The interaction of fibre and dye is therefore complex and the contrast that is obtained with anionic dyes does not depend solely upon the chemical differences between the fibres.

Chantler *et al.*[183], for example, examined the influence of a number of factors and found that the dyebath conditions affected the degree of contrast obtainable considerably. Other factors relating to the individual dye structure were also important eg, the degree of sulphonation, the position of the sulphonic acid group, the nature and ionic character of other groups and the size and shape of the dye molecule.

Nevertheless with careful dye selection a variety of multicoloured effects can now be obtained on all-nylon fabric from a single dyebath[184]. Progress so far has been most rapid in the field of tufted nylon carpets. In the United States, for example, about 70% of nylon carpet yarn production is piece-dyed, mainly as tufted carpeting on the winch, and about 80% of this is in the form of differential-dyeing designs[185]. Filament yarns of a variety of deniers are now also available for use in apparel, candlewick fabrics, curtains and upholstery[183].

2.4.3.2 Polyester

Almost all of the polyester produced is made by the condensation polymerisation of terephthalic acid and ethylene glycol:



The fibres are very hydrophobic and do not contain any specific dyesites; they are therefore dyed with disperse dyes. However, dyeing proceeds very slowly at 100°C so the process is generally carried out under pressure, at 130-140°C, or at the boil in the presence of a carrier. (Carriers are plasticisers which assist dyeing by lowering the glass transition temperature, ie. the temperature at which the chain segments in the amorphous regions become mobile producing holes into which the dye molecules can move).

Modification of polyester designed to produce fibres with differential-dyeing properties is carried out on both the homopolyester and copolyesters. Acid- and basic-dyeable fibres have thus been obtained, as well as fibres possessing different levels of substantivity for disperse dyes. At the same time many of the fibres produced have increased resistance to pilling[162].

Modification of the homopolyester is carried out during manufacture by using shorter molecular chains, altering the spinning conditions or including supplementary condensation reactants[186]. In this way physically modified homopolyester fibres such as Dacron 35 (Du Pont) and Trevira WA (FH) can be produced showing either a decreased or an increased substantivity for disperse dyes respectively.

In the case of Trevira WA (FH) the fibre structure is opened up to such an extent that the increased rate of diffusion and dye uptake which results produces rapid exhaustion which can give rise to non-uniform adsorption; at the same time little or no carrier is required[162].

Infrared laser radiation has also recently been suggested as a way of producing differential-dyeing polyester, enabling patterns to be traced out on a fabric by a laser under computer control[106]. Laser treatment of the conventional homopolyester has thus been shown to increase disperse dye uptake in the treated zones, the effect increasing with increasing energy dose. This behaviour was explained on the basis of reduced orientation and changes in the crystalline structure of the fibre.

The laser treated areas of the fibre were also observed to adsorb cationic dye whilst the untreated portion remained virtually unstained. This was attributed to the formation of carboxyl groups within the fibre which could act as sites for basic dyes; these, it was suggested, could be produced by laser irradiation as a result of hydrolytic, oxidative or pyrolytic degradation[106,179].

The dyeability of polyester fibres has also been claimed to be remarkably improved by heat treatment above their melting point while maintaining their mechanical properties at a satisfactory level. Differential-dyeing properties could be conferred to the yarns by applying a liquid with a high latent heat of vapourisation to some of the fibres before the high temperature treatment - the dyeability of those fibres to which the liquid was applied remaining unchanged by the heat treatment.

The great majority of modified polyester fibres are, however, copolyesters having poly(ethylene terephthalate) as the main component and incorporating a relatively small quantity of a comonomer, which need only be of the order of 2 mol% to produce a significant change in the dyeability of the fibre. The compounds used commercially for this purpose have been surveyed comprehensively[188] and include iso-phthalic acid, vanillic acid, p-hydroxy-benzoic acid, 4,4'-sulphonyl-dibenzoic acid and alkylene oxides.

Copolymerisation with alkylene oxides, for example, as in Dacron 64 (Du Pont) and Fiber K (Monsanto), and with aliphatic long chain carboxylic acids, which are used in small amounts, improves the substantivity for disperse dyes by opening up the physical structure of the fibre[189] (Figure 18).

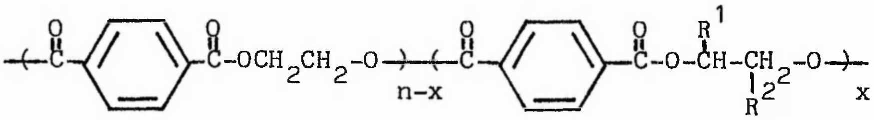


Figure 18. Deep-dyeable polyester - alkene oxide copolymer.

Such fibres are stated to be preferentially dyed by disperse dyes of high molecular weight[190]. Higher resistance to abrasion is also conferred on the fibre.

The incorporation of non-ionic compounds gives increased substantivity for disperse dyes by increasing the extent of the amorphous regions in the fibre, whilst cationic compounds, particularly those containing nitrogen[191], impart substantivity for acid dyes, which can often be improved by partial hydrolysis of the copolyester.

Acid-dyeable fibres can also be produced by incorporating into the fibre basic groups capable of being protonated in the presence of acid. Sulphonate-containing anionic compounds eg. 5-sulphoisophthalic acid, on the other hand, confer affinity for basic dyes (Figure 19):

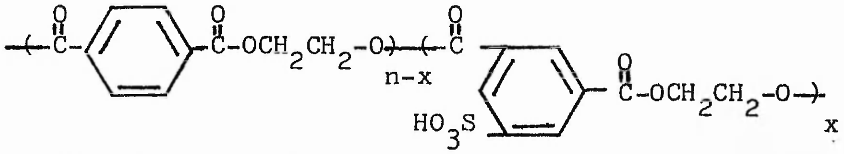


Figure 19. Basic-dyeable polyester - 5-sulphoisophthalic acid copolymer.

The dyeability of all copolyester fibres is better than that of unmodified fibres, the presence of the modifying component serving to interrupt the packing efficiency of the molecular chains, so reducing the degree of crystallinity and orientation. In addition, the amorphous regions of the fibre are frequently enlarged and the mobility of the chains in this region increased, relative to the homopolyester, allowing dyes to diffuse into the fibre more easily and rapidly[162].

Tone-on-tone effects can thus be produced with disperse dyes on mixtures of regular and acid- or basic-dyeable fibres, as well as on the more usual combination of regular and deep-dyeable polyester fibres. Mixtures of regular and deep-dyeable polyester fibres have thus been used extensively in the carpet trade for the production of pale and dark tone-on-tone effects - the deep-dyeable fibre sometimes also being used alone to obtain carpets that are more easily piece-dyed at atmospheric pressure[178].

Although acid- and basic-dyeable polyester fibres are not yet used in the carpet industry to the same extent as deep-dyeable fibres they are available in the form of filament and staple for use in both knitted and woven fabrics. They are also frequently used in combination with other fibres eg. nylon, cellulosics (including polynosic rayon) and wool[178].

In combination dyeings the poor light fastness properties of many disperse and basic dyes on basic-dyeable polyester fibres is particularly noticeable, however, the fastness to light of many of the modified fibres can be improved by incorporating small amounts of manganese terephthalate, preferably with a colour stabiliser, eg. phosphorous compounds[192].

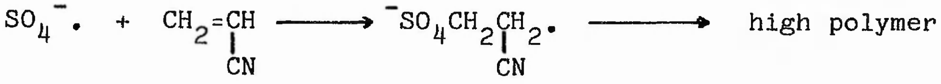
Further details concerning the principles involved in dye selection and the optimisation of dyebath conditions to obtain a variety of multi-coloured tone-on-tone and contrast effects on differential-dyeing polyester may be found in the literature[193,194].

2.4.3.3 Polyacrylonitrile

Acrylic fibres are those which contain at least 85% by weight of acrylonitrile. They also usually contain 10-15% of a neutral comonomer such as vinyl acetate or methylmethacrylate to modify the thermoplasticity of the fibre, reduce it's glass transition temperature, Tg, and so make dyeing easier. These contain no functional groups but improve the diffusion of disperse dyes by reducing the compactness of the fibre structure[22].

Commercial acrylic fibres also contain some acidic dye sites in the form of sulphate end groups which result from the redox catalysts used in the polymerisation:

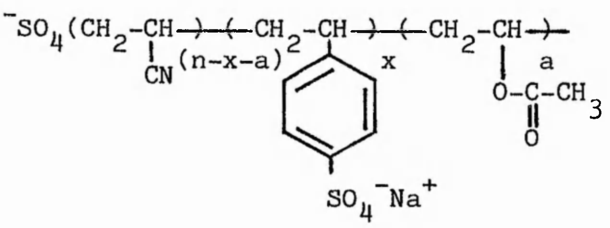
$$S_2O_8^{2-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-}\bullet$$



$$SO_4^{-}\bullet + \underset{\displaystyle CN}{CH_2{=}CH} \longrightarrow {}^{-}SO_4CH_2\underset{\displaystyle CN}{CH}CH_2\bullet \longrightarrow \text{high polymer}$$

These sites impart affinity for basic (cationic) dyes but their concentration is very low allowing only pale shades to be dyed. By introducing a third comonomer, however, acrylic fibres may be dyed deep shades and dye-variant yarns with particular dyeing properties produced.

Additional anionic sites can be introduced into the fibre in the form of side-groups by carrying out the polymerisation in the presence of 1-2% of an acidic comonomer such as sodium vinylbenzene sulphonate or methacrylic acid. Acidic monomers such as these containing sulphonic, phosphoric or carboxylic acid groups, confer substantivity for basic dyes whilst, at the same time, producing fibres with virtually no affinity for acid dyes[162]:



<u>Figure 20.</u> Basic-dyeable regular acrylic - acrylonitrile copolymer (n>85%) containing sodium vinylbenzene sulphonate (x%) and vinyl acetate (a%) comonomer.

Basic monomers, on the other hand, containing amine and pyridine groups (for example, vinyl pyridine and substituted vinylpyridines), when incorporated into the polymer impart affinity for anionic dyes (inlcuding acids and directs), whilst virtually no substantivity is shown for basic dyes.

The basicity of these groups is lower than that of the basic groups present in nylon and wool, hence when dyeing acid-dyeable acrylic it is usual to employ stronger acids, such as sulphuric, to obtain a pH of 2 so favouring protonation of available amine groups and ensuring that good yields and fastness properties are given by acid dyes, and that basic dyes reserve the acid-dyeable fibres[195].

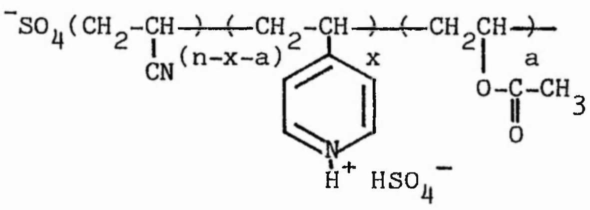


Figure 21. Acid-dyeable acrylic - acrylonitrile copolymer (n>85%) containing vinylpyridine (x%) and vinyl acetate (a%) comonomers.

Monomers containing no functional groups, such as hydrocarbons, can also be used to improve the dyeability of the fibre simply by altering it's physical structure whilst, at the same time, polar, non-ionisable monomers, such as alcohols, ethers and ketones also increase the general level of dye adsorption, not only by altering the physical structure of the fibre, but also by providing groups capable of non-ionic interaction with dyes[162].

The introduction of hydrophilic groups can also increase the substantivity of acrylic fibres for dyes, epoxy compounds, urea and certain quaternary ammonium compounds having been mentioned in this connection[196].

Differential-dyeing acrylic fibres are thus available. For example, Acrilan 16 and 36 (Monsanto) and Orlon 42 and 44 (Du Pont) are, respectively, the regular basic-dyeable and acid-dyeable acrylic fibres for each named manufacturer.

The use of these fibres to produce multi-coloured effects has been discussed by Beutler[197] and Schork[174]. In common with all differential-dyeing systems involving synthetic polymer fibres careful dye selection is essential for good results. The important factors to be taken into account when selecting dyes are their reserving properties, compatibility, and fastness to light and washing on the chosen substrate. The effects of dye concentration, pH, and dyebath additions on the results must also be considered[174].

Nevertheless colour-and-white and true two-tone effects can be produced, each fibre being dyed with its appropriate class of dye[198,199]. However, tone-on-tone effects are more usually obtained from mixtures of regular basic-dyeable acrylic and modacrylic fibres because this type of fibre shows differences in substantivity for disperse and basic dyes[178].

(Modacrylic fibres are acrylonitrile polymers containing more than 15% comonomer, added in order to impart special properties.

Differential-dyeing modacrylic fibres thus have varying substantivity for disperse and basic dyes and usually no substantivity for acid dyes).

Although differential-dyeing yarns were introduced primarily for the carpet industry, the principle could also prove of value to the designer of patterned knitted fabrics[200] and, in fact, mixtures of regular and acid-dyeable acrylic fibres have already been used in the apparel field[201].

In the carpet industry a greater emphasis has been placed on mixtures of basic-dyeable fibres with different substantivities for basic dyes, allowing the production of tone-on-tone effects. Differential-dyeing acrylic fibres in the form of acid- and regular basic-dyeable fibres have been available commercially for some years but market penetration has been limited[202].

Recently, however, the rapid growth of investment in continuous piece-dyeing by manufacturers has led to the development of acrylic fibres with three different dyeing levels for continuous piece-dyeing end-uses, the intention being to offer designers the same scope with differential-dyeing acrylics as is available with the multi-dye-level nylon fibres usually processed on piece-dyeing equipment.

The three dye variants will normally be reduced-affinity basic, regular or deep-basic, and acid-dyeable fibres for both tone-on-tone and contrast effects. These fibres have the advantages of rapid dye uptake and sufficient dye-sites to give dark colours within the fixation time normally encountered in continuous dyeing[202].

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Introduction

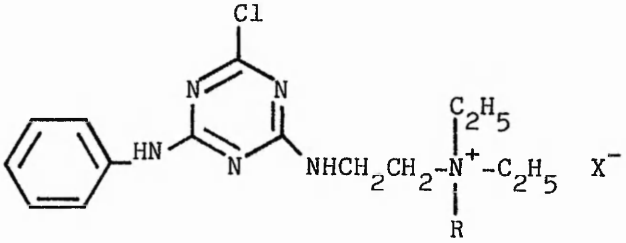
The main objective of this investigation was the preparation of colourless cationic and anionic compounds capable of reacting with cellulose under conditions similar to those used with reactive dyes and to apply them to cotton, or other cellulosic fibres, so as to produce differential-dyeing fibres showing preferential uptake of anionic and cationic dyes respectively.

In this way a variety of tone-on-tone effects could be produced on all-cotton goods woven from treated and untreated fibres, or from fibres and yarns treated to varying extents with, for example, a cationic reagent and dyed in a single dyebath. Similarly cotton yarns or fabrics produced from a mixture of cationic and anionic fibres could be dyed in a single bath containing, for example, a yellow acid dye and a blue basic dye to produce a cross-dyed, multi-coloured effect with considerable savings in time and energy.

3.2 Synthesis of reagents

3.2.1 Cationic reagents

A series of reactive compounds was prepared prior to an investigation of their use as potential reagents, based on the general formula (I):



(I)

where R = CH_3, C_2H_5, C_4H_{11}, C_6H_{13}, C_6H_{11}, $C_6H_5CH_2$, $C_{10}H_{21}$, $(C_6H_5)_2CH$, $C_{10}H_7CH_2$.

and X = Cl, Br, I or other simple anion.

These compounds all contain a labile chlorine atom capable of reacting with cellulose under alkaline conditions and a quaternary group which imparts water-solubility as well as acting as a site for anionic dyes.

They were prepared by first reacting cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) with a large planar aromatic group, containing an active hydrogen atom (usually aniline) to confer greater substantivity for cotton to the final reagent[203]. The reactivity of the three chlorine atoms in the triazine nucleus is such that careful control can be exercised over the degree of substitution of the final product. Replacement of the first chlorine atom (carried out at 0-5°C) has a deactivating effect on the remaining chlorines so that further substitutions of chlorine can generally be carried out at increasingly higher temperatures in a step-wise fashion[204].

The 2-anilino-4,6-dichloro derivative was thus reacted under reflux with a diamine containing a tertiary amine end group[205], capable of being quaternised with a variety of alkyl halides to produce a range of colourless quaternary reactive dye analogues. By carrying out the quaternisation as the final stage of the reaction, isolation of the quaternary end product was considerably simplified due to its very limited solubility in acetone.

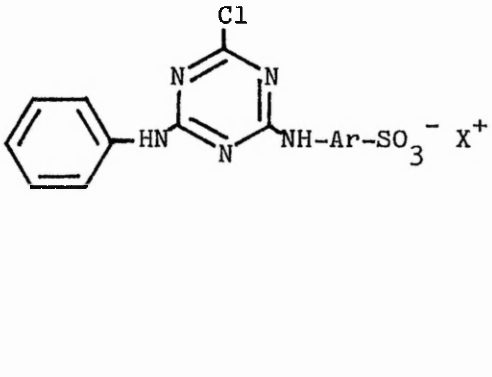
A scheme for the preparation of cationic reagent I, which was selected for use in most of the subsequent studies because it gave optimum contrast between treated and untreated fibre, is given below in Figure 22 and may be taken as being typical of the series (3.6.1).

3.2.2 Anionic reagents

The preparation of anionic reagents was less extensively studied, since most of the dyes commonly used with cellulose are anionic in character (at least in their application stage) and would therefore be more likely to require cationic rather than anionic sites.

Two reagents, II and IV (see below) were prepared, again based on the s-triazine ring system, each containing a labile chlorine atom for reaction with cellulose and a sulphonic acid group (instead of a quaternary ammonium group) to impart water-solubility as well as providing anionic sites for basic (cationic) dyes.

The general formula for the colourless anionic reagents may be given as:



where Ar = C_6H_4 (II)

$C_{10}H_6$ (IV)

and X = Na or other simple cation.

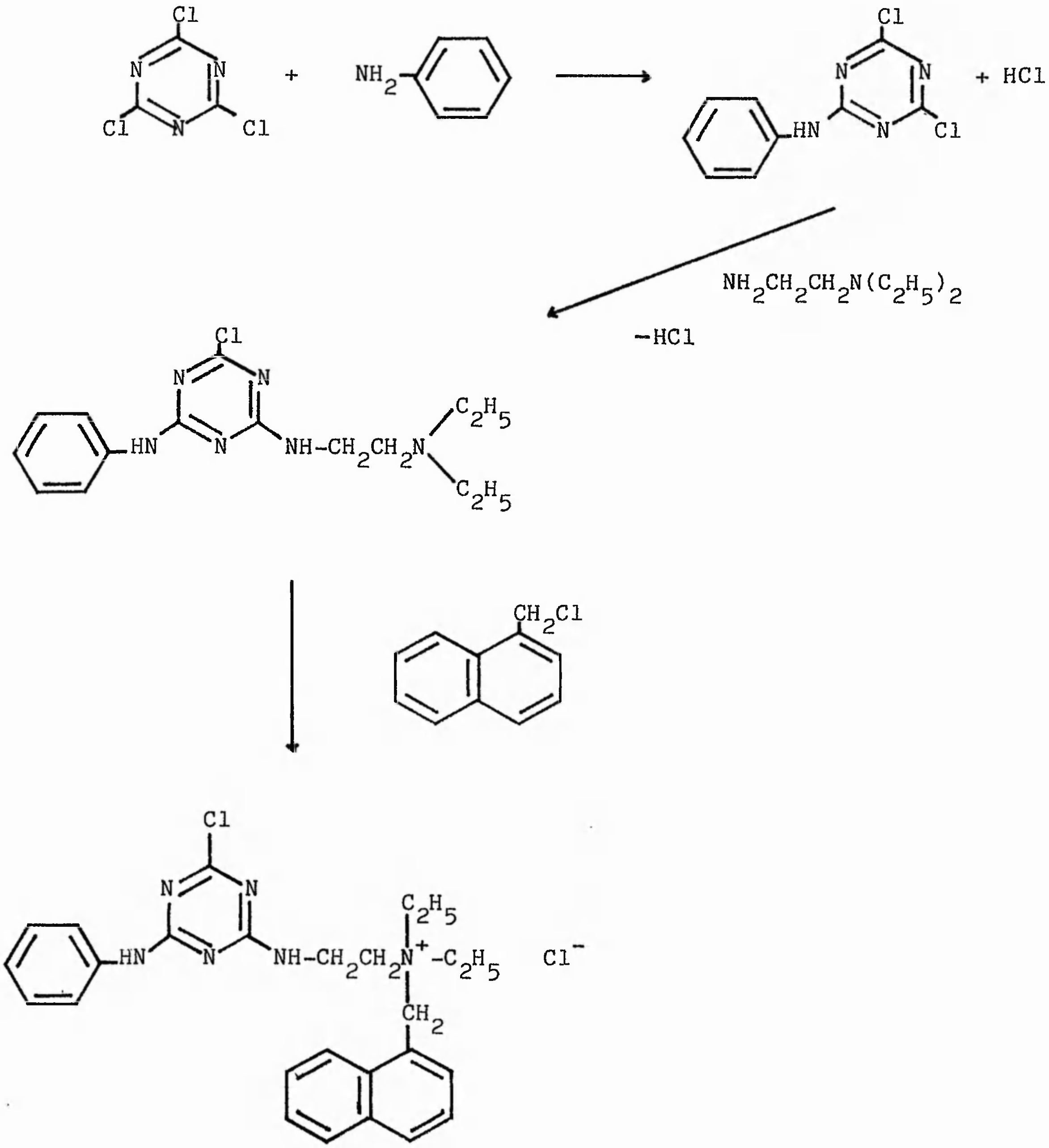


Figure 22. Preparation of Reagent I - 2-anilino-4-chloro-6-N-[2'-N-ethyl-N-(1-naphthylmethyl)ethylamino] amino-1,3,5-triazine ethochloride.

These anionic reagents were used mostly in cross-dyeing studies where both positive and negative groups were incorporated into cellulose to provide sites for anionic and cationic dyes respectively, enabling multi-coloured effects to be obtained from a single dyebath.

Another type of reagent used in the course of this work was a commercial preparation known as Sandospace R which is now no longer available. Manufactured by Sandoz and described in the technical literature as "a heterocyclic compound used as a reserving agent for dyeing polyamides"[205], nylon fibres treated with Sandospace R showed reduced affinity for anionic dyes and increased affinity for basic dyestuffs, whilst the affinity for disperse dyes remained unchanged[207].

No reference to the use of Sandospace R with cellulosic fibres could be found in the literature, however, treatment of cotton yarn with the compound, under conditions similar to those used for reactive dyeing, followed by washing to remove unreacted reagent and subsequent dyeing, resulted in preferential dye uptake by the treated samples in the cases of two basic dyes of widely differing structural types when treated and untreated cotton samples were dyed together in one bath.

3.3 Preparation of differential-dyeing cotton

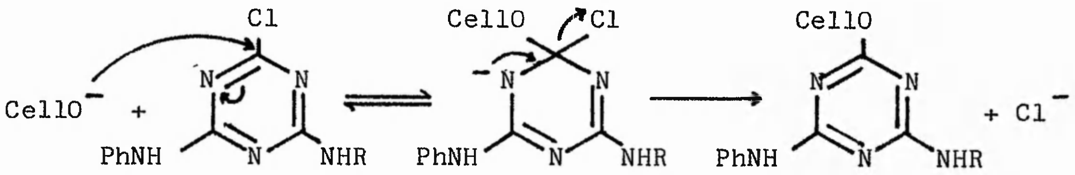
3.3.1 Theoretical principles of reagent application

Taking into account the mono-halogenated heterocyclic nature of the reagents prepared, it was decided to apply them to cotton yarn under conditions similar to those used with hot dyeing fibre-reactive dyes. In practice these are applied by first exhausting the dye onto the fibre in the presence of neutral electrolyte (usually sodium chloride) at about 40°C and then fixing the dye at 80°C in situ, under alkaline conditions, by the addition to the dyebath of dissolved sodium carbonate.

The reaction which these colourless quaternary reagents undergo with cellulose may be considered to be analogous to the type of acylation reaction which occurs between coloured reactive halogeno heterocyclic compounds, ie. the fibre-reactive dyes and cellulose[208].

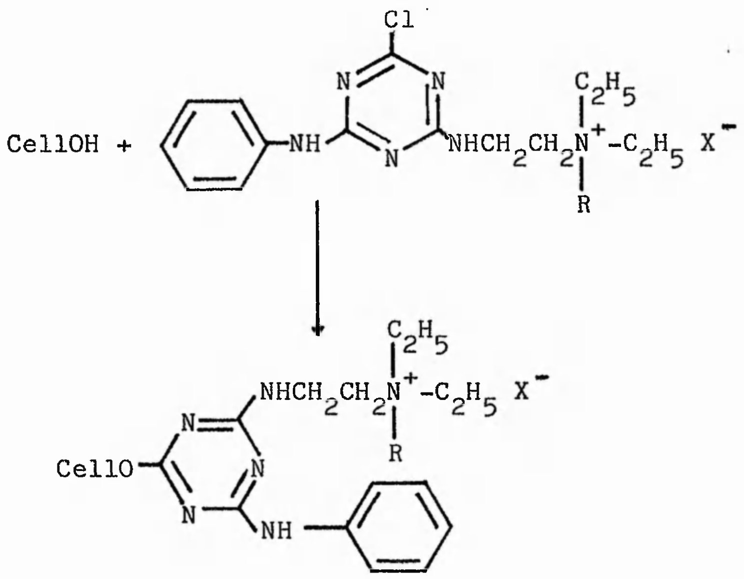
Halogen atoms attached to s-triazine rings are considerably more labile than are similar atoms attached to non-activated benzene rings, the hetero-nitrogen atoms causing a deficiency of electrons on the carbon atoms of the hetero ring, on account of their electronegativity, and in this way activating the system towards nucleophilic substitution.

The chlorine atoms, which tend to polarise the carbon-chlorine bond, $C^{\delta+} - Cl^{\delta-}$, contribute towards this build-up of positive charge on the carbon atom, so that nucleophilic attack can take place by a nucleophile such as HO^- or, in the case of the reactive dyeing of cellulose, the Cell.O^- radical.



The function of the alkali is thus to greatly increase the concentration of the cellulosate anions which are capable of reacting with the acylating agent; without the alkali no reaction occurs.

In general then the reaction taking place between these reactive quaternary reagents and cellulose may be given as:



where R = CH_3, C_2H_5, C_4H_{11}, C_6H_{13}, C_6H_{11}, $C_6H_5CH_2$, $C_{10}H_{21}$, $(C_6H_5)_2CH$, $C_{10}H_7CH_2$

and X = Cl, Br, I or other simple anion.

At the same time, however, there is a competing reaction involving the hydrolysis of the reagent taking place. Any difference in the molecular structure of the reagents which resulted in more of the reactive compound becoming adsorbed on the cellulose would therefore be likely to increase the probability of the reagent reacting with the latter rather than with the hydroxyl ions in the treatment bath.

An increased degree of reagent fixation would in turn increase the preferential dye uptake by the treated yarn and thus the degree of contrast obtainable when treated and untreated samples were dyed simultaneously in a single bath.

In the case of reactive dyes the distribution of dye between fibre and bath is dependant upon two factors, the affinity of the dye and the dyeing conditions. Although it would be possible to prepare reactive dyes of high affinity by using the direct dye type of structures the tendency has been to use dye structures of relatively low affinity so that the removal of hydrolysed dye is facilitated, otherwise the full wet fastness properties of the dye are not realised and hydrolysed dye held to the fibre only by physical adsorption (and obviously less fast than the covalently bound dye) continues to 'bleed'.

Similar considerations might therefore be expected to come into play when treating the fibre with a colourless reactive compound where the fastness of the treatment will ultimately depend on the effectiveness with which the hydrolysed reagent is removed,leaving only those positively charged sites which are covalently bound to the fibre.

Low affinity reactive compounds would also tend to have high rates of diffusion and therefore very attractive levelling and penetration properties before reaction occurs. Increasing the affinity of reagents might therefore incur serious disadvantages whilst the use of low affinity compounds as reagents would necessitate the selection of treatment conditions that favoured optimum exhaustion in order to render the process more economically viable.

There are, however, several dyebath variables which may be expected to affect the amount of fixation occurring in the reaction above. In order to examine their influence on the adsorption of reagents, particularly the cationic reagents, since there are far more anionic dyes which are substantive to cellulose, it was determined to establish which of the cationic reagents when applied to cotton produced the greatest degrees of preferential dye uptake, and to use these particular reagents in subsequent studies of the effects of several variables on the adsorption process. Accordingly, two reagents, I and III - the 1-(chloromethyl) naphthalene and the benzyl chloride derivatives of (I) respectively (see section 3.2.1) - were selected for use in further investigations.

3.3.2 Determination of the degree of adsorption of the reagent on cellulose

The amount of reagent adsorbed on the cellulose substrate was determined by applying a known weight of the colourless water-soluble reagent and then subtracting the amount known to be remaining in solution when exhaustion was complete. This latter quantity was measured using Beers Law ($A = \varepsilon cl$) after first determining the extinction coefficients, ε, for both of the selected reagents and checking that there were no deviations from linearity over a wide range of concentrations.

Since both cationic reagents I and III were necessarily colourless the wavelengths of maximum absorbance (λmax) for each were found to be in the uv region of the electromagnetic spectrum (see Figures 23 and 24). The uv absorption spectrum of the reagent derived from methyl iodide is also given in Figure 25. Absorbance measurements

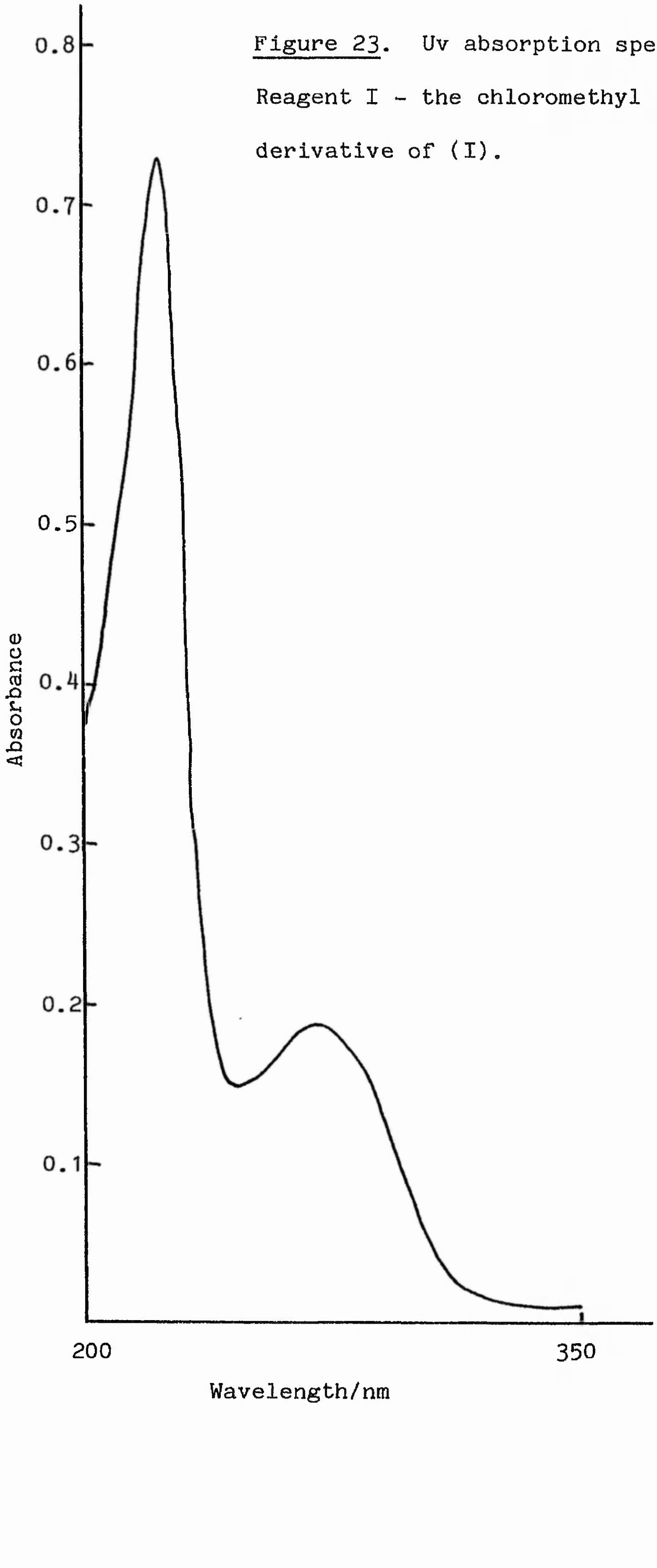


Figure 23. Uv absorption spectrum of Reagent I - the chloromethyl naphthalene derivative of (I).

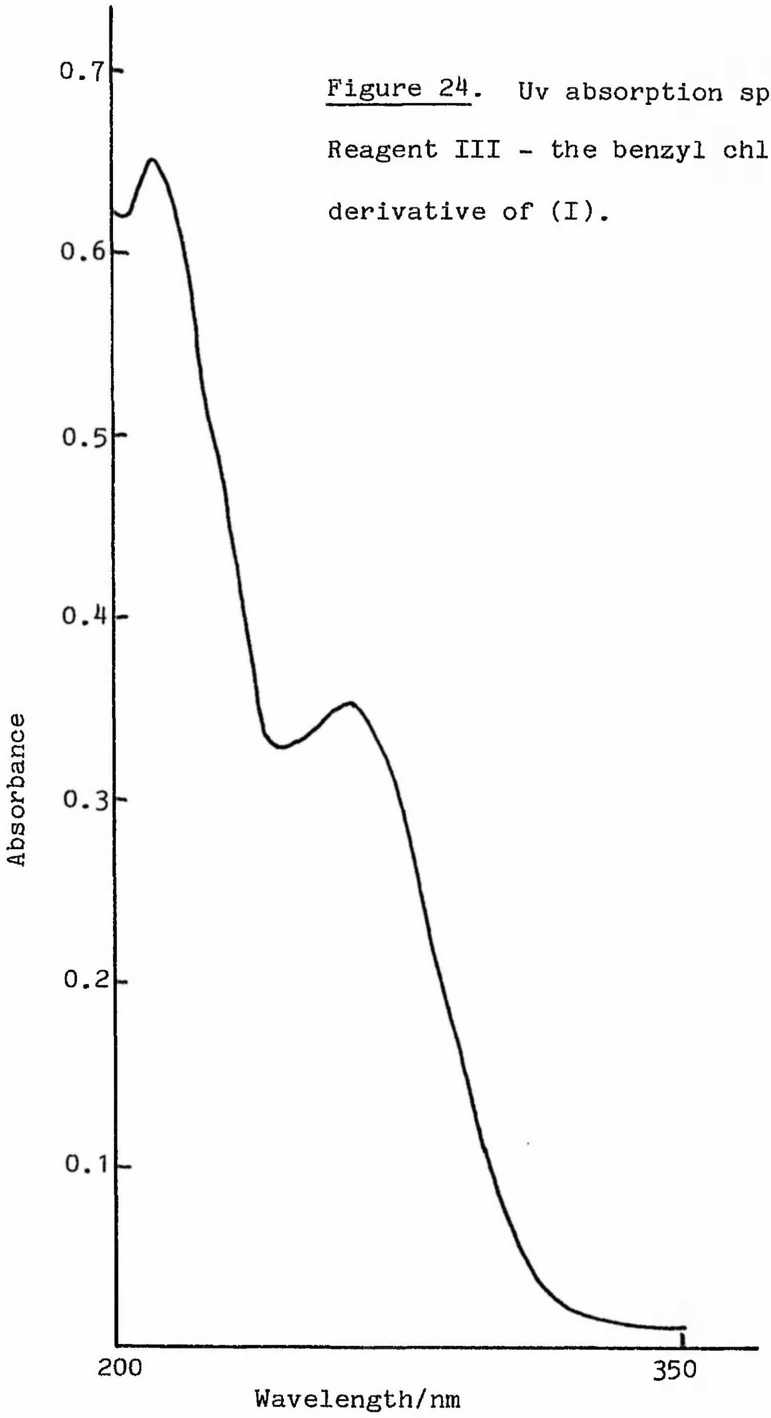


Figure 24. Uv absorption spectrum of Reagent III - the benzyl chloride derivative of (I).

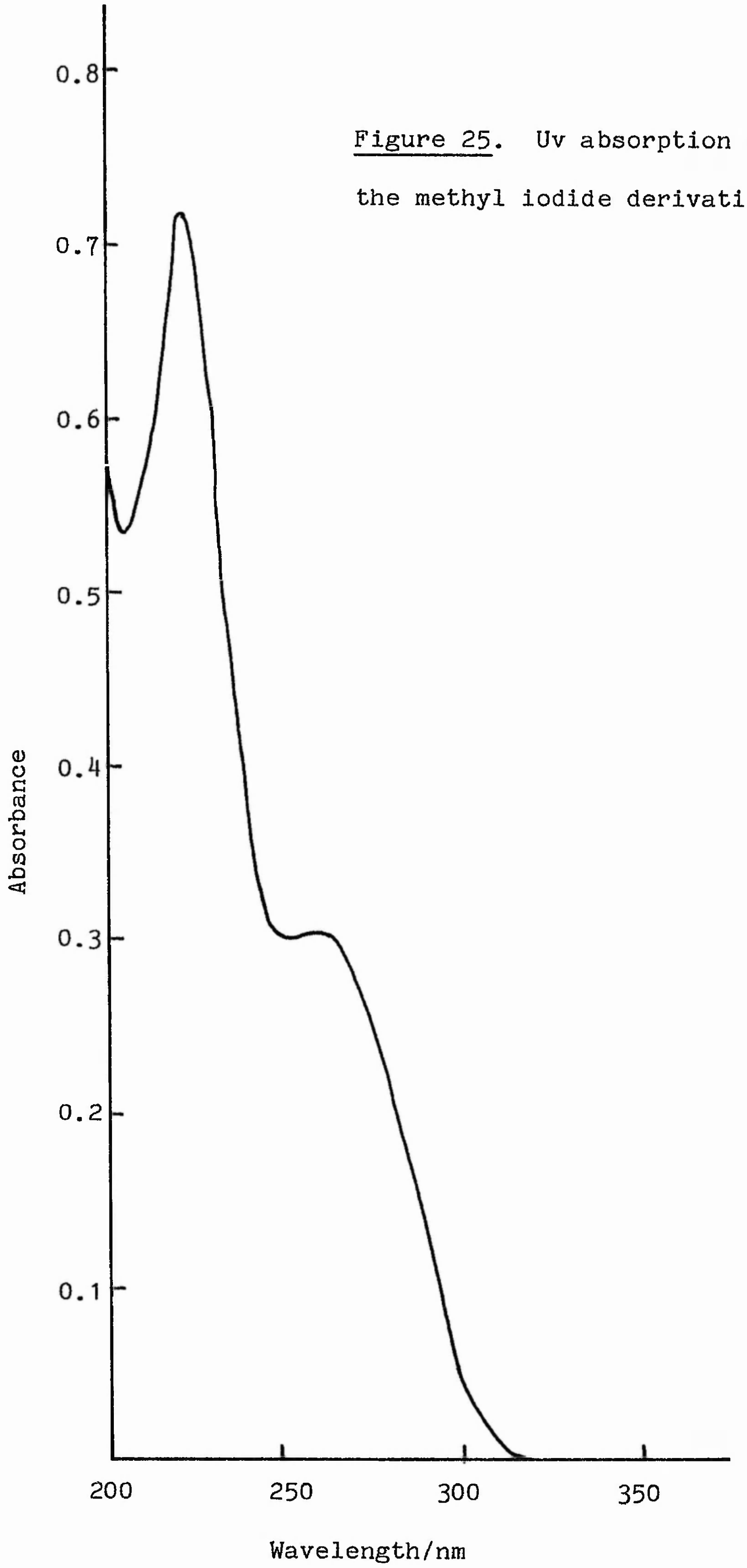


Figure 25. Uv absorption spectrum of the methyl iodide derivative of (I).

were therefore carried out using a Perkin Elmer uv/visible spectrophotometer at λmax = 270 nm ($\varepsilon = 1.83 \times 10^4$) and λmax = 262.5 nm ($\varepsilon = 1.65 \times 10^4$) for reagents I and III respectively, taking into account the fact that in each case the absorption at the shortest wavelength appeared to be more sensitive to the presence of dyebath assistants such as sodium chloride.

Beers Law calibration plots for reagents I and III together with that obtained for the methyl iodide derivative of (I) - see section 3.2.1 - are given in Appendix I.

3.3.3 Determination of the concentration of cationic sites in modified cotton

3.3.3.1 Introduction

In order to determine the optimum conditions for reaction of the cationic reagent I with cellulose the effect of a number of selected variables on the level of reagent fixation had to be examined and hence a method of determining the extent of reaction was required.

Two approaches to the problem were examined; one based on an ion-exchange technique and the other on a dye uptake method.

3.3.3.2 Ion-exchange method

The concentration of cationic sites incorporated into cotton yarn (C1) modified in bulk with 5% o.w.f. of reagent I was determined for a 20 g sample using the ion-exchange method outlined in section 5.7.1. Essentially the method involved exchanging the chloride counter-ion for hydroxyl ions and then determining the concentration of hydroxyl counter-ions by their neutralisation reaction with a known volume of standard hydrochloric acid. The site content of the yarn (C1) could then be determined from the following equation:

$$\text{Site content } (\text{mmolsKg}^{-1}) = (a-b).\ C_{OH}.\ x.\ 2.5$$

where a = titre (cm^3) for the initial HCl solution

b = titre (cm^3) for the HCl solution after the neutralisation reaction

C_{OH} = NaOH concentration

x = volume of HCl used.

$a = 11.7\ cm^3$

$b = 10.7\ cm^3$

$C_{OH} = 0.0099\ \text{molsdm}^{-3}$

$x = 300\ cm^3$

Site content = $\underline{7.4\ \text{mmolsKg}^{-1}}$

The result is given in Table 1 together with that obtained for the same yarn by the dye uptake method (described later) for comparison.

3.3.3.3 Dye uptake method

Since the modifying process involves incorporating cationic sites into cellulose the number of moles of an anionic dye taken up by the treated cotton should relate to the concentration of sites present, assuming a 1:1 interaction between the quaternary ammonium groups in the fibre and the sulphonic acid residues on the dye (see section 3.7.1) and that little or no diffuse adsorption occurs.

Table 2. Classification of yarns treated in bulk (500 g).

(see section 5.6.3 for details of bulk preparations).

	Site content mmolsKg^{-1}		Denoted
	a)	b)	
Cotton yarn (R220/2) treated in hank form in bulk with 5% o.w.f. of the cationic reagent I	7.4	7.1*	C1
Cotton yarn (R220/2) treated in bulk on a package dyeing machine with 10% o.w.f. of the cationic reagent I	-	35.5	C2

Key:

a) Ion exchange method

b) Dye uptake method

* as determined by extrapolation

Taking account of this latter consideration, a small monosulphonic acid dye, C.I. Acid Orange 7, (whose structure is given below - Figure 26) was selected, since it was unlikely to engage in a significant degree of diffuse adsorption.

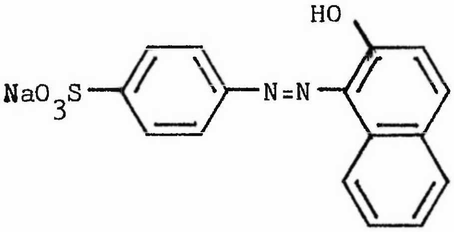


Figure 26. C.I. Acid Orange 7 - C.I. 15510.

The values of εmax and λmax were obtained from the literature[209] and $[Df]_\infty$ versus $[Ds]_\infty$ measurements carried out to obtain an equilibrium isotherm.

As can be seen in Figure 27 saturation of the available sites appeared to occur at a $[Df]_\infty$ of 6.6 mmolsKg^{-1}, where a plateau region of the isotherm was observed, followed by diffuse adsorption of dye onto the fibre. However, by extrapolation a site content of 7.1 mmols Kg^{-1} was obtained, which was slightly closer to the figure of 7.4 mmols Kg^{-1} obtained earlier for C1 by the ion-exchange method.

The above method was thus used to determine the site content of the cotton yarn treated in bulk with 10% o.w.f. of the cationic reagent I, (C2) and a value of 35.5 mmolsKg^{-1} was obtained by extrapolation (Figure 28). A second portion of cotton treated with 5% o.w.f. of reagent I, this time on a small scale, was also examined and a site content of 18.0 mmolsKg^{-1} obtained (see Figure 29), which was more in keeping with the result obtained for C2 and confirmed that the original 5% o.w.f. bulk treatment was less efficient than expected possibly because of too high a liquor to goods ratio.

Table 3. Equilibrium adsorption measurements for C.I. Acid Orange 7 on treated cotton (C1).

$[Ds]_o$ molsdm^{-3} x 10 ^{3}	A λmax 486 nm	Dilution Factor	$[Ds]_\infty$ molsdm^{-3} x 10 ^{3}	$[Df]_\infty$ molsKg^{-1}x 10^3	Colour strength
0.204	0.303	10	0.135	3.45	37.60
0.510	0.849	10	0.377	6.60	49.45
0.714	0.528	25	0.587	6.35	56.10
1.020	0.799	25	0.888	6.60	54.92
1.530	0.618	50	1.373	7.85	60.18
2.040	0.422	100	1.876	* 8.20	61.45
2.550	0.536	100	2.382	8.40	63.18

* Calculation of intercept by a 3 point regression analysis

Intercept	7.13
Slope	0.54
Correlation coefficient	0.99

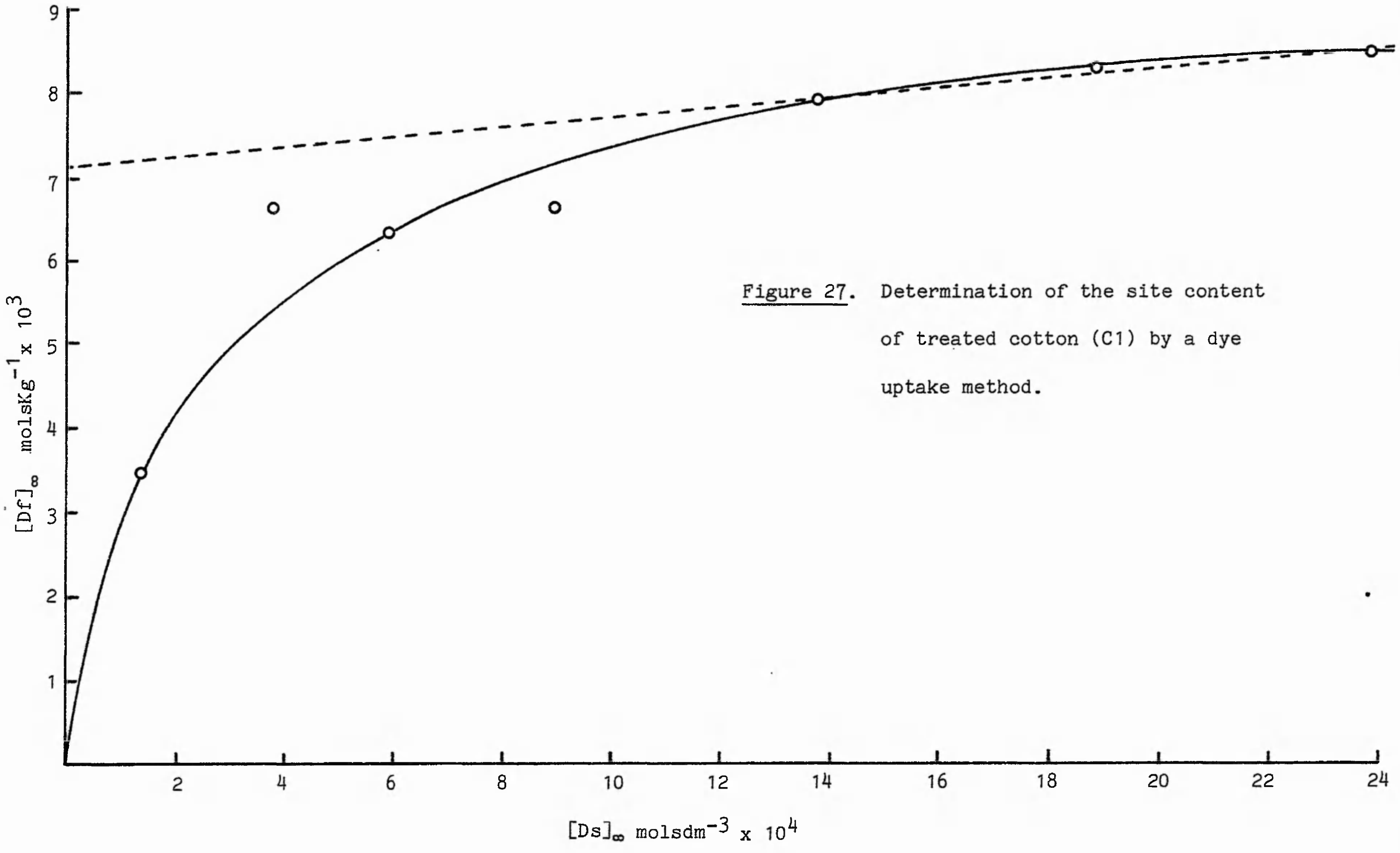


Figure 27. Determination of the site content of treated cotton (C1) by a dye uptake method.

Table 4. Equilibrium adsorption measurements for C.I. Acid Orange 7 on treated cotton (C2).

$[Ds]_o$ molsdm^{-3}x10^4	Aλmax 486 nm	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^4	$[Df]_\infty$ molsKg^{-1}x10^3
2.90	0.149	-	0.066	14.17
7.25	0.843	5	1.87	26.88
14.50	0.713	25	7.92	32.89
21.75	0.663	50	14.73	35.08
29.00	0.489	100	21.73	36.33
36.25	0.330	200	29.33	34.58

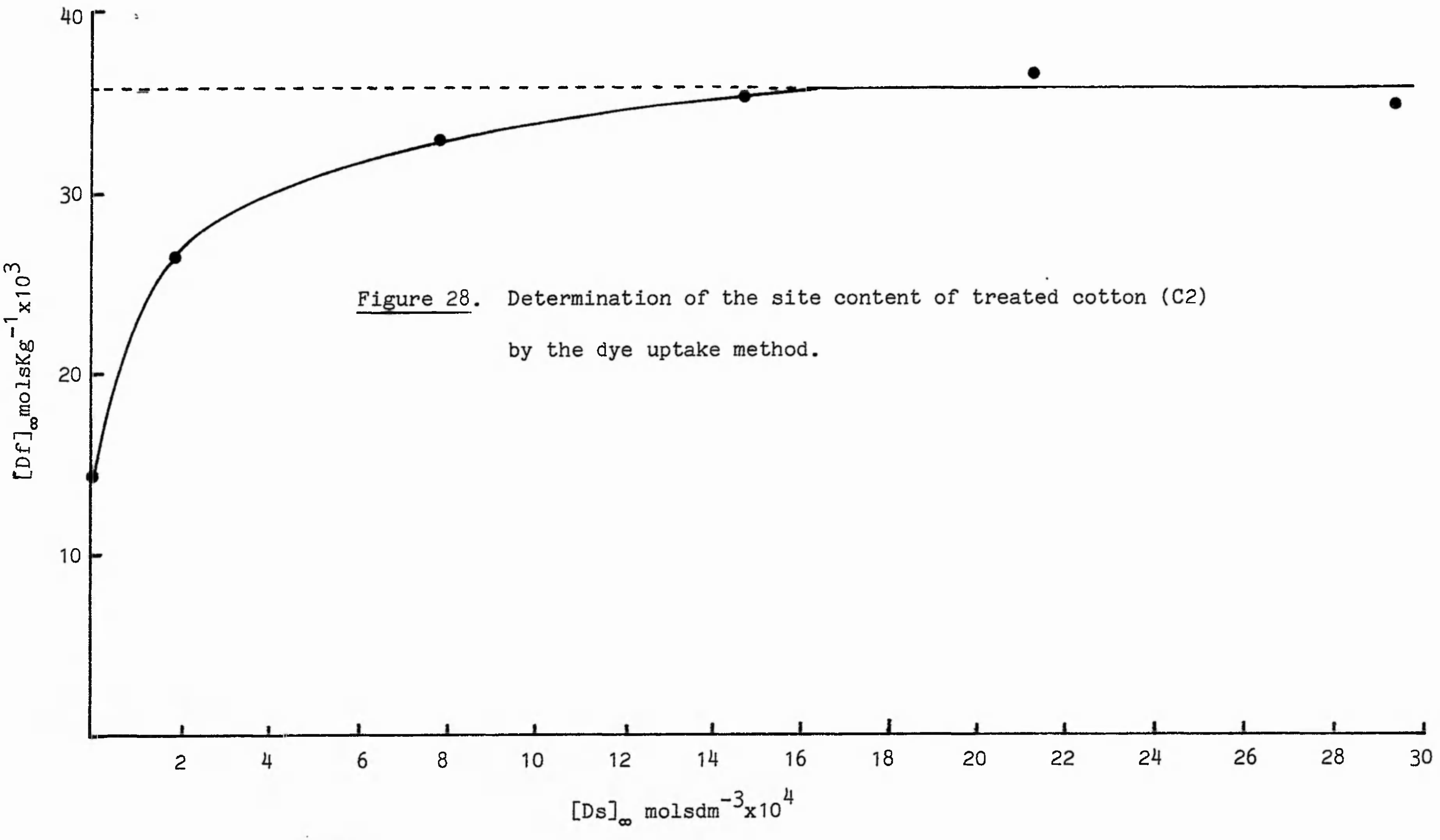


Figure 28. Determination of the site content of treated cotton (C2) by the dye uptake method.

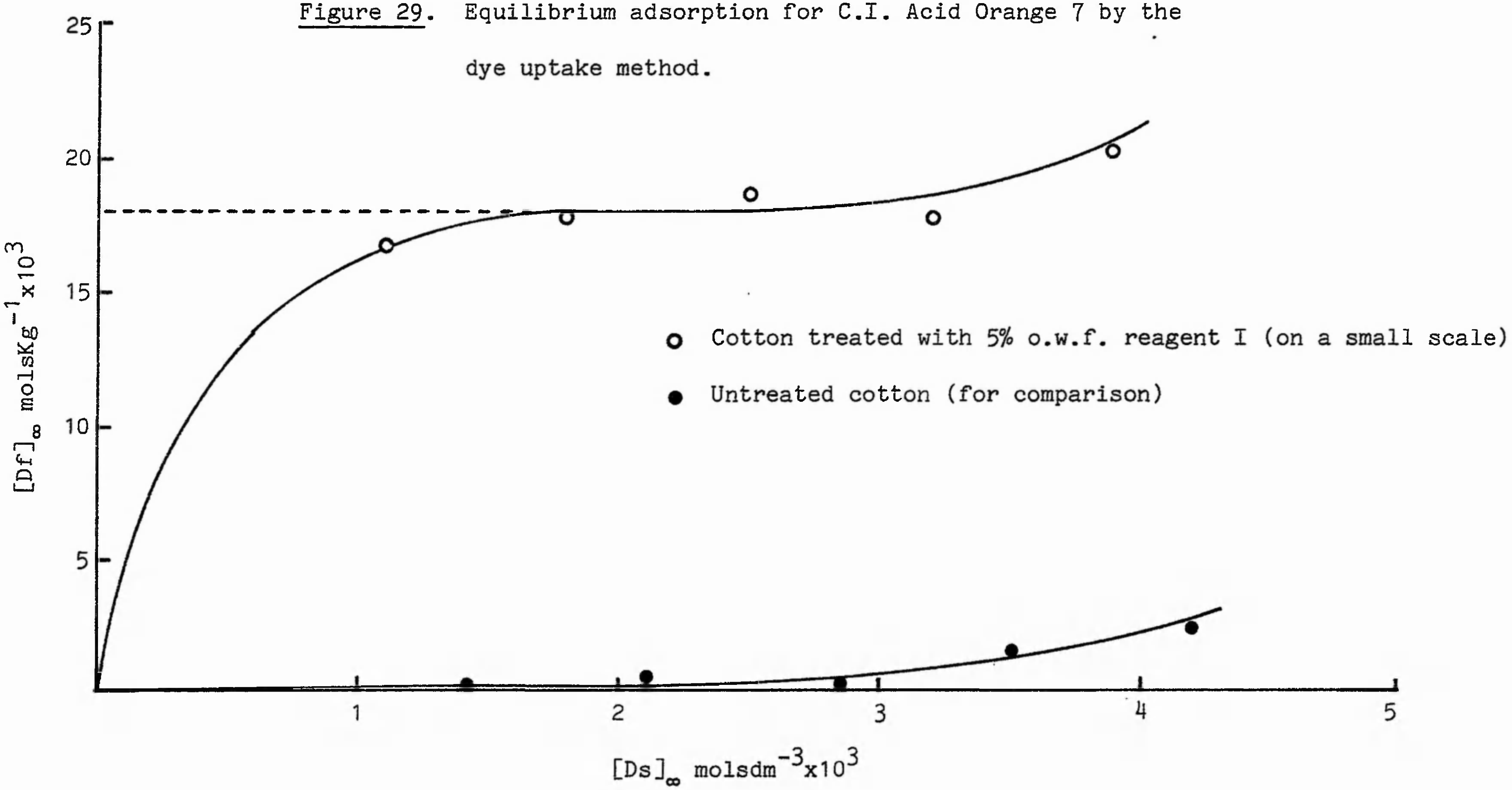
Table 5. Equilibrium adsorption measurements for C.I. Acid Orange 7 on cotton treated with 5% o.w.f. of reagent I on a small scale.

$[Ds]_o$ molsdm^{-3}x10^3	Aλmax 486 nm	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^3	$[Df]_\infty$ molsKg^{-1}x10^3
1.429	0.197	125	1.094	16.71
2.143	0.322	125	1.789	17.71
2.857	0.449	125	2.494	18.14
3.571	0.579	125	3.217	17.71
4.286	0.699	125	3.883	20.14

Table 6. Equilibrium adsorption measurements for C.I. Acid Orange 7 on untreated cotton for comparison.

$[Ds]_o$ molsdm^{-3}x10^3	Aλmax 486 nm	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^3	$[Df]_\infty$ molsKg^{-1}x10^3
1.429	0.257	125	1.428	0.06
2.143	0.384	125	2.133	0.48
2.857	0.514	125	2.856	0.07
3.571	0.638	125	3.544	1.33
4.286	0.764	125	4.244	2.10

Figure 29. Equilibrium adsorption for C.I. Acid Orange 7 by the dye uptake method.



3.3.4 Determination of the extent of reaction between cationic reagents and cellulose by Colour Strength measurements

The extent of reaction occurring between the reagent and cellulose can be directly related to the number of cationic sites successfully incorporated into the substrate and hence, as was shown in section 3.3.3.3, to the concentration of anionic dye taken up by the modified fibres.

In the dyeing industry reflectance measurements on dyed samples have been related to dye concentrations enabling the dye content of unknown samples to be quickly determined from measurement of their reflectance under identical conditions. The method is restricted to substrates which have a reasonably white appearance but since treatment with the colourless reagent brings about very little discoloration of the bleached cotton this was not considered to be a problem.

A similar method was therefore developed for quickly determining the extent of reaction between the reagent and cellulose and hence the efficiency of the fixation process under a given set of conditions. Dyeing of treated samples was carried out using either acid or direct dyes and reflectance measurements taken using the wavelength of maximum absorption (minimum reflectance).

The relationship between colourant concentration and reflectance is, however, not linear but straight-line relationships are possible between the concentration, c, and some function, F, of reflectance at a particular wavelength so that

$$Kc = F(R) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where K is a constant for a particular colourant, wavelength and substrate.

There are a number of ways in which the reflectance function can be determined, however, the simplest generally useful function of reflectance, having widespread applications was developed by Kubelka and Munk[210]. This states that

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R} \quad \text{.....................(2)}$$

where K = absorption coefficient

S = scattering coefficient

R = fractional reflectance (on a scale of 0-1)

Beers Law indicates that K is proportional to concentration, but S is independent of concentration. Combination of equations (1) and (2) leads to equation (3).

$$K.c = \frac{(1-R)^2}{2R} \quad \text{...........................(3)}$$

Using equation (3) the reflectance can be related to the colourant concentration. It is, however, only applicable if the reflectance of the substrate is 100%, although normally the substrate has an absorption coefficient which adds to that of the colourant. The fractional reflectance of the substrate must also therefore be determined, leading to equation (4).

$$Kc = \frac{(1-R)^2}{2R} - \frac{(1-Rt)^2}{2Rt} \quad \text{.................(4)}$$

where Rt = fractional reflectance of the substrate.

At high concentrations of dye on the fibre the reflectance function of the substrate is small enough by comparison to be ignored. It can however be completely removed by measurement of the reflectance of the dyed sample against a sample of the undyed substrate rather than against an arbitrary white standard.

The applicability of the Kubelka-Munk theory to a particular system can be assessed by means of a logarithmic expansion of equation (1) to give

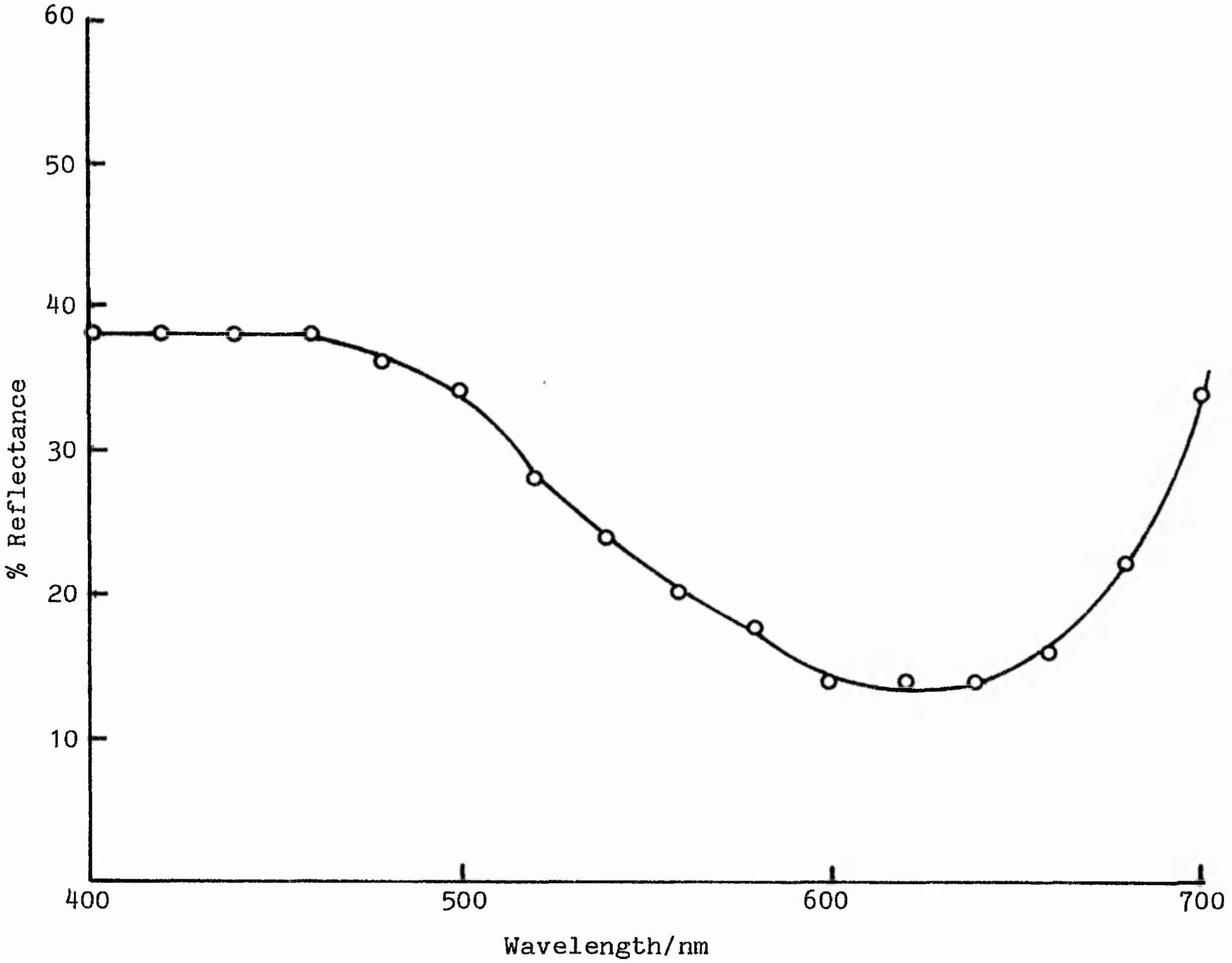
$$\log K + \log c = \log F(R) \qquad \text{.....................(5)}$$

Thus if the theory holds for a particular situation a plot of log F(R) versus log c should be linear with a slope of unity. The constant K has to be initially evaluated by the construction of a calibration plot involving measurement of the reflectance of a series of treated samples dyed to a known concentration.

A number of dyeings of treated cotton were therefore carried out employing 0.1-3.0% o.w.f. of a commercial sample of C.I. Direct Blue 1 (liquor ratio 50:1). Samples treated with 5% o.w.f. of reagent I (C1) were added to the 0.1-0.75% o.w.f. dyebaths and cotton treated with 10% o.w.f. reagent I were dyed in the baths containing 1-3% o.w.f. C.I. Direct Blue 1, so as to ensure complete exhaustion in each case and at the same time level dyeings.

Measurement of the reflectance of a 10% treated sample dyed with C.I. Direct Blue 1 against an undyed sample as standard across the visible region gave λmax = 620 nm (Figure 30).

Figure 30. % Reflectance *versus* Wavelength/nm for C.I. Direct Blue 1 on cotton treated with 10% o.w.f. of cationic reagent I (C2)



Dyeing was carried out for 4 hours at 96°C on a Rotadyer after which time the tubes were cooled. Reflectance measurements were then carried out on the dyed samples at λmax = 620 nm against an undyed 5 or 10% o.w.f. treated sample as appropriate. The results are given in Appendix II together with the data required to examine the application of the Kubelka-Munk reflectance function to this particular dye-substrate system. A graph of Dye on fibre concentration (% o.w.f.) versus the Kubelka -Munk reflectance function (Figure 31) confirmed that a good straight-line relationship existed between the two. A plot of log (concentration) versus log (reflectance function) (Figure 32) , drawn up to examine the applicability of the data to analysis by the Kubelka-Munk treatment, was found to be linear with a slope of 0.85 which fairly closely approached the ideal value of 1, indicating that for this particular dye-substrate system the reflectance data fitted the mathematical model of the Kubelka-Munk theory reasonably well (any deviation from unity possible being due to the specific surface characteristics of the substrate).

Reflectance data in conjunction with the Kubelka-Munk expression could thus be used for determining the amount of dye taken up by the treated fibre and hence the extent of reaction occurring between the cationic reagent I and cellulose treated under a given set of conditions.

A more modern approach to the measurement of the intensity of the colour of a specimen was, however, investigated using the International Colour Systems Micromatch Spectrophotometer. Using this instrument the reflectance for a given sample could be measured at 16 different wavelengths from 400-700 nm at 20 nm intervals and an average value

Figure 31. Dye on fibre concentration versus Kubelka-Munk reflectance function

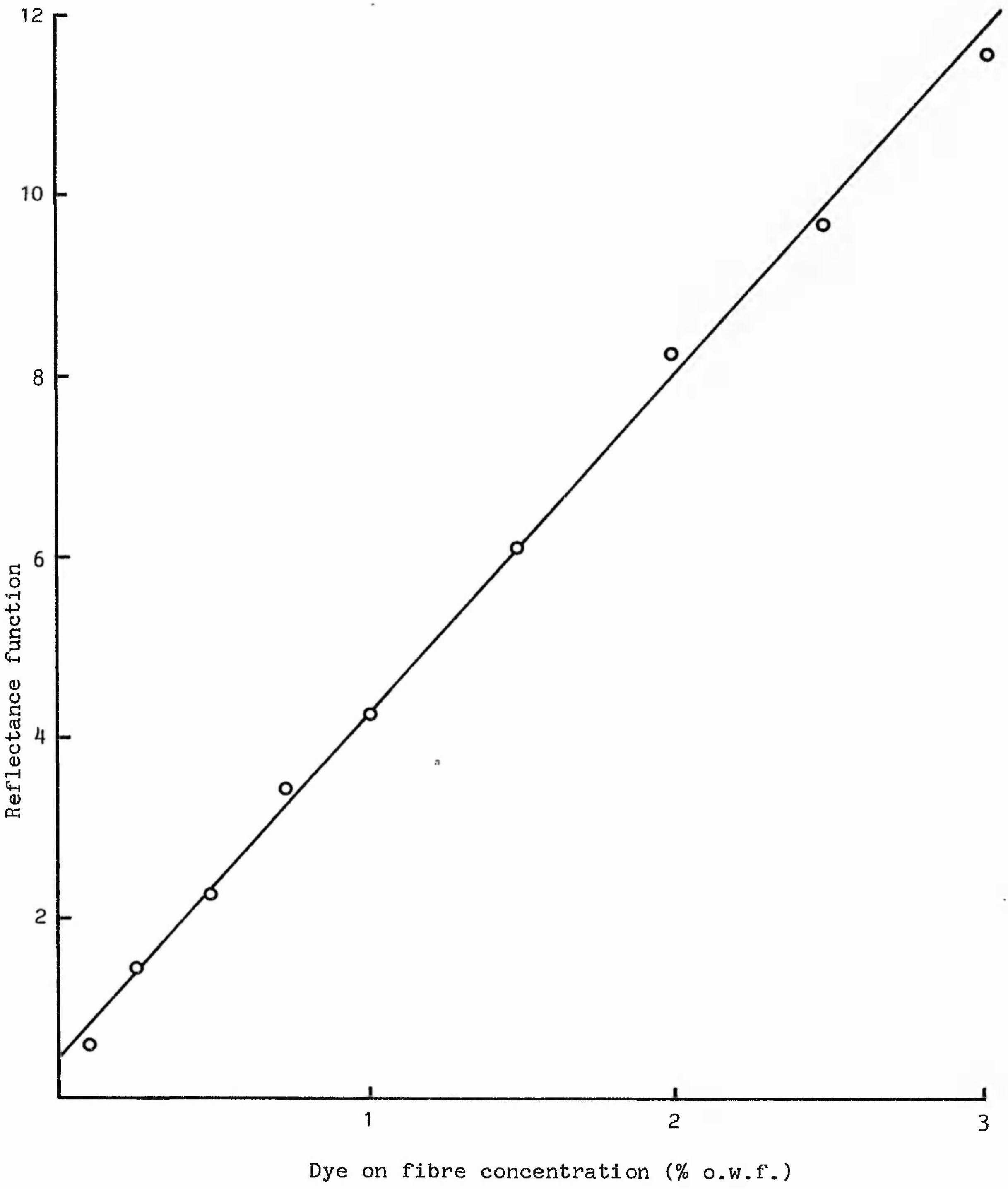
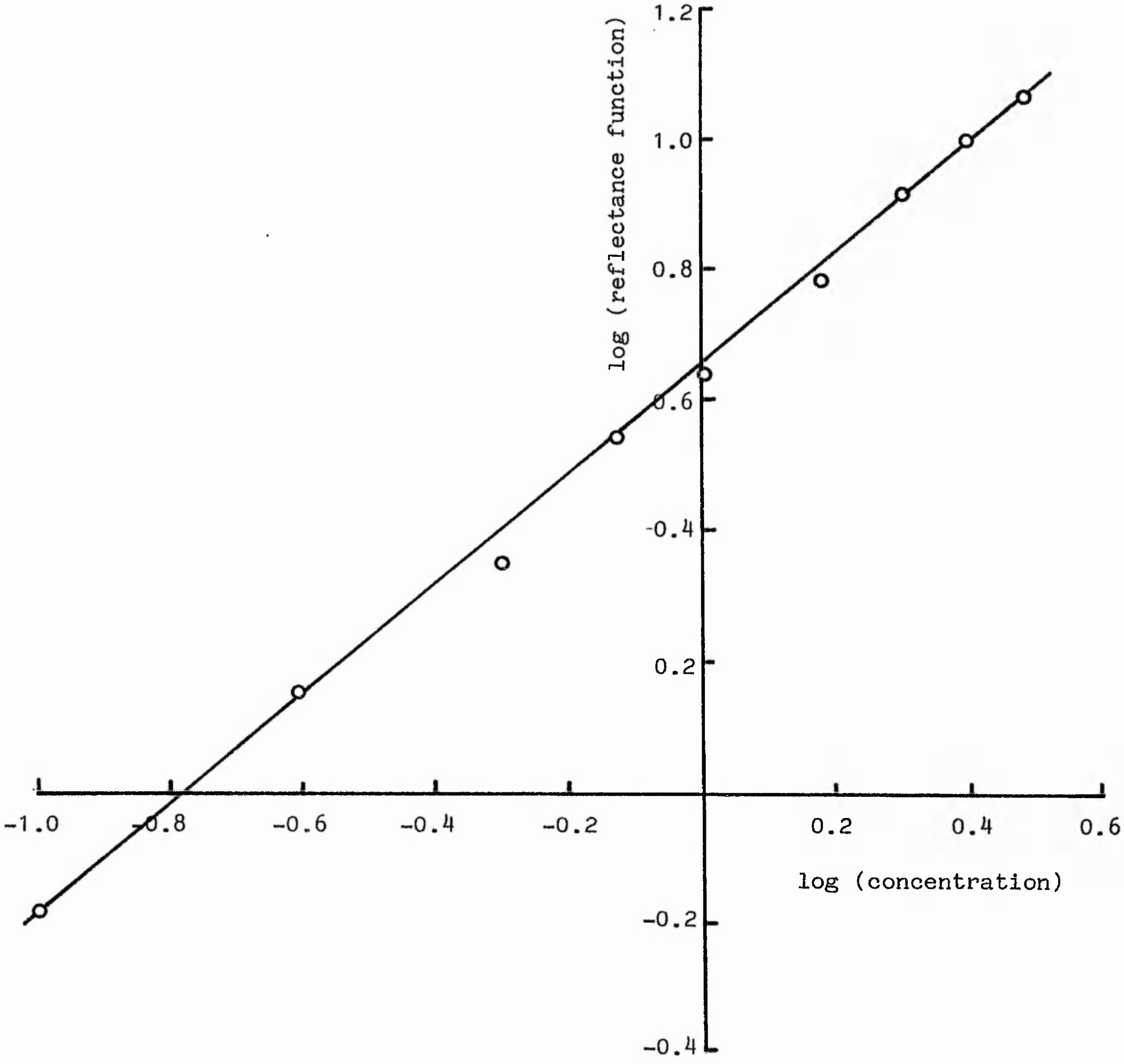


Figure 32. Plot of log (concentration) *versus* log (reflectance function).



given for the 'Colour Strength' over these 16 values. The Colour Strength is the ratio of the absorption to scattering coefficients for the dyed sample against that for the undyed substrate which acts as a standard:

$$\text{Colour Strength} = \frac{\text{Sum K/S sample}}{\text{Sum K/S standard}}$$

where $K/S = \frac{(1-R)^2}{2R}$ R = reflectance on a 0-1 scale

Using the dyeings obtained earlier the Colour Strengths of the samples were determined taking an average of four readings for each sample. The results are given in Table 3. In theory a plot of Colour Strength *versus* Concentration should give a straight line with an intercept of 1, which corresponds to the point where the sample and substrate are identical.

As can be seen from Figure 33 a good straight line relationship was obtained on plotting Colour Strength *versus* Concentration although the value at the intercept of 2.72 did not comply with the theoretical requirement of 1. This was to be expected bearing in mind the slight deviation from ideality noted earlier in the analysis of the data by the Kubelka-Munk treatment, and perhaps reflects the greater sensitivity of the treatment to differences in the surface characteristics of the substrate.

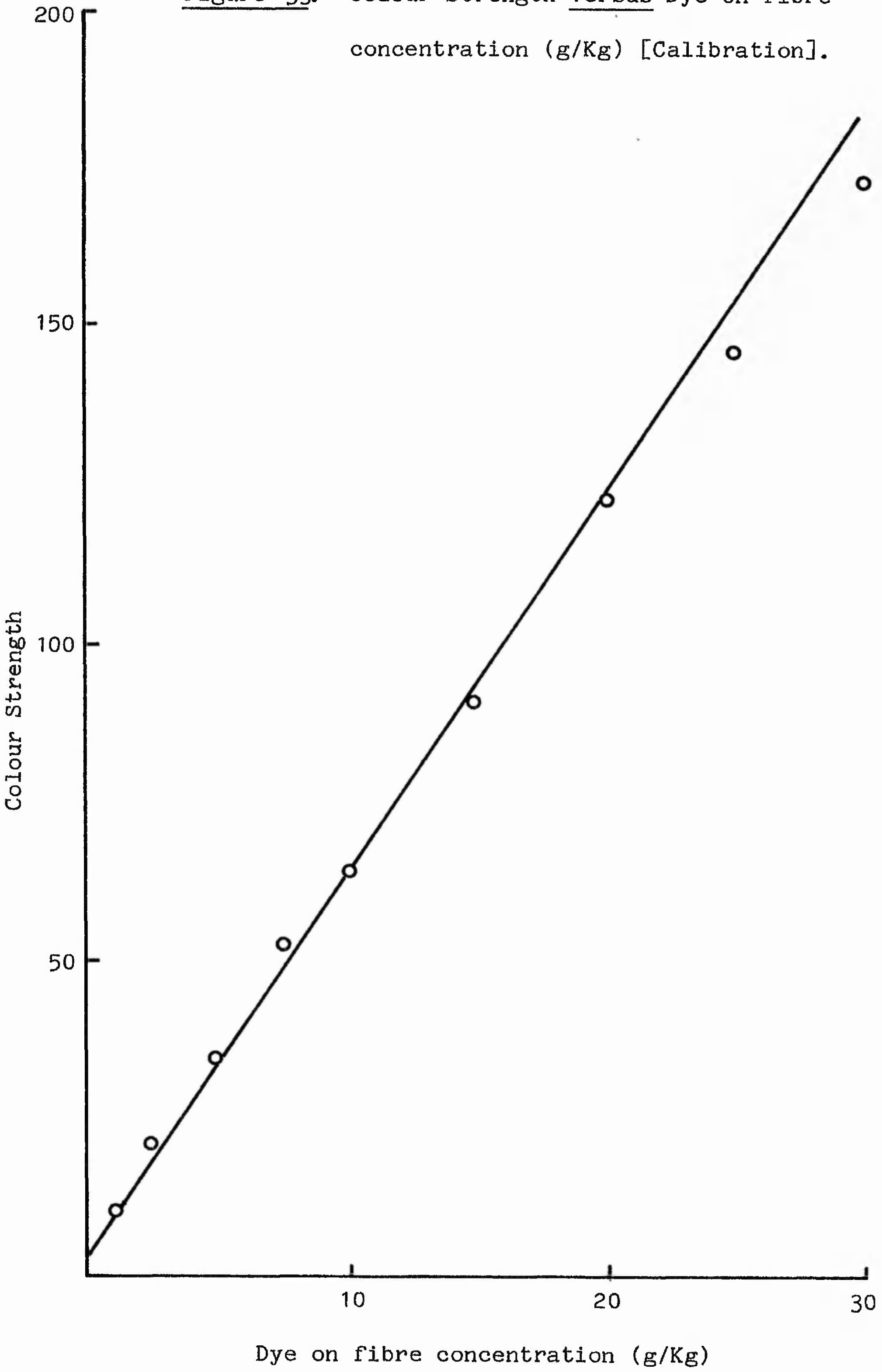
Table 7. Colour Strength *versus* Concentration of dye on treated cotton (g/Kg).

Dye concentration % o.w.f.	 g/Kg	Colour Strength
0.1	1.0	10.54
0.25	2.5	22.33
0.5	5.0	34.61
0.75	7.5	52.48
1.0	10.0	64.78
1.5	15.0	91.54
2.0	20.0	122.15
2.5	25.0	145.35
3.0	30.0	172.65

Regression analysis of a plot of Colour Strength *versus* Concentration of dye on treated cotton (g/Kg).

Intercept	2.717
Slope	5.810
Correlation coefficient	0.998

Figure 33. Colour Strength *versus* Dye on fibre concentration (g/Kg) [Calibration].



Colour Strength measurements of samples treated with the cationic reagent I, and dyed with C.I. Direct Blue 1 can thus be used directly as a measure of the degree of fixation occurring between the reagent and the fibre or converted into dye on fibre concentrations (g/Kg) using the Colour Strength versus Concentration calibration graph and by fitting an equation to the line using the regression analysis data, dye on fibre concentrations can be determined at higher Colour Strengths ie. >200:

$$\text{Dye on fibre (g/Kg)} = (\text{Colour Strength} - 2.72)/5.81$$

Molar concentrations of dye on the fibre may also be calculated from a knowledge of the structure of C.I. Direct Blue 1 (Figure 56 section 3.7.1.2) and hence its molecular weight (992), the purity of the commercial dye sample used having been previously determined as 20.87%.

3.4 Factors influencing the adsorption of cationic reagents on cellulose

3.4.1 Effect of temperature

Taking the lowest temperature to be examined (30°C) the time taken for the system to reach equilibrium was first determined by carrying out six identical 5% o.w.f. treatments of cotton yarn using the cationic reagent I, in the presence of sodium chloride (40 g/l) but without the addition of alkali.

The treatments were carried out in sealable polypropylene tubes at a liquor ratio of 50:1, using a 'Rotadyer' constant temperature bath, samples being removed at regular intervals over a 2 hour period. The amount of reagent remaining in solution was then determined and a graph of % Exhaustion versus Time drawn up (Figure 34).

For the cationic reagent I, at 30°C equilibrium can be seen to have been reached within 2 hours, and thus it could be assumed that at higher temperatures equilibrium would be attained within this time.

Five further runs were therefore carried out for 2 hours at 40°C, 50°C, 60°C, 70°C and 80°C, removing samples at regular intervals, and these results are also shown in Figure 34.

As expected the exhaustion of the treatment bath at equilibrium was generally found to increase with decreasing temperature. The only exception occurred when the reagent was applied at 80°C when the equilibrium % exhaustion was apparently higher than that obtained at 60°C or 70°C although this was more than likely due to the occurrence of a considerable degree of reagent hydrolysis as a result of exposure to an excessively high bath temperature. (The recommended exhaustion temperature for similar monochlorotriazinyl type reactive dyes does not usually exceed 60°C). Similar increases in the apparent exhaustion were also observed at 60°C and 70°C after prolonged exposures of more than an hour at these temperatures.

In most cases, however, equilibrium can be seen to have been reached in an hour, the highest equilibrium adsorption after 1 hour (69%) being obtained at the lowest temperature employed (30°C) compared to only 37.9% exhaustion after 1 hour at 60°C. Such behaviour is typical of monochlorotriazinyl reactive dyes of low molecular weight

Table 8 . Effect of temperature on the exhaustion of cationic reagents.

Time (mins)	% Exhaustion at constant temperature					
	30°C	40°C	50°C	60°C	70°C	80°C
15	64.0	55.7	45.4	33.0	33.3	35.1
30	66.7	58.3	45.8	35.6	30.0	38.0
45	67.6	58.7	49.6	34.7	27.6	43.7
60	69.0	59.7	48.7	37.9	28.8	41.6
90	69.3	57.5	49.0	47.9	36.3	31.8
120	70.5	60.4	48.5	52.5	34.9	31.5

and is attributed to the fact that they posses high rates of diffusion into the fibre.

It is questionable, however, whether or not there would be any advantage in starting the treatment in the cold since, by analogy with a typical monochlorotriazinyl reactive dyeing which also requires a temperature of at least 70°C for reaction with the fibre to occur, raising the bath temperature may cause the reagent to rapidly redistribute itself so that by the time a temperature of, for example, 70°C is reached there may be little difference between the amount of reagent on the fibre and the amount which would have been present if the treatment had been started hot.

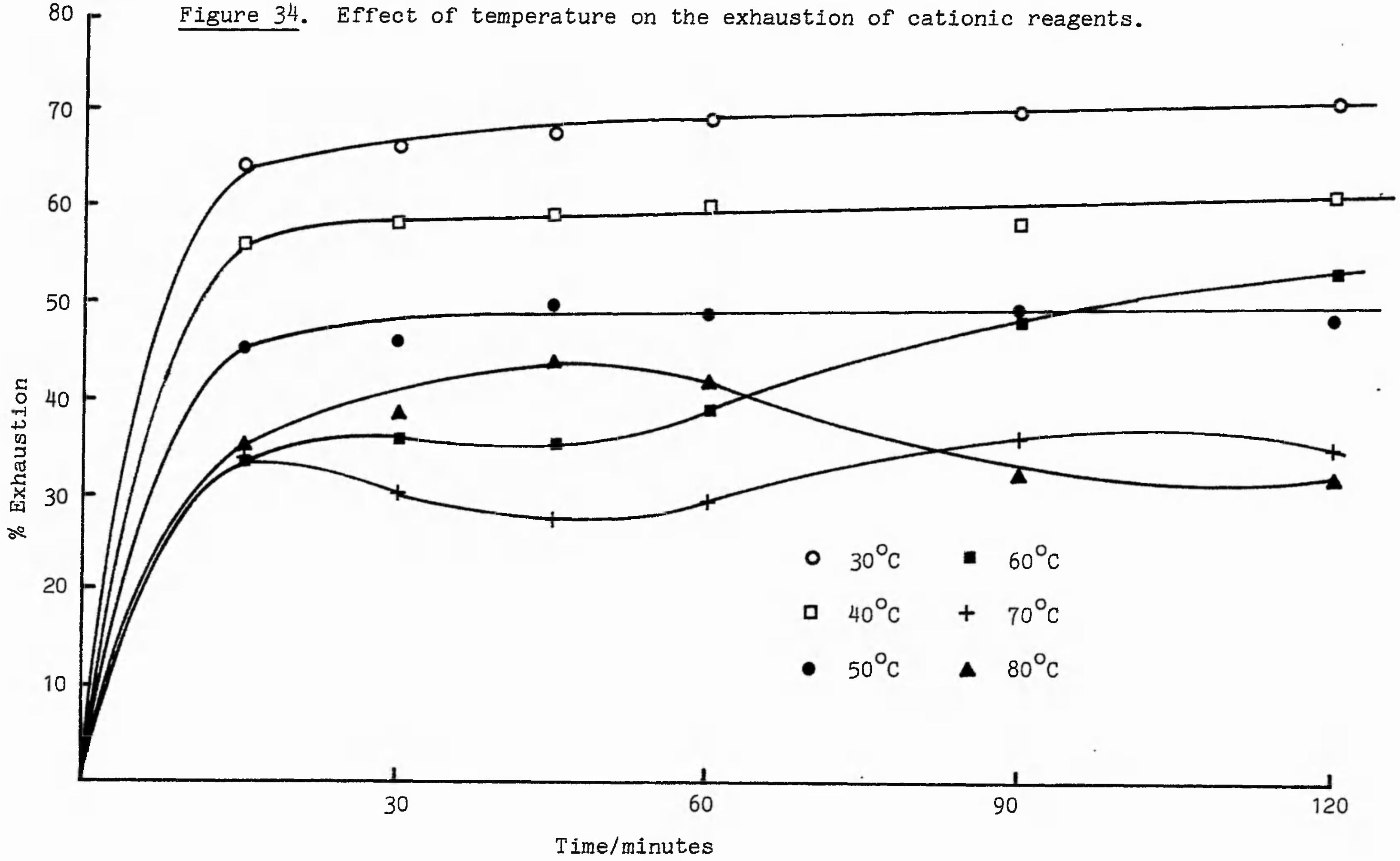


Figure 34. Effect of temperature on the exhaustion of cationic reagents.

3.4.2 Effect of electrolyte concentration

In order to examine the effect of varying the concentration of neutral electrolyte on the adsorption of the cationic reagent I, on cellulose, six 5% o.w.f. treatments of cotton yarn were carried out (liquor ratio 50:1) in the absence of alkali. Exhaustion was carried out for 1 hour at 40°C in the presence of sodium chloride concentrations in the range 0-1 molsdm^{-3} using an Ahiba thermostatically controlled sample dyeing machine (see section 5.6) which ensured good agitation for all of the samples simultaneously. Evaporation was prevented using the seals provided although it was assumed to be virtually negligible at this temperature.

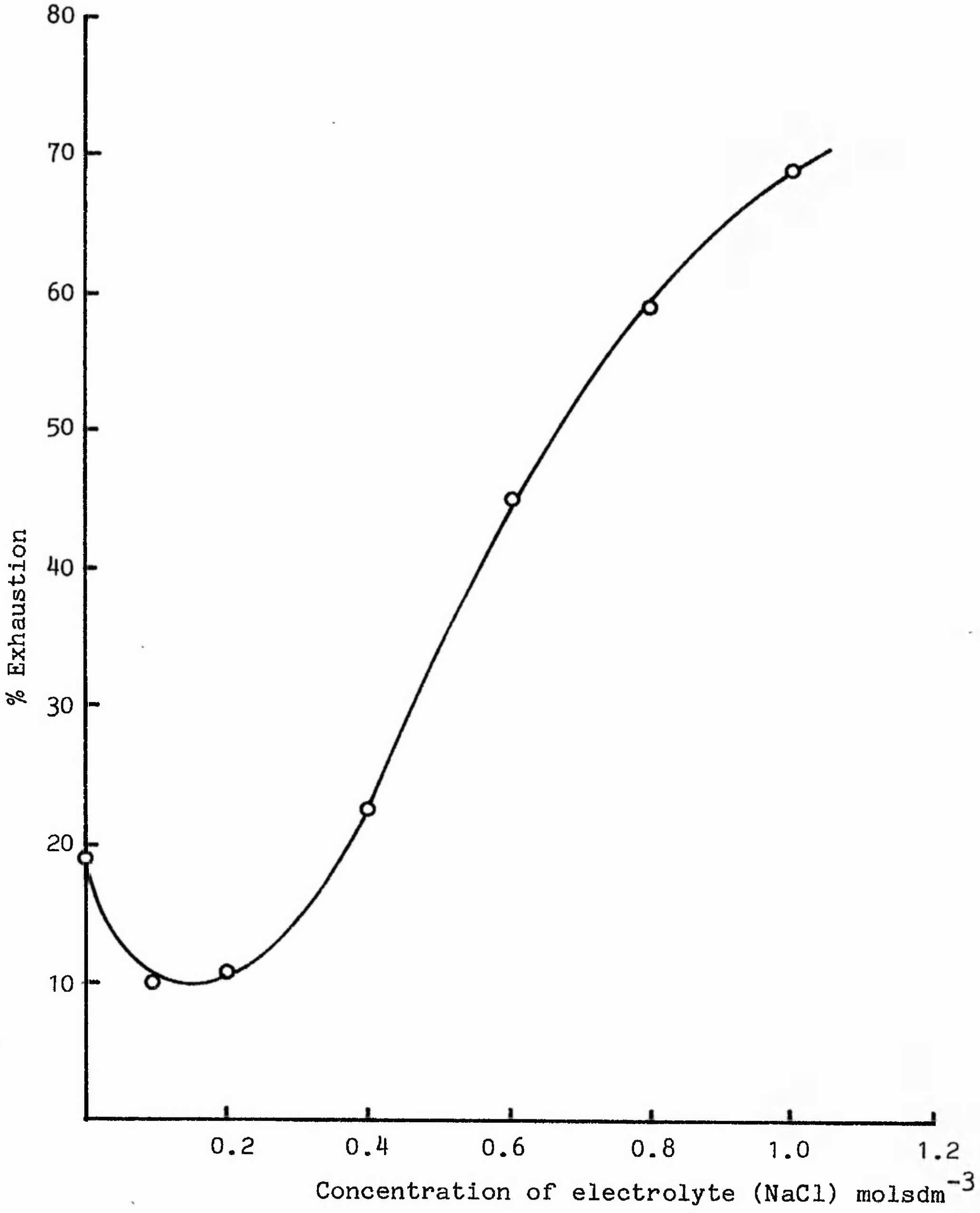
The % exhaustion was then determined at each electrolyte concentration and the results plotted (Figure 35). As can be seen exhaustion of the reagent onto the fibre generally increased with increasing electrolyte concentration from 0.1-1.0 molsdm^{-3}. This type of behaviour is typical of reactive dyes, which behave in neutral solution like direct dyes, except that much higher sodium chloride concentrations are generally involved. From an economic standpoint it can be seen that there would be little to be gained by increasing the sodium chloride concentration much beyond 1.0 molsdm^{-3} (58.5 g/l) as any increase in exhaustion would tend to be offset by the cost of the extra sodium chloride required.

Interestingly, however, in the case of the treatment carried out in the complete absence of electrolyte a significantly greater degree of exhaustion (18.8%) was obtained than that which had occurred at a concentration of 0.1 molsdm^{-3} (10.0%). This effect manifested itself in the form of a minimum in the graph which occurred at a sodium chloride concentration of approximately 0.1 molsdm^{-3} (see Figure 35).

Table 9. Effect of electrolyte concentration (NaCl) on the adsorption of cationic reagents at 40°C.

[NaCl]	% exhaustion
0	18.8
0.1	10.0
0.2	10.9
0.4	22.3
0.6	44.8
0.8	58.7
1.0	68.3

Figure 35. Effect of electrolyte concentration (NaCl) on the adsorption of cationic reagents at 40°C.

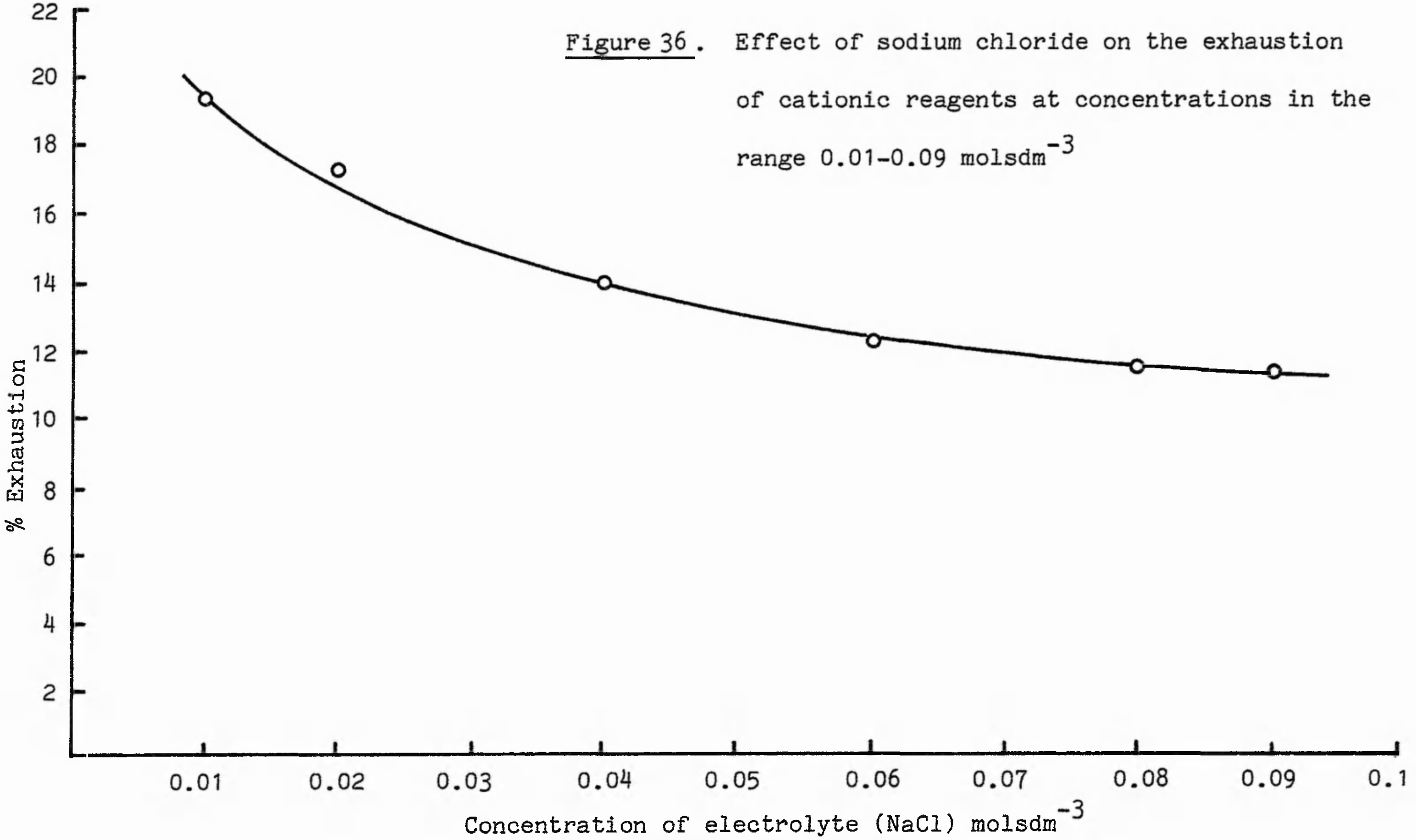


A more detailed examination of the effect of sodium chloride on the adsorption of the cationic reagent I at lower concentration levels in the range of 0.01-0.09 molsdm^{-3} using the same method as described earlier confirmed this to be the case (see Figure 36).

It was therefore decided to determine whether or not the nature of the electrolyte had any effect on the occurrence of this minimum by examining the exhaustion characteristics of reagent I in the presence of a number of different neutral electrolytes.

Table 10. Effect of sodium chloride on the exhaustion of cationic reagents at 40°C employing concentrations in the range 0.01-0.09 molsdm^{-3}.

[NaCl]	% exhaustion
0.01	19.3
0.02	17.2
0.04	14.0
0.06	12.2
0.08	11.3
0.09	11.2



<u>Figure 36</u>. Effect of sodium chloride on the exhaustion of cationic reagents at concentrations in the range 0.01-0.09 molsdm^{-3}

3.4.3 Effect of the nature of the electrolyte

3.4.3.1 Effect of the anion

The effect of several neutral electrolytes on the adsorption of the cationic reagent I on cellulose was examined using the same procedure as outlined in section 3.4.2, in each case substituting varying concentrations of the electrolyte in question for sodium chloride. The electrolytes employed were all monovalent sodium salts, apart from one - sodium sulphate, $Na_2SO_4.10H_2O$ (or 'Glaubers salt') - which is divalent, and hence the only variable in each run was the anion. Those investigated included the fluoride, bromide, iodide, sulphate, nitrate and thiocyanate anions. The results are illustrated overleaf and it should be noted that particular attention was given to low levels of electrolyte concentration in the range 0-0.18 $molsdm^{-3}$ ie. approximately in the region where a minimum was first observed with sodium chloride. Where appropriate, the results obtained with sodium chloride have also been included for comparison. Also, for the sake of clarity, the results for those electrolytes bringing about widely differing reagent exhaustion characteristics have been shown separately.

As can be seen from Figure 37 a minimum % exhaustion of 2.7% was obtained with sodium sulphate (by extrapolation) at an electrolyte concentration of 0.07 $molsdm^{-3}$. Once the minimum was reached the exhaustion again began to increase with increasing sodium sulphate concentration as had been observed with sodium chloride previously.

The occurrence of such a minimum is thought to be due to the operation of opposing effects. These may involve an initial attraction

Table 11. Effect of the anion on the adsorption of cationic reagents at 40°C.

NaCl		$Na_2SO_4.10H_2O$	
Concentration	% exhaustion	Concentration	% exhaustion
0.01	19.3	0	20.1
0.02	17.2	0.031	11.4
0.04	14.0	0.062	3.1
0.06	12.2	0.124	7.7
0.08	11.3	0.155	11.2
0.09	11.2		
0.124	11.3		
0.155	12.2		

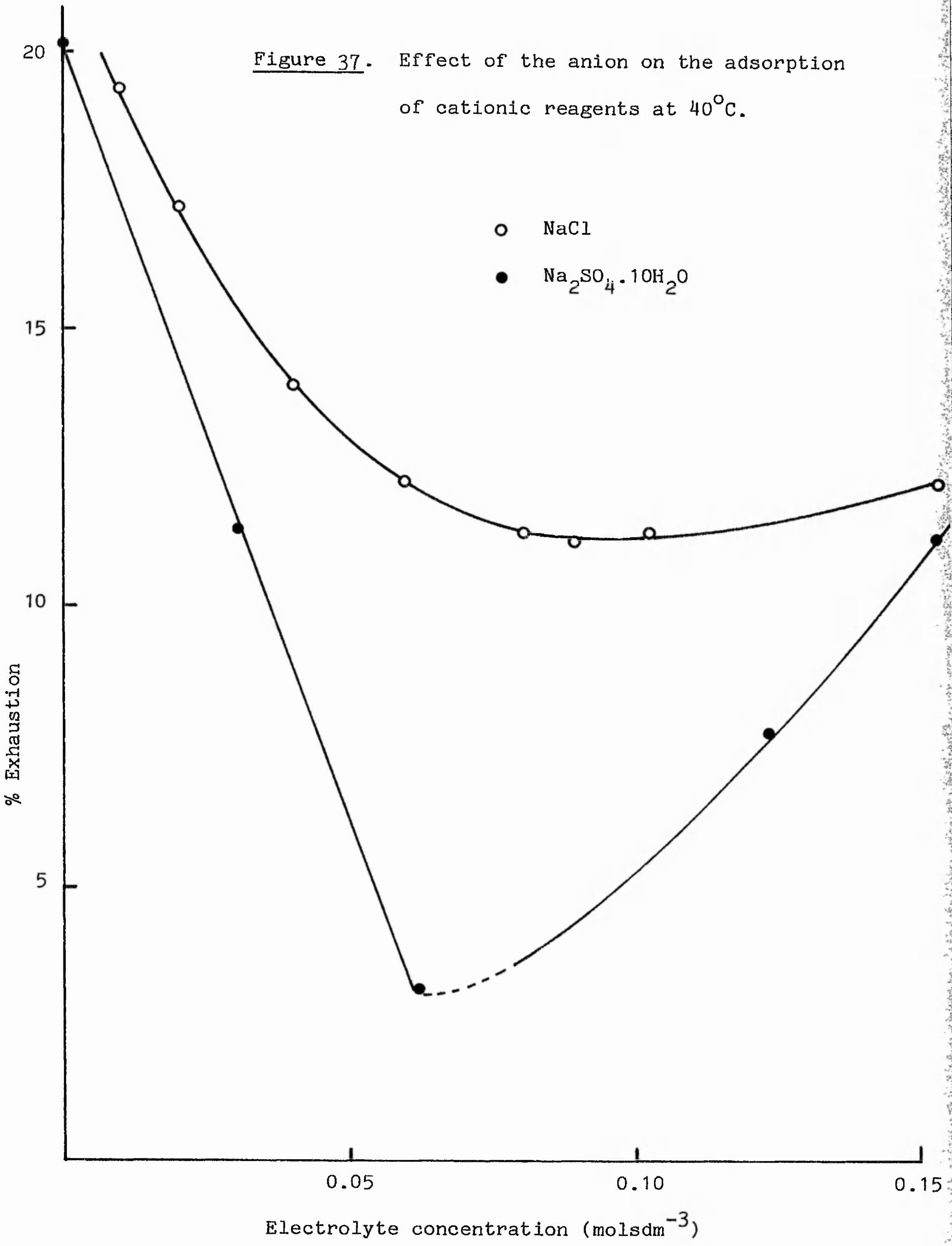


Figure 37. Effect of the anion on the adsorption of cationic reagents at 40°C.

of the positively charged quaternary ions for the cellulose, which acquires a negative surface charge on immersion in water (which would give rise to the unexpectedly high exhaustion observed in the absence of electrolyte and would tend to decrease with increasing electrolyte concentration) followed by a gradual increase in the chemical potential of the reagent due to the addition of electrolyte. This latter effect, would tend to cause an increase in the exhaustion, as the cationic reagent is salted out of solution and into the fibre and would be expected to become dominant as concentrations of electrolyte increased.

Similar exhaustion minima were also obtained with sodium bromide and sodium nitrate (see Figures 38 and 39) but in the case of electrolytes such as sodium iodide and sodium thiocyanate no such minima were observed, presumably because the balance between the two opposing forces operating in the system had been lost. In fact, very high levels of exhaustion of 91% and 94%, for the iodide and thiocyanate ions respectively, were obtained at relatively low concentrations of <0.1 $\mathrm{molsdm^{-3}}$ indicating the greatly increased 'salting out' powers of these anions (see Figure 40).

Sodium thiocyanate is however, more usually considered to be a 'salting in' (or solubilising) agent. Nevertheless as the Hofmeister (or lyotropic) series[211] of decreasing 'salting out' power was crossed from left to right for a series of anions the degree of reagent exhaustion at a given concentration (>0.02 $\mathrm{molsdm^{-3}}$) was observed to increase accordingly.

$$SO_4^{2-} < F^- < Cl^- < Br^- < NO_3^- < I < SCN^-$$

Table 12. Effect of the anion on the adsorption of cationic reagents at 40°C.

[NaX]	% Exhaustion		
	X = Br^-	I^-	NO_3^-
0.005	18.5	27.1	18.0
0.01	18.5	52.0	18.2
0.02	17.2	72.5	17.2
0.04	17.5	82.9	26.8
0.06	18.6	87.0	40.0
0.10	28.6	90.0	54.4
0.14	43.4	91.0	64.1
0.28	63.5		75.4
0.42	72.3		79.5
0.52	75.0		

$[F^-]$	% Exhaustion
0.01	20.7
0.02	16.0
0.04	13.1
0.06	10.3
0.08	8.7
0.10	10.4
0.16	9.6
0.20	9.3
0.24	10.1
0.32	9.1
0.40	9.9

Figure 38. Effect of the anion on the adsorption of cationic reagents at 40°C.

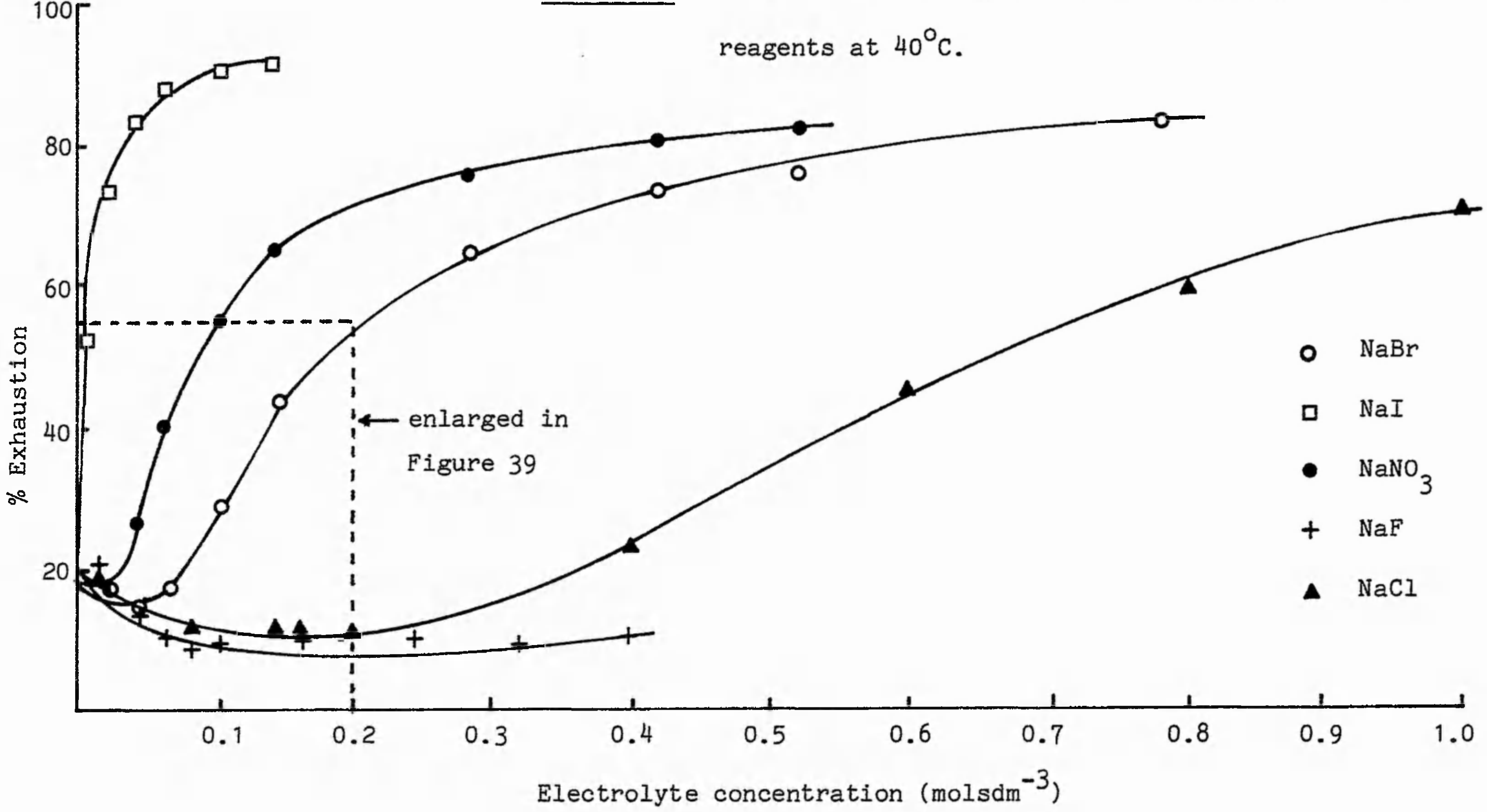


Figure 39. Effect of the anion on the adsorption of cationic reagents at 40°C.

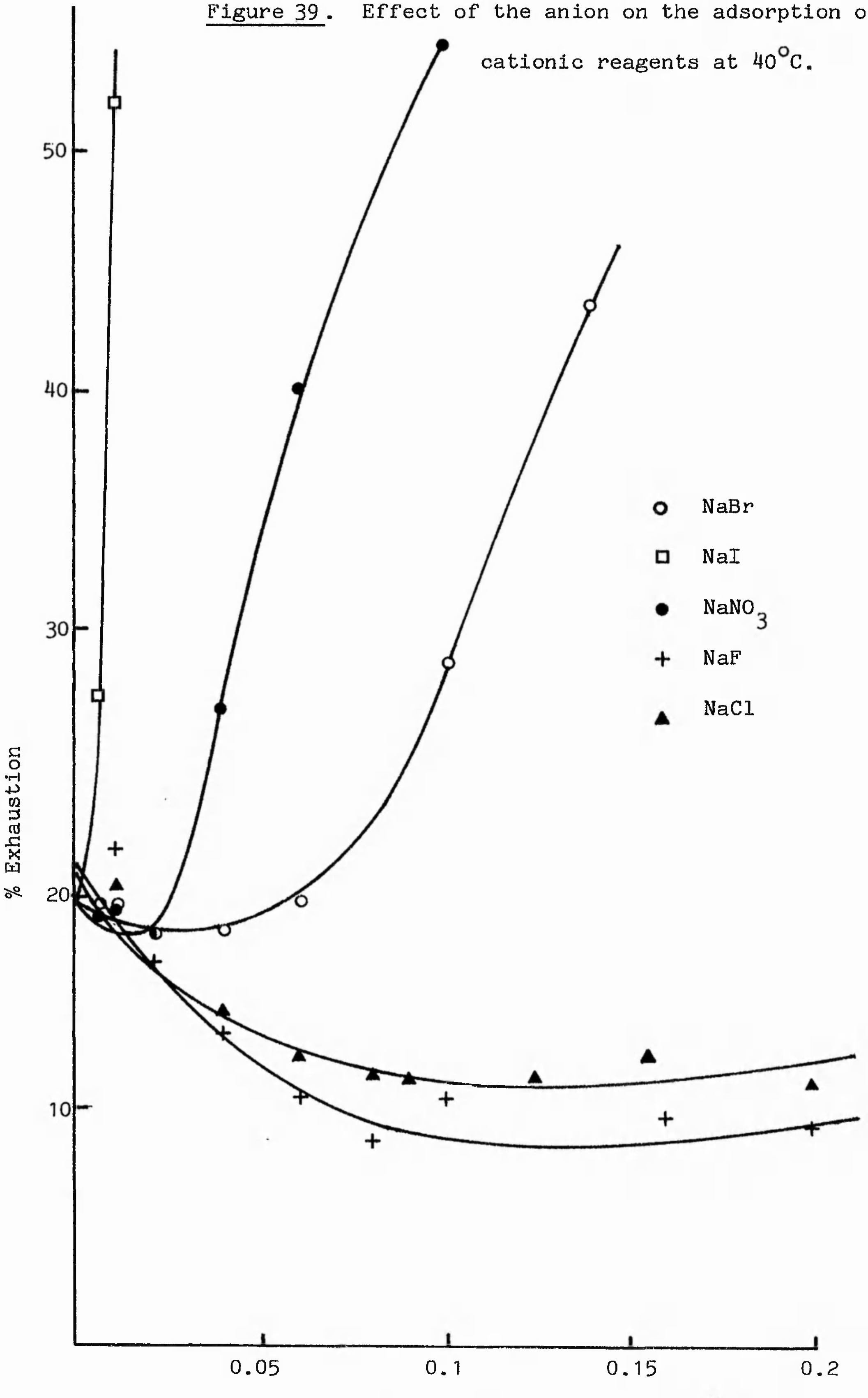


Table 13. Effect of sodium thiocyanate on the adsorption of cationic reagents at 40°C.

[NaSCN]	% Exhaustion
0	19.9
0.031	88.5
0.062	92.9
0.093	94.1
0.124	94.8
0.155	94.4
0.005	48.9
0.01	69.7
0.02	82.7
0.001	20.6
0.002	24.3
0.003	30.2

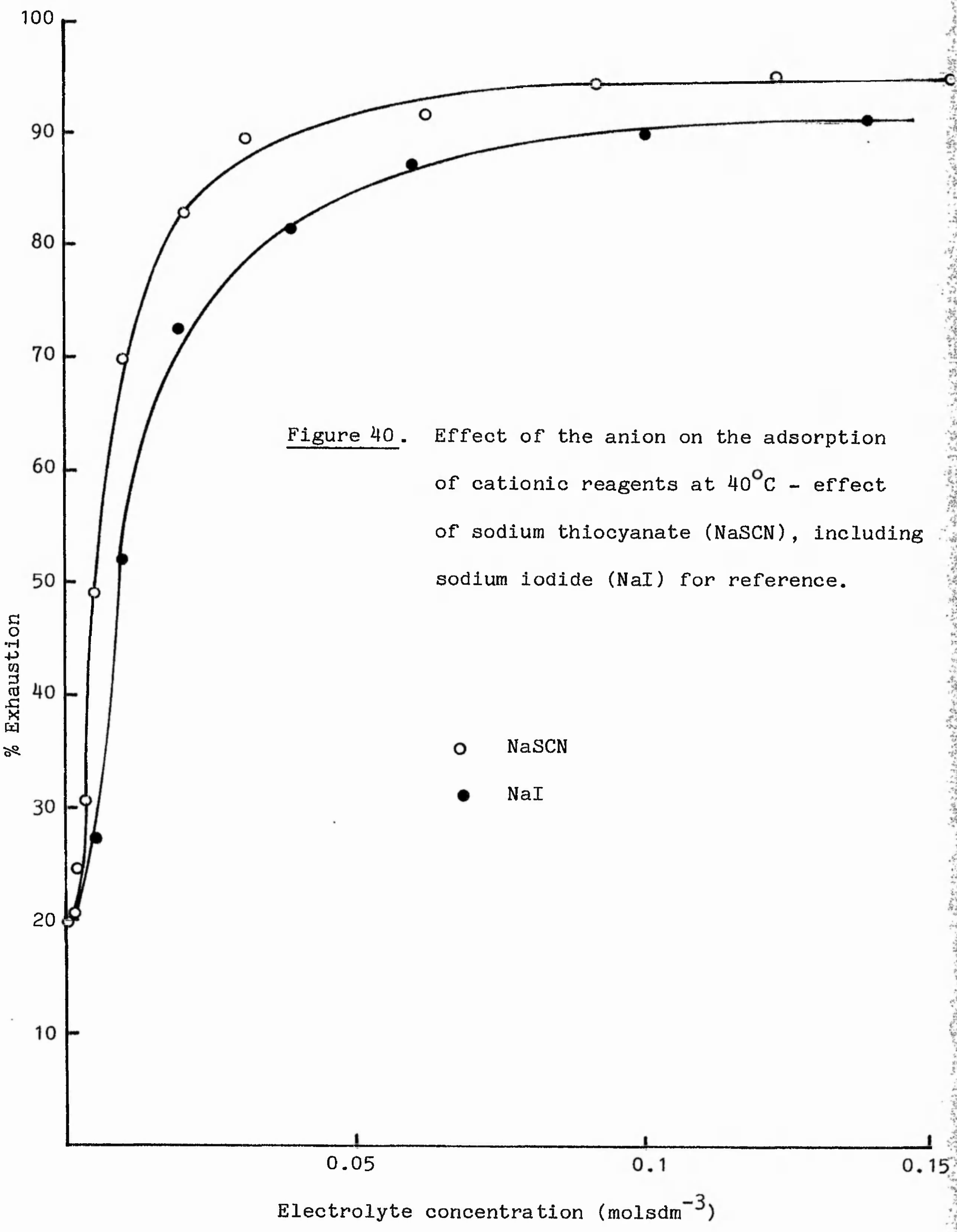


Figure 40. Effect of the anion on the adsorption of cationic reagents at 40°C - effect of sodium thiocyanate (NaSCN), including sodium iodide (NaI) for reference.

In this case the experimental evidence confirmed that the large thiocyanate anion did in fact appear to be acting as a 'salting out' agent.

Diamond[212] in his paper, concerned with the behaviour of large unhydrated univalent ions, describes how the solution of such hydrophobic compounds (which, for example, in the case of a quaternary ammonium compound, may be regarded as a molecule with a charge embedded in it) results in a tightening up of the water structure around the molecule, that is on the internal surface of the cavity surrounding the solute.

If, however, both the cation and the anion are large hydrophobic ions then the hydrogen-bonded water structure forces them together into a single larger cavity thereby maximising the water-water interactions and minimising the disturbance to itself. This 'water structure-enforced' ion-pairing, which is very different from the more usual electrostatic or Bjerrum type of ion-pairing, occurring as it does only in water or other highly hydrogen-bonded solvents and being greater the larger the ions and the smaller the charges, would appear then to account for the greatly increased reagent exhaustion exhibited in the presence of the larger, less hydrated, iodide and thiocyanate ions, presumably as a result of a reduction in the solubility of the reagent on ion-pair formation.

A further experiment confirmed that the increased exhaustion observed in the presence of the larger ions was not due to a rate effect. Identical exhaustion trials for sodium chloride and sodium thiocyanate carried out for 2 and 4 hours duration at a given electrolyte concentration of 0.075 molsdm^{-3} resulted in no significant increase in the percentage exhaustion obtained than had been observed with either electrolyte after only 1 hour (see Figure 41).

The presence in the treatment bath of increasing concentrations of urea (0.25-3.6 molsdm^{-3}), a solubilising agent, was however shown to bring about a gradual reduction in the increased exhaustion obtained in the presence of sodium thiocyanate. (Again a given concentration, 0.075 molsdm^{-3}, of sodium thiocyanate was used throughout the experiment). This suggested that the action of urea in dyeing systems, which is known to consist of the disaggregation of dye molecules, increasing the dielectric constant of the solution and the rupturing of hydrophobic bonds[213], must in this case be resulting in a reduction in the extent of water-structure enforced ion-pair formation (see Figure 42).

Interestingly, in the case of sodium fluoride although suppression of the negative surface charge on the cellulose took place at low fluoride concentrations (<0.1 molsdm^{-3}) reducing the attraction between reagent and fibre and a minimum percentage exhaustion was approached, the graph at this point levelled off and no increase in exhaustion was observed (Figure 38).

This was attributed to the small size of the fluoride ion and the fact that it is very highly hydrated which would tend to make it very unlikely that it would engage in water structure-enforced ion-pairing so bringing about increased exhaustion.

In fact this type of water structure-enforced association may also explain a related observation made recently during studies of the adsorption of chitosan (a positively charged polyelectrolyte) on cellulose when the degree of exhaustion was found to increase in the presence of sodium thiocyanate (0.1 molsdm^{-3}) relative to that obtained with sodium chloride at the same concentration[214].

Table 14. Effect of time on the adsorption of cationic reagents in the presence of sodium chloride and sodium thiocyanate (0.075 molsdm^{-3}).

Time (hours)	% Exhaustion	
	NaCl	NaSCN
1	11.5	93.9
2	10.2	92.5
4	7.3	92.9

Table 15. Effect of urea on the increased adsorption observed in the presence of sodium thiocyanate (0.075 molsdm^{-3}).

[Urea] molsdm^{-3}	% Exhaustion
0	94.8
0.25	93.5
0.50	92.5
1.00	90.4
1.60	84.3
3.6	63.7

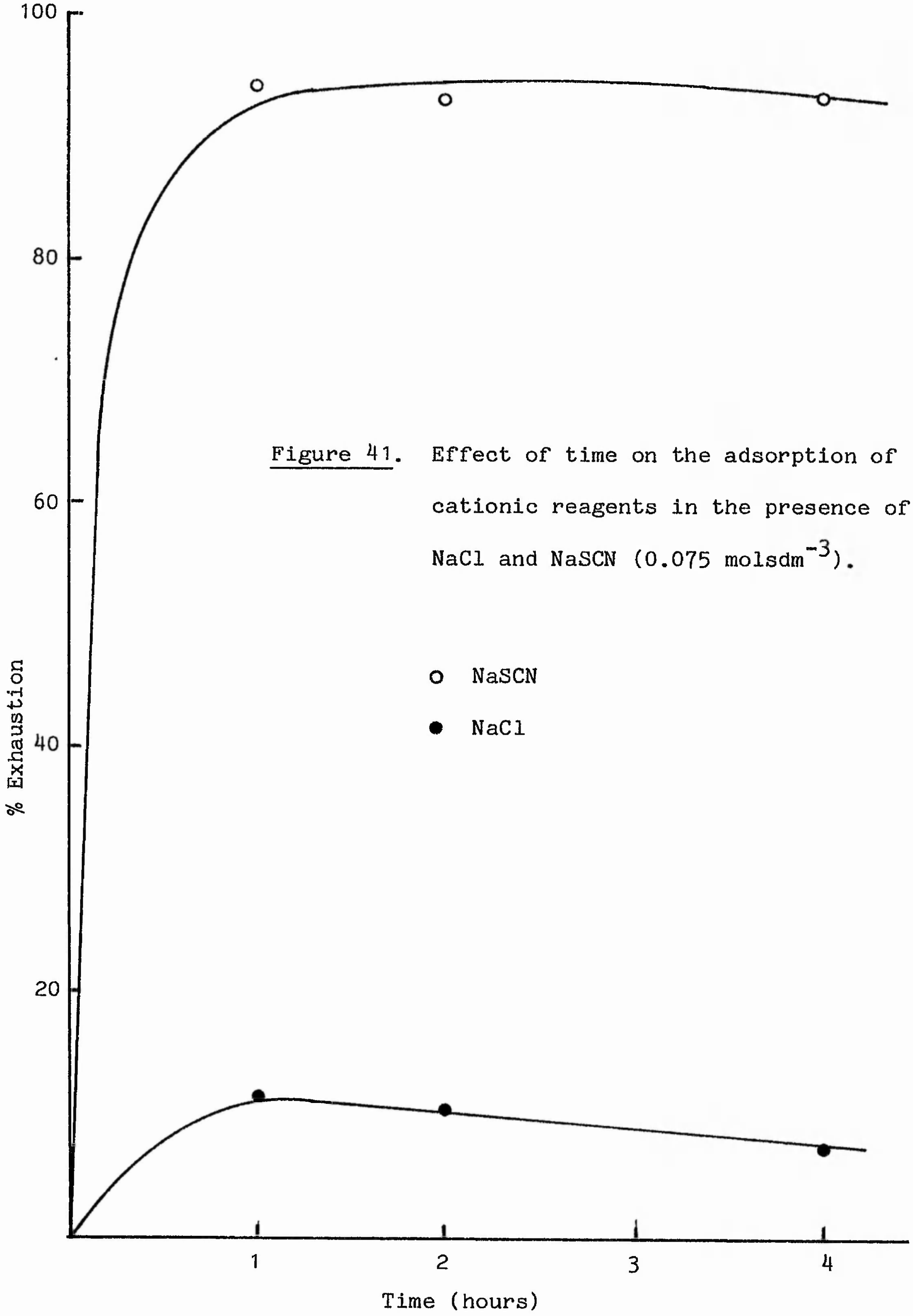


Figure 41. Effect of time on the adsorption of cationic reagents in the presence of NaCl and NaSCN (0.075 molsdm^{-3}).

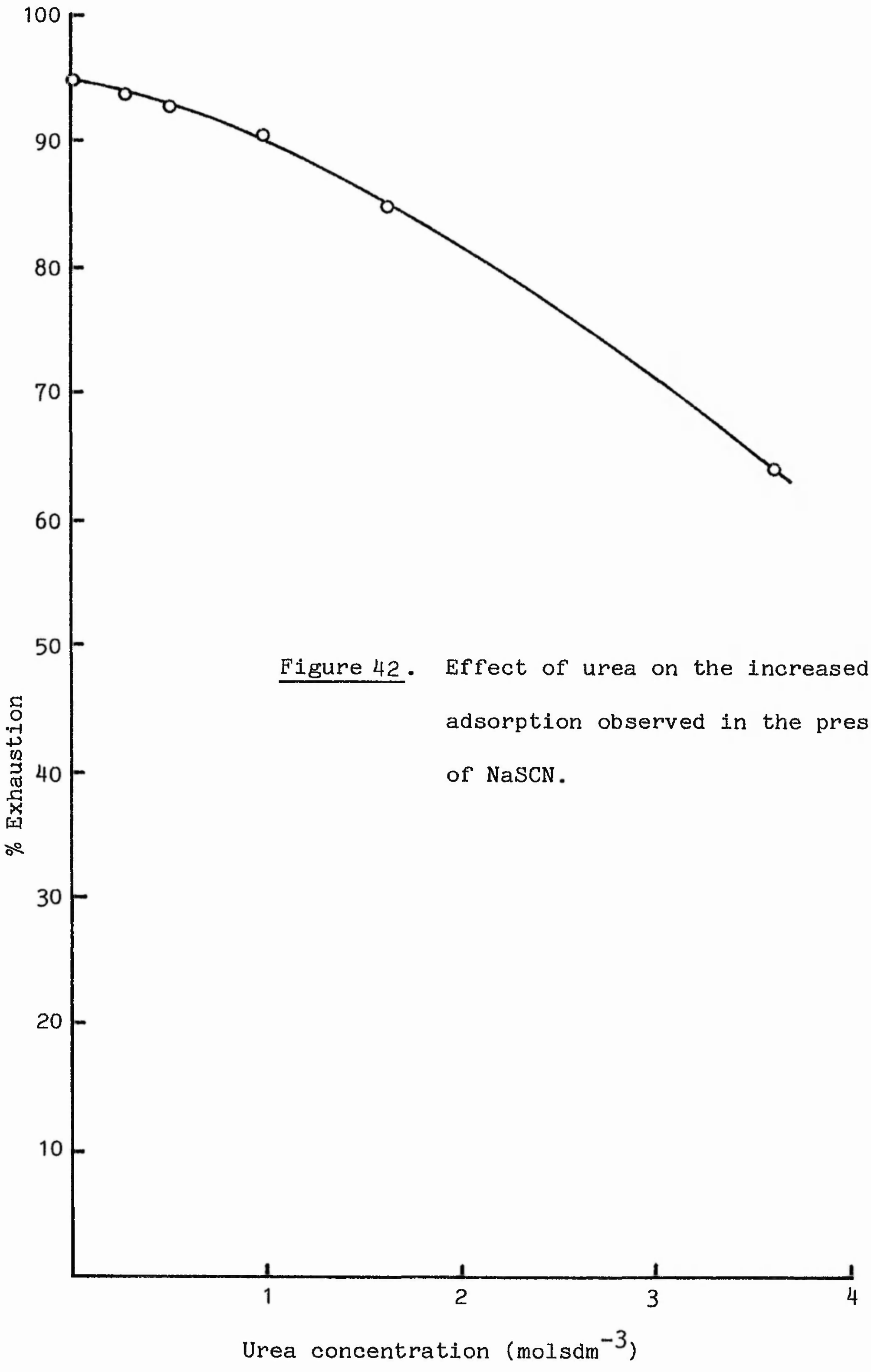


Figure 42. Effect of urea on the increased adsorption observed in the presence of NaSCN.

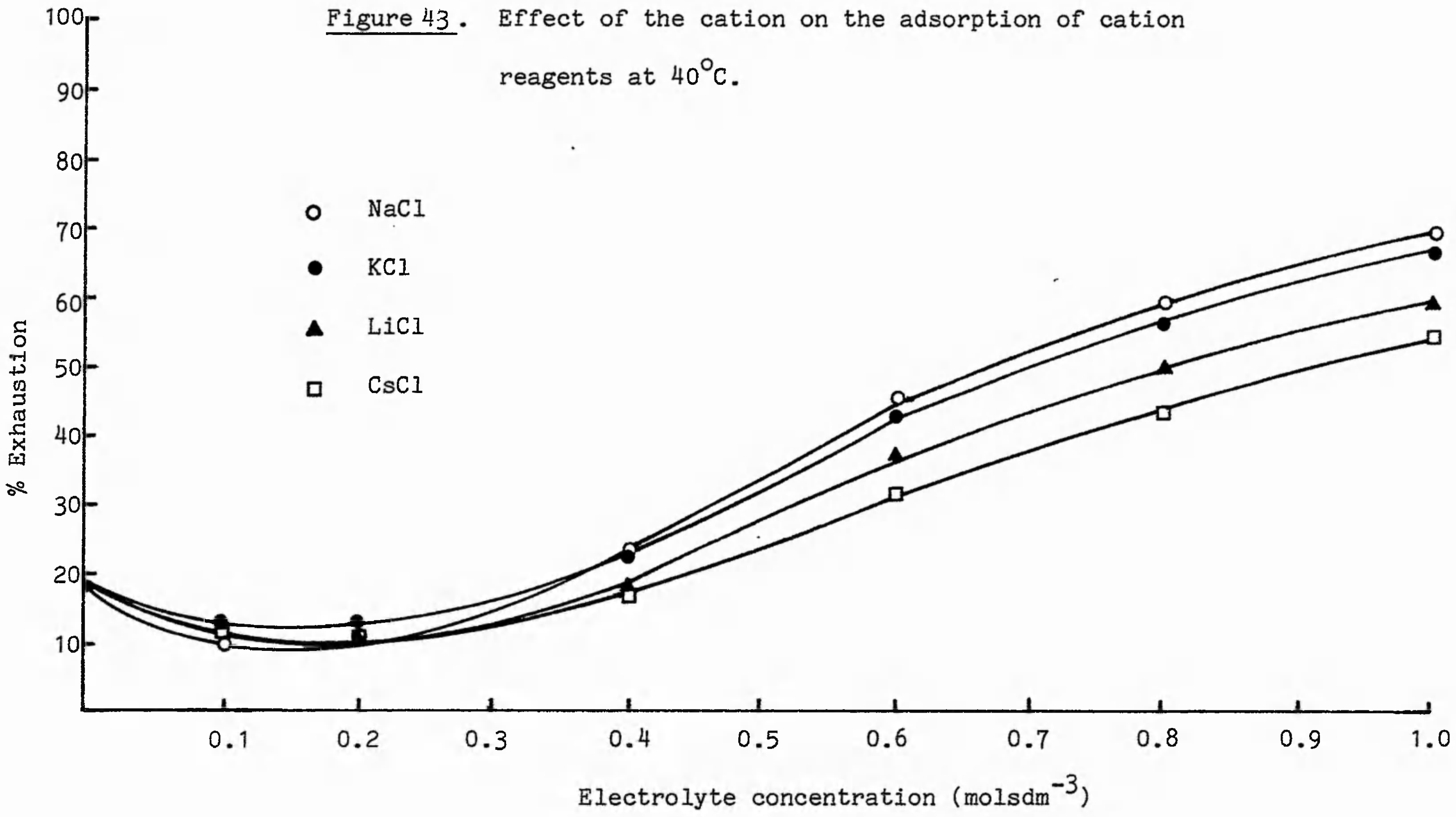
3.4.3.2 Effect of the cation

The effect of the cation on the adsorption of the cationic reagent I on cellulose was studied using the same experimental procedure as outlined in section 3.4.2, excepting that in this case a series of electrolytes were chosen in order that the cation varied whilst the chloride anion remained unchanged. 5% o.w.f. of reagent I was applied and exhaustion trials were carried out for 1 hour at 40°C using electrolyte concentrations of 0.1-1.0 molsdm^{-3}. The results are given in Figure 43.

Table 16. Effect of the cation on the adsorption of cationic reagents at 40°C.

Electrolyte concentration (molsdm^{-3})	% Exhaustion NaCl	KCl	LiCl	CsCl
0.1	10.0	12.5	12.5	11.8
0.2	10.9	12.5	11.6	10.7
0.4	22.3	21.9	18.1	16.8
0.6	44.8	42.6	36.5	31.0
0.8	58.7	55.1	49.4	42.5
1.0	68.3	65.4	58.9	53.6
0.0	18.8	18.8	18.8	18.8

Figure 43. Effect of the cation on the adsorption of cation reagents at 40°C.



Once again at low cation concentrations a minimum percentage exhaustion was observed in each case as the initial attraction of the positively charged reagent for the negatively charged cellulose surface was gradually reduced by the addition of electrolyte.

In the presence of higher concentrations of electrolyte (>0.4 $molsdm^{-3}$) the exhaustions again began to increase in the order:

$Cs^+ < Li^+ < K^+ < Na^+$

However, overall, the actual differences between the highest and lowest exhaustions achieved by varying the cation were far less pronounced compared to the results obtained using different anions, which would tend to support the view expressed earlier that water structure-enforced ion-pair formation between the cationic reagent and the larger more hydrophobic anions was more than likely the cause of the increased exhaustions previously observed. Since in this case the anion remained constant it might be expected that the percentage exhaustions should remain fairly similar throughout although the fact that there was a slight decrease in the degree of exhaustion from sodium to caesium was probably attributable to their relative positions in the lyotropic series of decreasing salting out power for the series of cations:

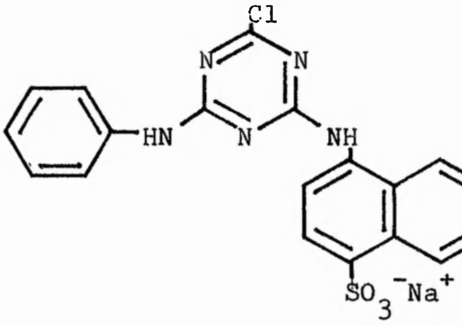
$Li^+ > Na^+ > K^+ > NH_4^+ > Rb^+ > Cs^+$

By comparison the sodium ion can be seen to be a good 'salting out' agent whilst caesium was the best 'salting in ' agent or 'water structure breaker' employed in the above investigation.

3.5 Factors influencing the adsorption of anionic reagents on cellulose

Since most of the dyes used with cellulose are anionic in character the use of treatments involving anionic reagents was expected to be restricted to mainly cross-dyeing applications. A full investigation into the effects of the various dyebath variables was therefore not felt to be warranted in this case, with the exception of the effect of added neutral electrolyte which was considered to be of particular interest bearing in mind the unexpected results obtained earlier for the cationic reagent I.

Since only small quantities of the two anionic reagents prepared earlier were available and the exact structure of the commercial sample 'Sandospace R' was unknown, a model compound of known chemical constitution was selected for use as an anionic 'reagent' on the grounds that, although a coloured molecule, it was a relatively simple structure based on a triazine ring system and very similar to the anionic reagent IV prepared earlier based on 1-naphthylamine-4-sulphonic acid (Figure 44).



Anionic reagent IV

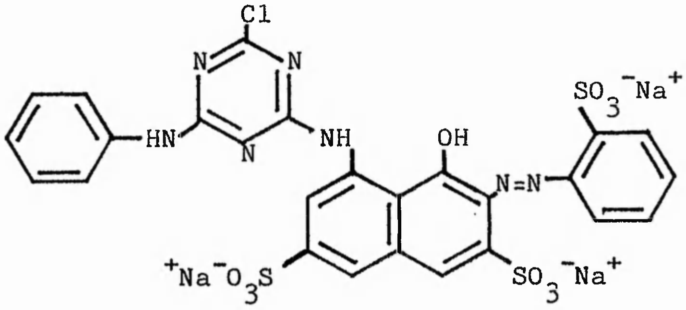


Figure 44. A comparison of the structures of anionic reagent IV and C.I. Reactive Red 3; C.I. 18159.

The uv/vis absorption spectrum of the dye was run (Figure 45) and the effect on it of large concentrations of electrolyte was determined. Consequently λmax = 512 nm was selected for use in the following investigation.

3.5.1 Effect of the nature and concentration of the electrolyte

3.5.1.1 Effect of the anion

In order to examine the effect of neutral added electrolyte on the adsorption of an anionic reagent on cellulose, the equivalent of a 1% o.w.f. shade of C.I. Reactive Red 3 was applied to cotton yarn, exhaustion being carried out for 2 hours at 40°C in the presence of a number of different electrolytes, in this case containing a range of anions namely the chloride, bromide, iodide and thiocyanate anions.

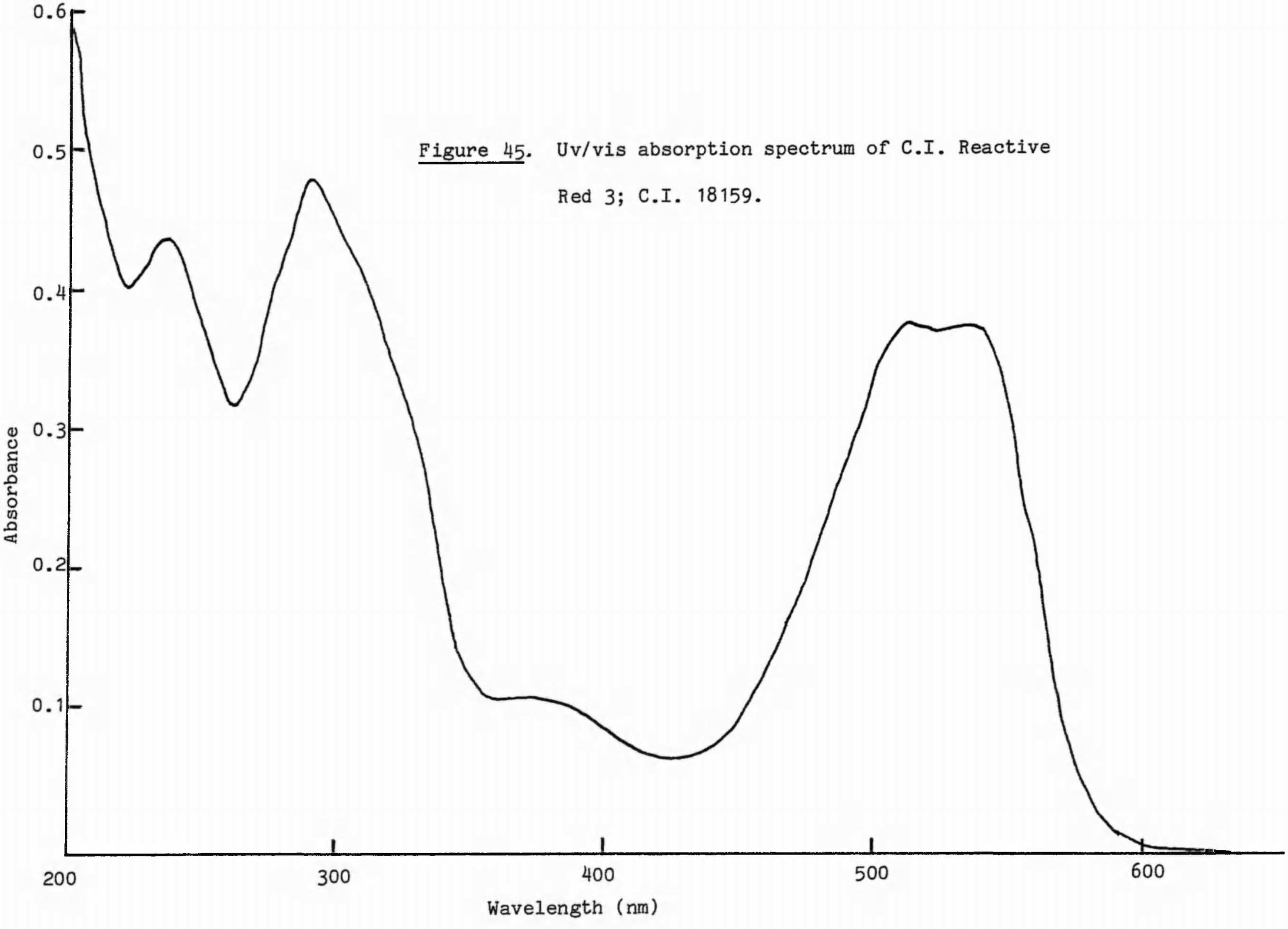


Figure 45. Uv/vis absorption spectrum of C.I. Reactive Red 3; C.I. 18159.

As can be seen in Figure 46 reagent exhaustion was observed to increase steadily over a concentration range of 0.1-1.0 molsdm^{-3} on all counts, with no evidence of any exhaustion minima, the percentage exhaustion for an anion at any one molar concentration decreasing in accordance with the lyotropic series of decreasing salting out power:

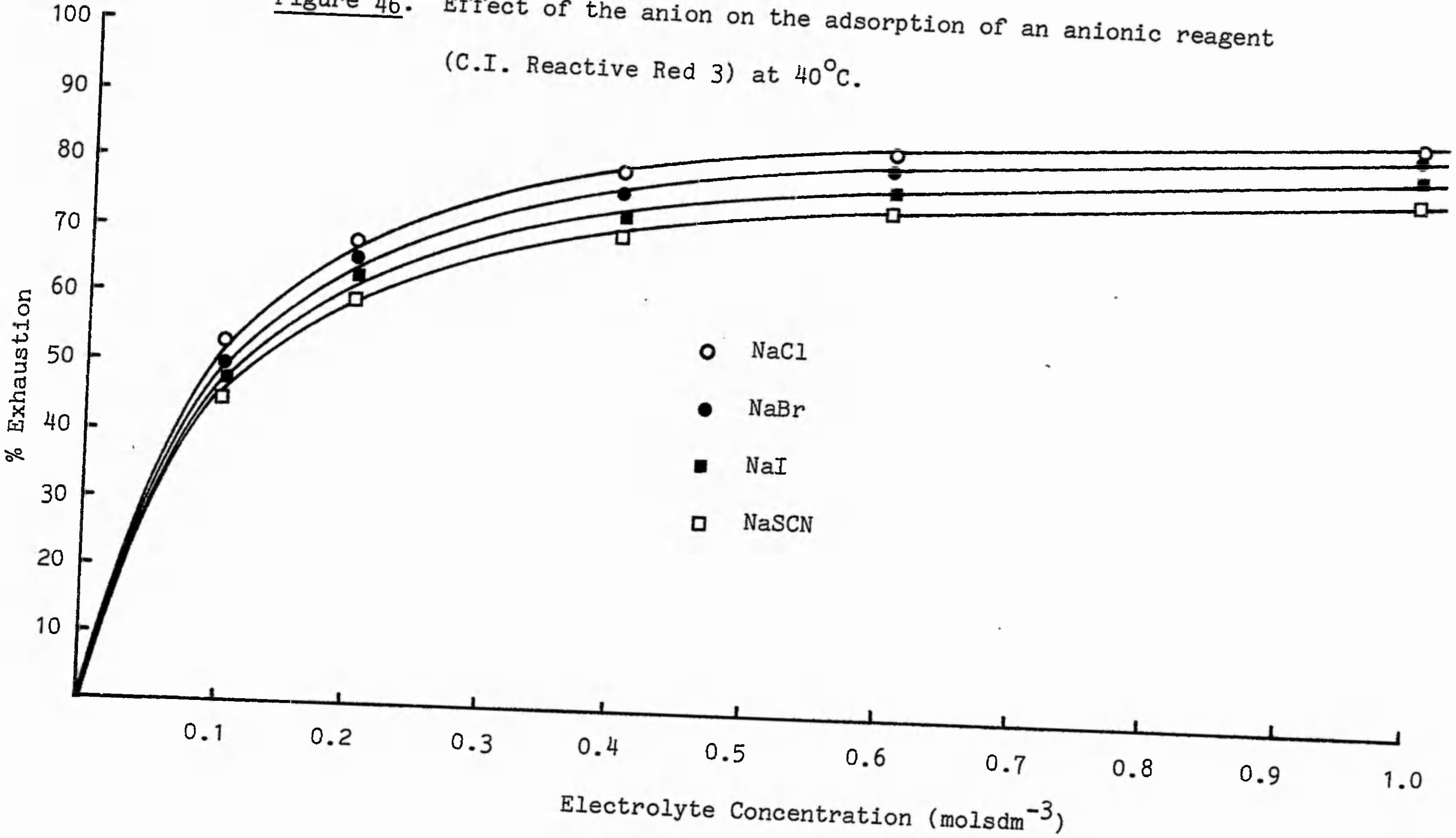
$Cl^- > Br^- > I^- > SCN^-$

It would appear then that, as might be expected, the role of the anion in the adsorption of an anionic reagent on cellulose is of far less importance than the part it plays in the adsorption of a cationic reagent, particularly since water structure-enforced ion-pair formation and solubility considerations appear to be essential parts of the process whereby the reagent is 'salted out' of solution into the fibre.

Table 17. Effect of the anion on the adsorption of an anionic reagent (C.I. Reactive Red 3) at 40°C.

Electrolyte concentration molsdm^{-3}	% Exhaustion NaCl	NaBr	NaI	NaSCN
0.1	52.2	49.8	47.1	44.3
0.2	68.0	65.4	63.0	59.0
0.4	79.1	76.3	73.0	69.8
0.6	82.9	80.9	77.5	74.0
1.0	86.8	85.0	81.6	77.7

Figure 46. Effect of the anion on the adsorption of an anionic reagent (C.I. Reactive Red 3) at 40°C.



3.5.1.2 Effect of the cation

The influence of the cation on the adsorption of an anionic reagent was examined using the procedure outlined in section 3.5.1.1, except in this case employing a series of electrolytes containing a range of different cations, the anion remaining the same. The electrolytes investigated included lithium chloride, potassium chloride and caesium chloride - the results for sodium chloride already having been obtained in the previous experiment.

As expected the cation was shown to play a more important part than the anion in determining the extent to which the anionic reagent was adsorbed onto cellulose. As can be seen in Figure 47 up to a concentration of 0.4 molsdm^{-3} the exhaustion was shown to increase with increasing electrolyte concentration with the exhaustion obtained with a given cation at any one concentration increasing in the order:

$Li^+ < Na^+ < K^+ < Cs^+$

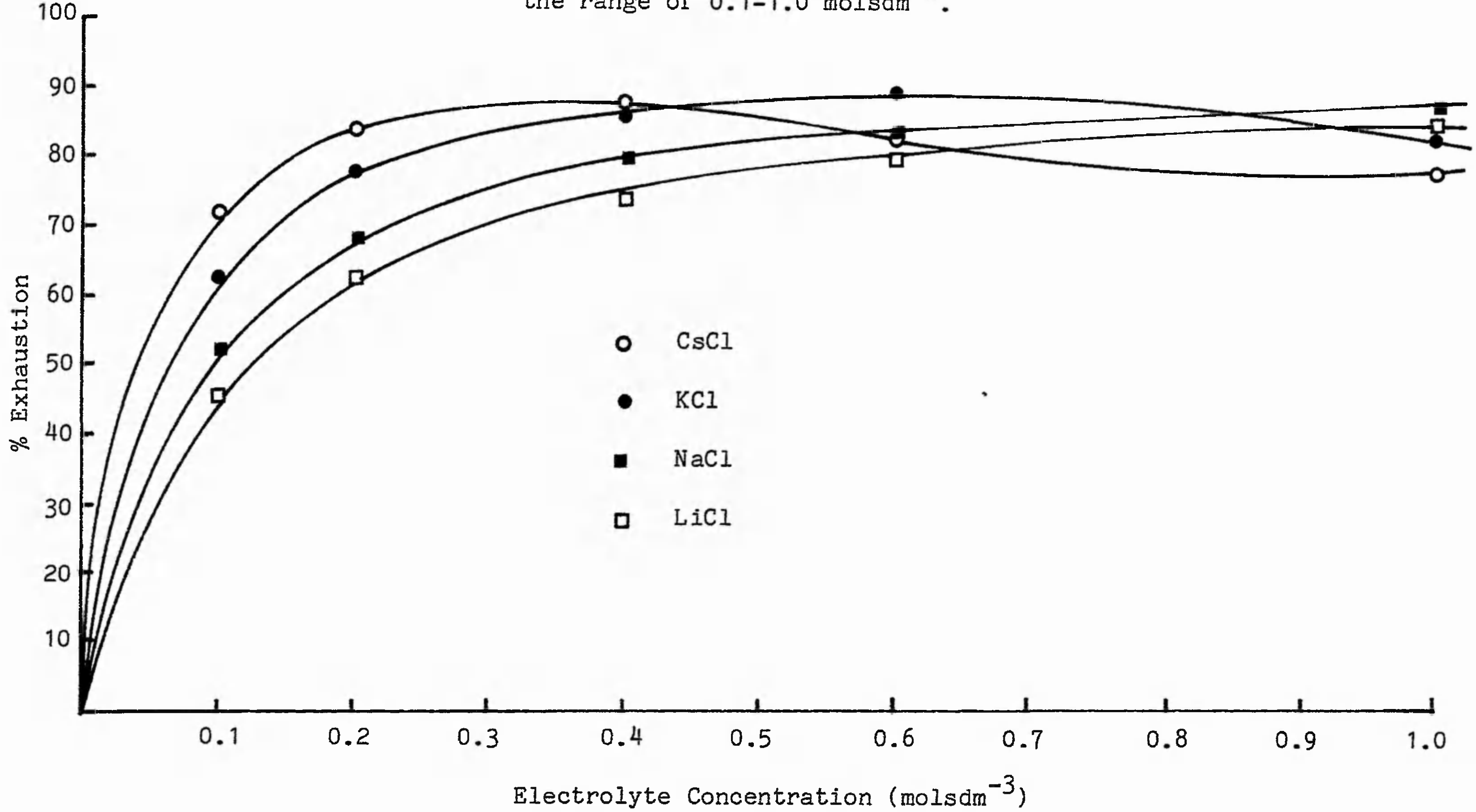
The greatest exhaustion was thus initially achieved with caesium, a large hydrophobic cation which is generally considered to be a good 'salting in' agent or 'water structure breaker', but which in this case would seem to be acting as a 'salting out' agent.

The presence of both a large hydrophobic cation and anion must therefore again result in water structure-enforced ion-pairing, since both ions require a considerable loss in water-water interactions to create their cavities and both contribute to a tightening up of their surrounding water structure. The tendency must therefore be for the water structure to force the pair into a single larger cavity to decrease the disturbance to itself, the opposite charges on the two

Table 18. Effect of the cation on the adsorption of an anionic reagent (C.I. Reactive Red 3) at 40°C at concentrations in the range 0.1-1.0 molsdm^{-3}.

Electrolyte concentration molsdm^{-3}	% Exhaustion CsCl	KCl	NaCl	LiCl
0.1	71.5	62.1	52.2	45.1
0.2	83.7	77.5	68.0	62.1
0.4	87.8	85.5	79.1	73.1
0.6	82.6	88.6	82.9	79.0
1.0	76.3	81.4	86.8	83.9

Figure 47. Effect of the cation on the adsorption of an anionic reagent (C.I. Reactive Red 3) at 40°C at concentrations in the range of 0.1-1.0 $molsdm^{-3}$.



ions serving to facilitate this association, so contributing to an overall lowering of the ionic free energy of the pair.

No initial exhaustion minima were obtained for any of the cations employed, however, in each case there appeared to be an optimum cation concentration at which maximum reagent exhaustion was achieved and above which the percentage exhaustion began to decrease, the concentration at which this maximum occurred being lower the larger the cation. Clearly, therefore, an additional factor must be coming into play at higher cation concentrations which is capable of reducing the extent to which reagent is adsorbed by the fibre.

Possibly, in the case of caesium for example, once the cation concentration at which ion-pair formation is at a maximum is exceeded additional caesium chloride may begin to affect the water structure in such a way as to impede the formation of ion-pairs by acting in its more usual capacity as a salting in (water structure breaking) agent.

Sodium on the other hand, being a relatively small hydrated cation and a good salting out (water structure making) agent has a much lesser tendency to form ion-pairs and maximum reagent exhaustion did not occur until a cation concentration of 2.5 molsdm^{-3} (compared with 0.4 molsdm^{-3} for caesium) was employed (Figure 48).

It would appear then that there are two opposing effects, the net result of which, in terms of ion-pair formation and thus reagent exhaustion, is dependant on the concentration of the cation and on its size; the larger, more hydrophobic and thus less hydrated cations such as caesium and potassium bringing about maximum reagent exhaustion at lower cation concentrations because of their increased

Table 19. Effect of lithium and sodium cations on the adsorption of the anionic reagent (C.I. Reactive Red 3) at 40°C at higher concentrations in the range 0.1-3.5 molsdm^{-3}.

Electrolyte concentration molsdm^{-3}	% Exhaustion NaCl	LiCl
0.1	52.2	45.1
0.2	68.0	62.1
0.4	79.1	73.1
0.6	82.9	79.0
1.0	86.8	83.9
1.25	87.6	84.5
1.5	88.7	86.1
2.0	89.5	88.3
2.5	92.5	89.8
3.0	91.9	91.3
3.5	90.8	91.7

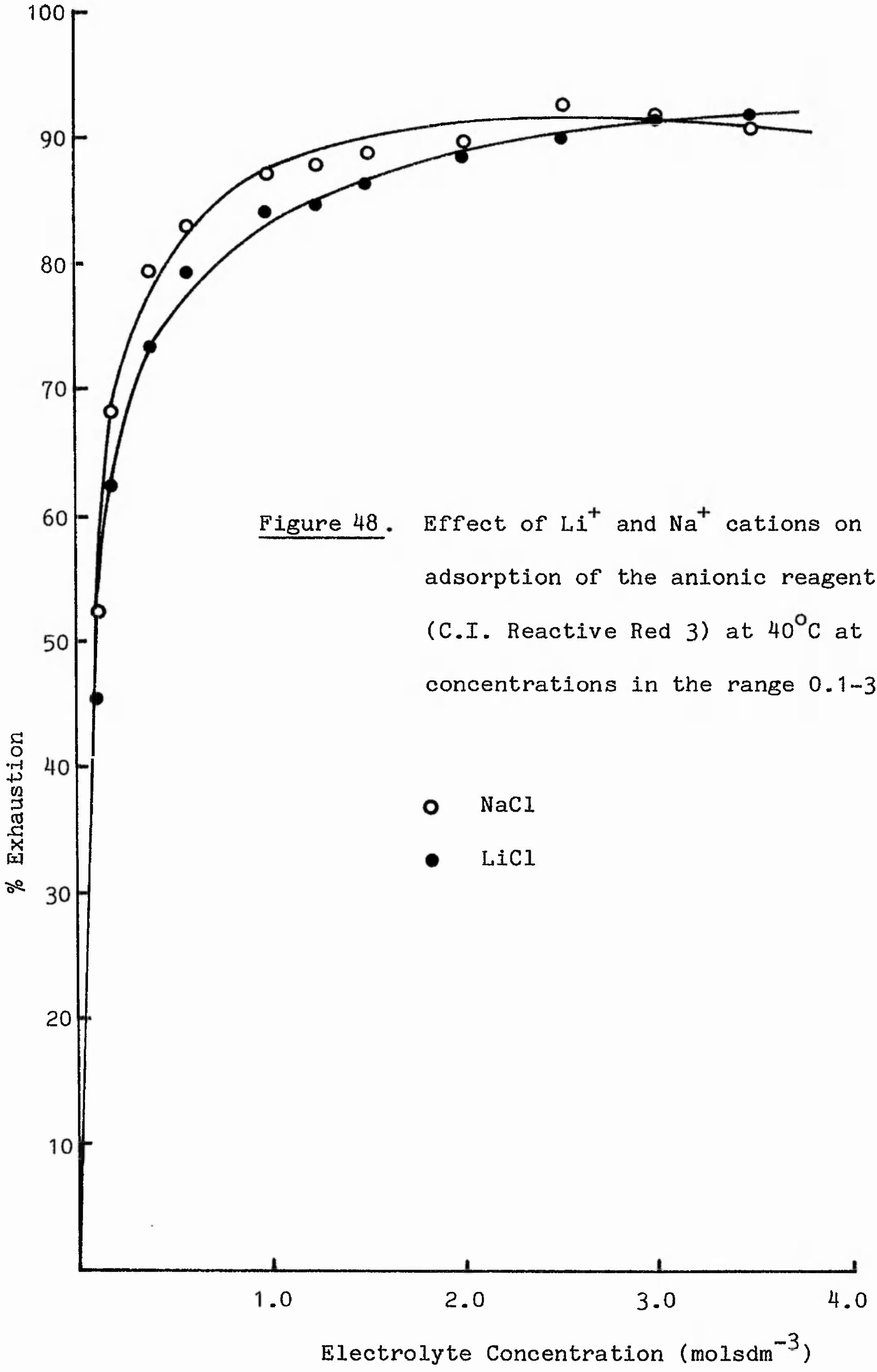


Figure 48. Effect of Li$^+$ and Na$^+$ cations on the adsorption of the anionic reagent (C.I. Reactive Red 3) at 40°C at higher concentrations in the range 0.1-3.5 molsdm^{-3}.

propensity towards water structure-enforced ion-pair formation.

At low cation concentrations ion-pair formation is thus the dominant effect until maximum ion-pair formation is achieved when the more usual solution behaviour of the respective cations in terms of their salting in/salting out characteristics prevails.

3.6 Factors influencing the extent of reaction between cationic reagents and cellulose

3.6.1 Effect of reagent structure

A series of monohalogenated heterocyclic quaternary reagents were prepared (see section 3.2.1) using a variety of alkyl and aryl halide quaternising agents, RX, of differing molecular weights and degrees of planarity. An equal weight of each reagent, 5% o.w.f., was applied to samples of bleached unwaxed cotton using the method outlined in section 5.6.1.

Each treated sample was then dyed with 1% o.w.f. C.I. Direct Blue 10 for 1 hour at 96°C in the presence of an equal weight of untreated cotton. The extent of reaction taking place between the reagents and the fibre and thus the degree of preferential dye uptake imparted by each individual treatment was then determined by taking Colour Strength measurements of the treated sample against the untreated sample as standard.

The results, given in Table 20, showed that all but two of the reagents prepared did impart a significant degree of preferential dye uptake to the treated cotton when it was dyed in the presence of an untreated cotton sample. The cationic reagent I, (the chloromethyl naphthalene derivative of [I]) - see section 3.2.1 - was observed to give the greatest degree of preferential dye uptake, which was attributed to its greater molecular weight and degree of planarity compared with those of the other reagents, which would tend to improve its exhaustion characteristics on cellulose, bearing in mind the importance of these factors in determining the substantivity of direct dyes for cellulose.

Table 20. Colour Strength measurements for cotton samples treated with a series of potential cationic reagents - derivatives of (I) - see section 3.2.1.

Derivative of (I) RX	Colour Strength % o.w.f. treated 5%	 10%
CH_3I	23.08	25.02
C_2H_5I	7.60	-
C_4H_9I	8.69	-
$C_6H_{13}I$	6.52	-
$C_{10}H_{21}I$	11.86	-
$C_6H_5CH_2Cl$	48.34	70.33
$C_{10}H_7CH_2Cl$	61.36	77.49
$C_6H_{11}I$	0.79	-
$(C_6H_5)_2CHCl$	0.75	-

The fact that steric considerations may play an important part in determining whether or not a reagent will modify cellulose so as to produce a differential-dyeing cotton was suggested by the fact that, whereas treatment with the hexyl iodide derivative of (I) resulted in the treated sample showing increased substantivity for direct dyes, treatment with the cyclohexyl iodide analogue did not (Colour Strength <1).

Since the hexyl and cyclohexyl groups have almost identical molecular weights the only other difference between the two which could have given rise to such an observation is the spatial arrangement of the atoms in the group - the hexyl group existing as a straight chain whilst the cyclohexyl group usually adopts the puckered ring conformation because of energy considerations. The fact that cotton treated with the diphenylmethyl derivative of (I) also did not show preferential dye uptake when dyed with the same direct dye in the presence of an untreated sample would also tend to support this view.

Bulky groups such as the diphenylmethyl or cyclohexyl radicals may therefore so reduce a compounds affinity for cellulose that it is effectively prevented from adsorbing on the fibre surface and hence reaction with the fibre may be inhibited to such an extent that very few cationic sites are incorporated into the fibre and hence little if any preferential dye uptake on the 'treated' cotton occurs.

3.6.2 Effect of reagent concentration

The effect of reagent concentration on the degree of fixation was examined in order to determine whether or not the use of higher treatment levels, of for example 10-15% o.w.f., would bring about significant increases in the degree of reaction occurring between the reagent and the fibre. Six treatments of cotton yarn were carried out employing from 1-15% o.w.f. of the cationic reagent I together with sodium chloride (40 g/l). Exhaustion was carried out for 1 hour at 30°C and, after the addition of sodium carbonate (20 g/l), fixation was continued for 6 hours at 80°C to ensure that equilibrium was reached for all the samples.

After soaping and drying, the treated hanks were dyed with 0.5-7.5% o.w.f. of commercial C.I. Acid Orange 7 (Figure 26), a small monosulphonic acid of low affinity for untreated cellulose, thus keeping diffuse adsorption to a minimum. The amount of dye applied was also determined with this end in view ensuring that, whilst an excess of dye was present in every case, at the same time none of the treated samples were exposed to a vast excess.

Dyeing was carried out under reflux for 6 hours at the boil, none of the baths coming close to exhaustion. The samples were then soaped and dried and Colour Strength measurements taken using an undyed, untreated sample of bleached cotton as the standard.

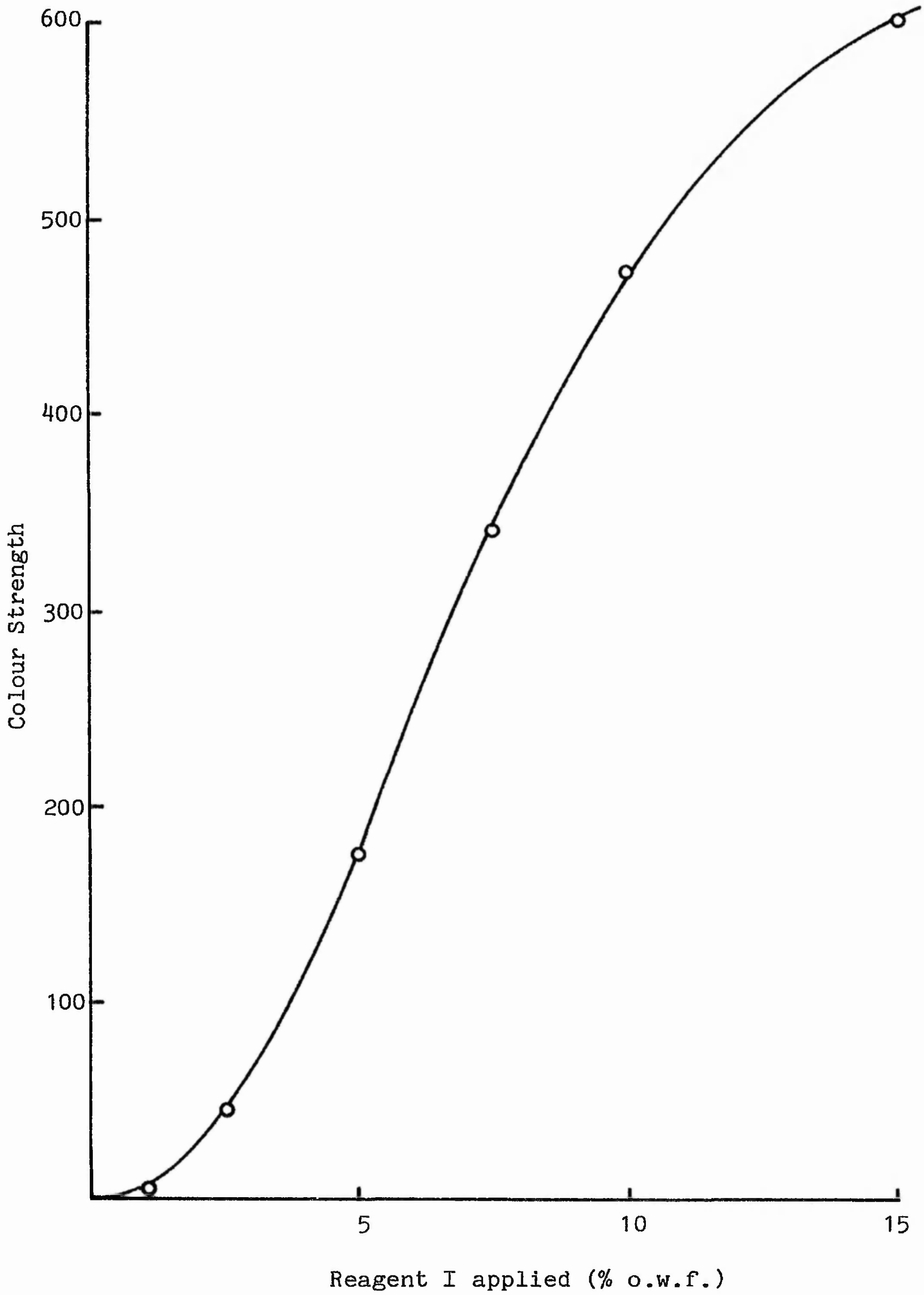
As can be seen in Figure 49 a sigmoid graph was obtained on plotting Colour Strength versus the % o.w.f. treatment for each of the samples. This was probably due to the fact that at low concentrations the solubility of the reagent was such that the degree of fixation was low, whilst at high concentrations the process became less efficient, perhaps due to repulsion of the positively charged ions from the cellulose surface, which itself had now acquired a positive charge, and/or between the positively charged groups already incorporated into the fibre.

It would appear then that, in so far as increasing the degree of fixation is concerned, there is less and less to be gained by increasing the concentration of reagent applied beyond the 15% o.w.f. level since small increases in the degree of fixation occurring would have to be off set against the cost of the extra reagent required.

Table 21. The effect of reagent concentration on the degree of fixation - as indicated by uptake of C.I. Acid Orange 7; C.I. 15510.

% Treatment (o.w.f.)	Colour Strength
1.0	4.44
2.5	44.54
5.0	175.35
7.5	347.30
10.0	474.52
15.0	602.50

Figure 49. Colour Strength *versus* % Reagent I applied, using C.I. Acid Orange 7.



3.6.3 Effect of temperature

The temperature at which the fixation process was carried out was expected to have a profound effect on the extent of reaction occurring between the reagent and the fibre. Coloured, although otherwise analogous, monochlorotriazinyl compounds are referred to in the technical literature as 'hot-dyeing' reactive dyes (as opposed to the 'cold-dyeing' dichlorotriazine dyes) and in general recommended fixation temperatures are in the range of 60-80°C.

The temperature at which maximum reagent fixation occurred was therefore determined by carrying out six 5% o.w.f. treatments of cotton yarn (2x2 g samples) using the cationic reagent I, exhausting for 1 hour at 30°C using sodium chloride (40 g/l) and fixing in the presence of sodium carbonate (20 g/l) at six different temperatures in the range 30-80°C, in each case removing one sample after 1 hour and 2 hour fixation times respectively.

One sample for each temperature and time of fixation was then dyed with 2% o.w.f. C.I. Direct Blue 1 in the presence of a similar weight of untreated cotton and, after soaping well, Colour Strength measurements were taken for the treated sample against an undyed sample of 5% o.w.f. treated cotton as standard.

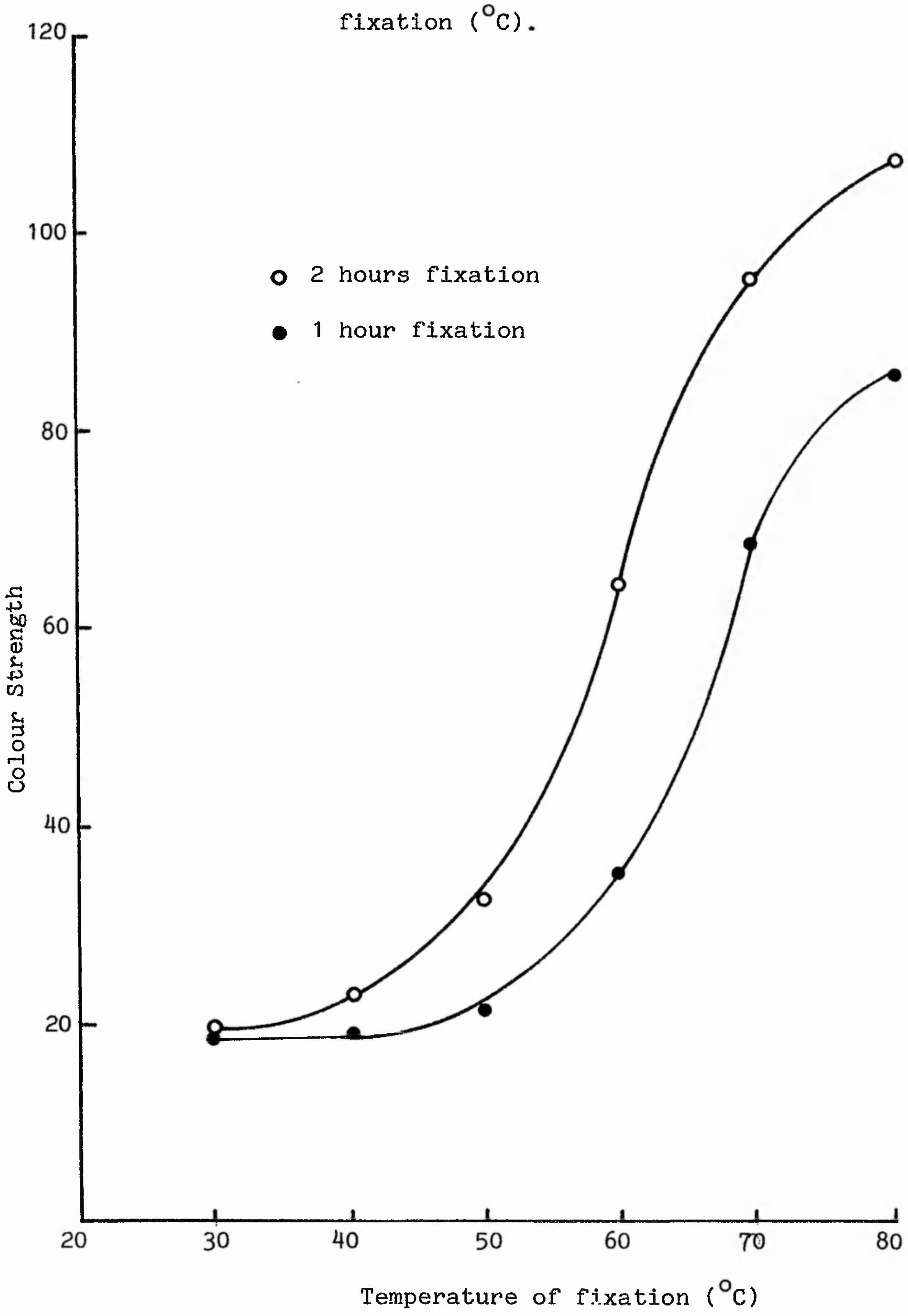
The results given in Figure 50 (Table 22) show clearly that elevated temperatures were required for efficient fixation, maximum fixation occurring after 2 hours at 80°C, although at this stage it was not yet clear whether or not equilibrium had been reached.

In the case of treated samples fixed at <70°C large quantities of dye were removed at the soaping off stage, presumably having been merely adsorbed to the cellulose surface in the absence of cationic sites.

Table 22. Effect of temperature on the degree of fixation of reagent I on cellulose - as indicated by uptake of C.I. Direct Blue 1.

Temperature of fixation (^{o}C)	Colour Strength @ 1 hour	@ 2 hours
30	18.53	19.85
40	19.10	23.04
50	21.79	32.93
60	35.69	64.47
70	68.27	95.39
80	85.82	107.35

Figure 50. Colour Strength versus Temperature of fixation (°C).



3.6.4 Effect of time

The effect of time on the extent of reaction between the cationic reagent I and the cellulose substrate was examined to determine whether the reaction was complete after 2 hours or if, in fact, equilibrium was only achieved after several hours.

A 5% o.w.f. treatment was therefore carried out simultaneously on six cotton hanks in the same bath using reagent I (L.R. 50:1), exhausting for 1 hour at 30°C using sodium chloride (40 g/l) and fixing for a maximum of 6 hours at 80°C in the presence of sodium carbonate (20 g/l), one hank being removed at hourly intervals.

Six individual 3% o.w.f. dyeings were then carried out using C.I. Direct Blue 1 (L.R. 50:1) for 1 hour at 96°C in the presence of an equal weight of untreated cotton.

After soaping them well at 60°C in 2% Sandozin NI, Colour Strength measurements were then taken for the treated samples against an undyed sample of 5% o.w.f. treated cotton as standard (Table 23). The results are plotted in Figure 51 and show that at 80°C fixation was effectively complete after 2 hours, since no further dye was taken up by the treated samples.

Table 23. Effect of time on the degree of fixation of reagent I on cellulose - as indicated by uptake of C.I. Direct Blue 1.

Time (hours)	Colour Strength
1	117.71
2	136.51
3	138.31
4	138.70
5	136.79
6	139.79

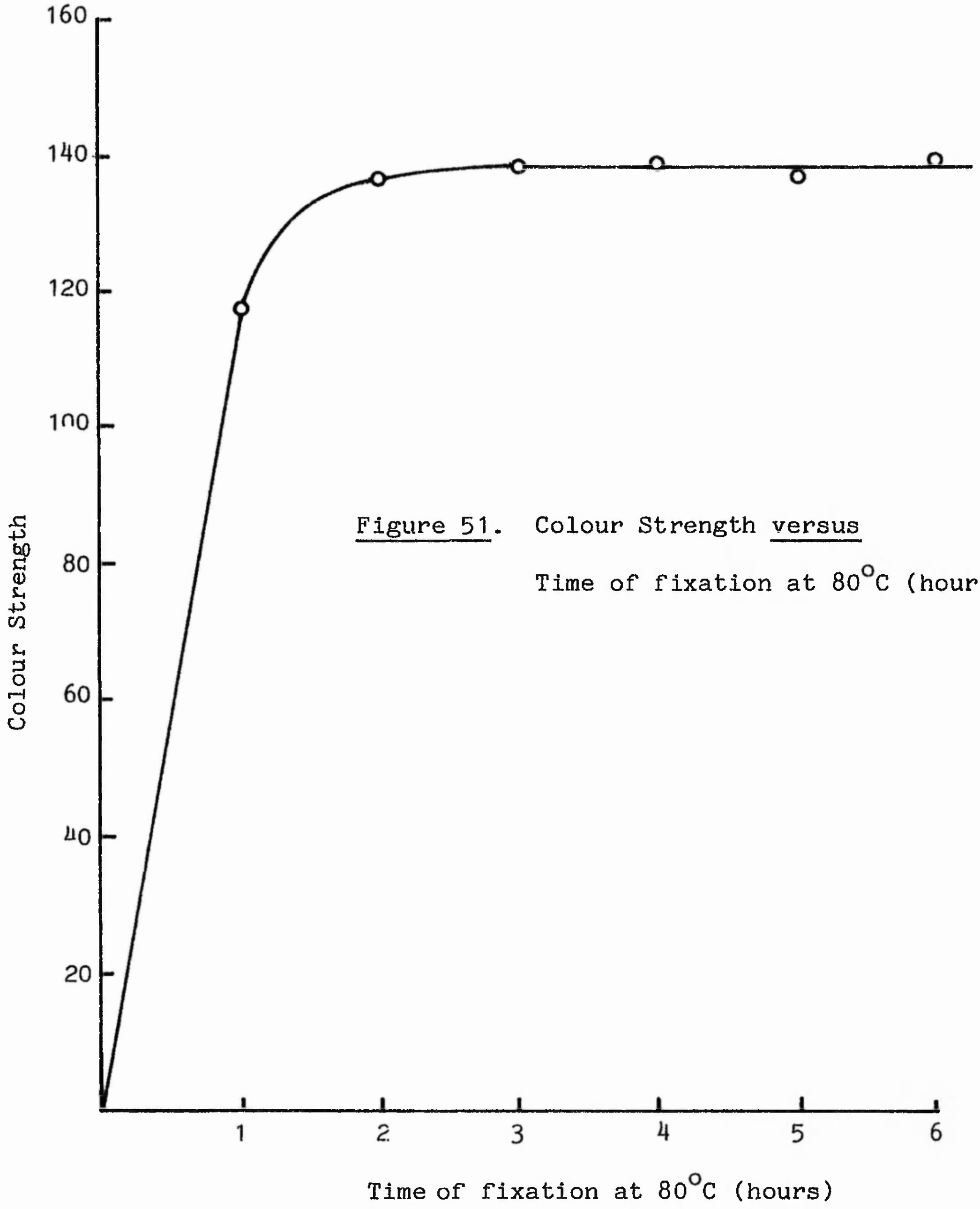


Figure 51. Colour Strength *versus* Time of fixation at 80°C (hours).

3.6.5 Effect of the nature and concentration of the alkali

The effects of two different alkalis, sodium carbonate and sodium hydroxide were examined at each of three concentrations in order to determine their influence on the degree of reagent fixation.

Six 5% o.w.f. treatments of cotton yarn were therefore carried out (L.R. 50:1), exhausting for 1 hour at 30°C using sodium chloride (40 g/l). Fixation was carried out for 3 hours at 80°C in the presence if 0.1, 0.2 and 0.3 molsdm^{-3} sodium carbonate, respectively, and for 3 hours at 60°C in treatment baths containing 0.05, 0.1 and 0.2 molsdm^{-3} sodium hydroxide - a stronger alkali, for which lower fixation temperatures are generally recommended.

After soaping and drying, the samples were dyed with 5% o.w.f. C.I. Direct Blue 1 for 2 hours at 96°C (L.R. 50:1) in the presence of an equal weight of untreated cotton, ensuring that the baths did not exhaust. Colour Strength measurements were then taken for the treated samples against an undyed sample of 5% o.w.f. treated cotton as standard.

The results are given in Table 24 (Figure 52) and indicate that, in general, fixation carried out in the presence of sodium carbonate was slightly more efficient, in terms of the number of dye sites incorporated into the fibre, than the same process carried out in sodium hydroxide solution and that sodium carbonate concentrations as low as 0.1 molsdm^{-3} (10.6 g/l) were just as effective as the higher concentrations used.

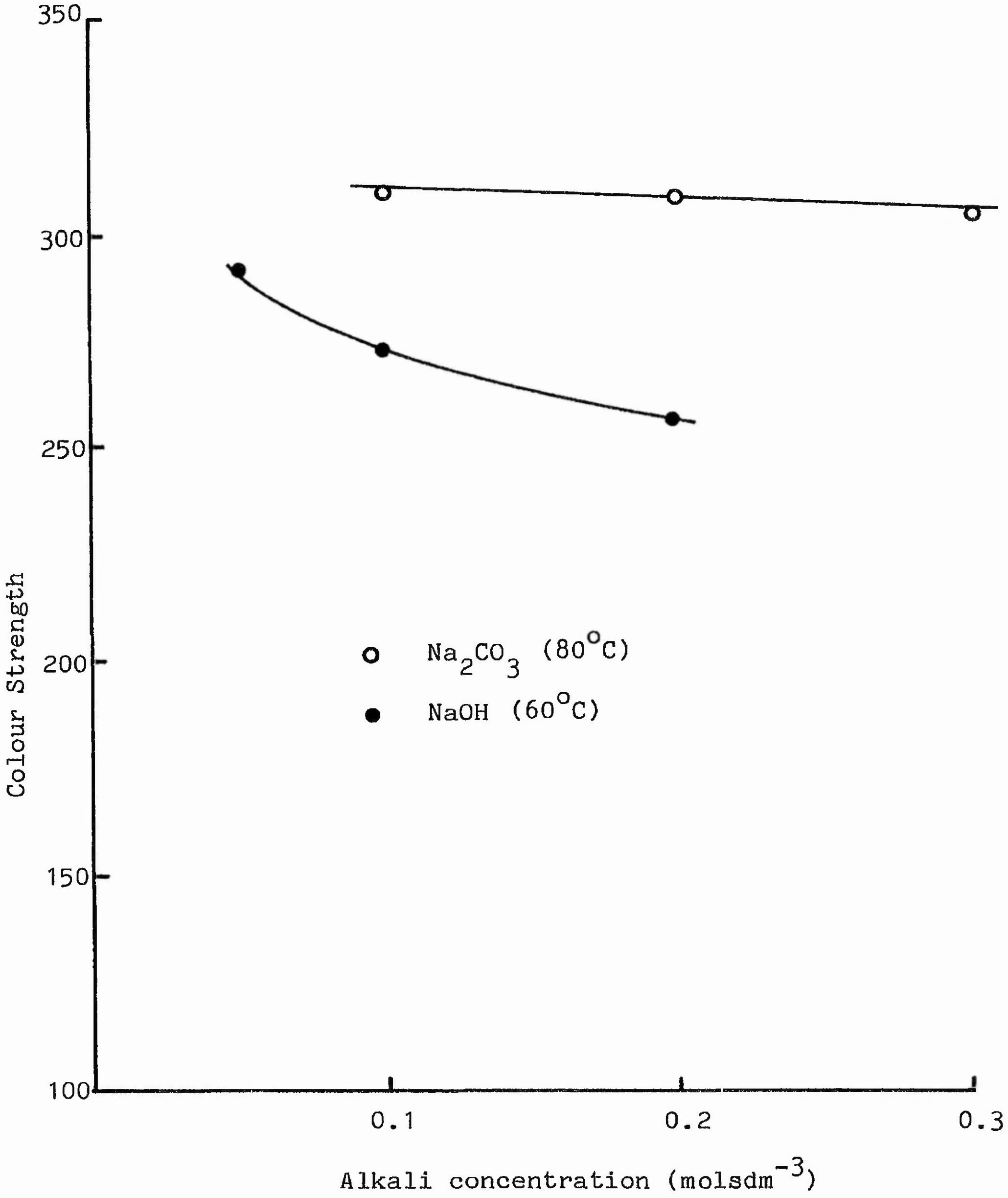
In large scale production of the treated yarn, however, the savings in energy to be gained by lowering the temperature of fixation from

80°C to 60°C would more than compensate for the slight loss in efficiency of sodium hydroxide, in which case a working concentration of $\leq$0.05 molsdm^{-3} would be recommended, as more concentrated solutions resulted in lower degrees of fixation, probably as a result of increased hydrolysis of the reagent.

Table 24. Effect of the nature and concentration of the alkali on the degree of fixation of reagent I on cellulose - as indicated by uptake of C.I. Direct Blue 1.

Alkali	Concentration molsdm^{-3}	g/l	Temperature of fixation (°C)	Colour Strength
Na_2CO_3	0.1	10.6	80	309.55
	0.2	21.2	80	308.32
	0.3	31.8	80	304.45
NaOH	0.05	2	60	291.23
	0.10	4	60	272.44
	0.20	8	60	254.70

Figure 52. Colour Strength versus Alkali concentration (molsdm^{-3}) for sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH).



3.6.6 Use of a commercial liquid alkaline buffer

In a further study the use of a commercially available liquid alkaline buffer, 'Alkaflo', was investigated to determine its effect on the degree of fixation of reagent I on cellulose. Recommended for use with reactive dyes, this colourless liquid consists of a mixture of tripotassium phosphate and potassium hydroxide and is claimed to provide adjustment of pH giving optimum conditions for dyestuff fixation. As a result less reagent hydrolysis and a greater degree of fixation would be expected to be achieved.

Four 5% o.w.f. treatments of cotton yarn were carried out using the cationic reagent I (L.R. 40:1) exhausting at 30°C using sodium chloride and fixing at 80°C. The various additions of sodium chloride and alkali, together with the exhaustion and fixation times employed are given in Table 25. Treatment 1 was the 'standard' treatment in which fixation was carried out for 2 hours in the presence of sodium carbonate (20 g/l) and against which the results obtained with 'Alkaflo' could be compared. Treatment 2 was the recommended procedure outlined for use with 'Alkaflo' . In each of treatements 2, 3 and 4, Alkaflo was employed at the specified concentration of 1.5 cm^3/l for a liquor to goods ratio of 40:1.

The samples were then dyed with 5% o.w.f. C.I. Direct Blue 1 for 2 hours at 96°C (L.R. 50:1), in the presence of an equal weight of untreated cotton. Colour Strength measurements were then taken for the treated samples against an undyed sample of 5% o.w.f. treated cotton as standard. The results are given in Table 25.

Table 25. The effect of replacing sodium carbonate with Alkaflo on the degree of fixation of reagent I on cellulose - as indicated by uptake of C.I. Direct Blue 1.

Treatment	Electrolyte	Time of exhaustion (minutes)	Alkali	Time of fixation (hours)	Colour Strength
1	NaCl	60	Na_2CO_3	2	263.82
2	NaCl	10	Alkaflo	1	154.22
3	NaCl	60	Alkaflo	1	162.21
4	NaCl	60	Alkaflo	2	200.21

As can be seen the use of 'Alkaflo' generally resulted in a lower degree of reagent fixation occurring, as indicated by the reduction in Colour Strengths obtained for samples 2, 3 and 4, compared to that obtained in treatment 1 with sodium carbonate. It is possible, however, that by reducing the fixation temperature (from say $80^{o}C$ to $60^{o}C$) or adjusting the concentration of Alkaflo in the treatment bath, improved levels of fixation might be achieved although, unfortunately, insufficient time was available for a more detailed study of the optimum conditions for the reaction.

In large scale production of the treated yarn, however, the use of an alkaline liquid buffer system, such as Alkaflo, would have several obvious advantages particularly in terms of the improvement of the levelness and reproducability of the treatment and in the ease of application.

3.6.7 Effect of increasing exhaustion with sodium thiocyanate

Owing to the very high degree of exhaustion of reagent I exhibited in the presence of relatively low concentrations of sodium thiocyanate (≤ 0.1 molsdm^{-3}) the effect of using this electrolyte (in conjunction with different alkalis) on the level of reagent fixation obtained warranted further investigation.

Three 5% o.w.f. treatments of cotton yarn were therefore carried out using the cationic reagent I, exhausting for 1 hour at 30°C in the presence of 0.1M sodium thiocyanate (L.R. 40:1) and fixing at 80°C, the alkalis and times of fixation employed being given in Table 26. Dyeing of the treated samples was carried out using 5% o.w.f. C.I. Direct Blue 1 for 1 hour at 96°C (L.R. 50:1) in the presence of an equal weight of untreated cotton. Colour Strength measurements were then taken against an undyed sample of 5% o.w.f. treated cotton as standard. The results indicated that, far from improving the level of reagent fixation, the use of sodium thiocyanate considerably reduced the degree of fixation occurring, regardless of the alkali used in the fixation step. In the case of treatment 1, the use of sodium thiocyanate (as opposed to sodium chloride) for exhaustion reduced the Colour Strength obtained in the presence of sodium carbonate from 263.82 to 153.13 and similarly large reductions in the Colour Strengths obtained (from 200.21-111.21) were observed using Alkaflo liquid alkaline buffer.

It would appear then that despite the high degree of exhaustion exhibited in the presence of sodium thiocyanate at ≤ 40°C, the alkaline conditions and high temperatures prevailing in the treatment bath resulted in much lower degrees of fixation than were obtained when exhaustion of reagent I was carried out in the presence of sodium chloride.

Table 26. The effect of increasing the exhaustion with sodium thiocyanate on the degree of fixation of reagent I on cellulose - as indicated by the uptake of C.I. Direct Blue 1.

Treatment	Electrolyte	Time of exhaustion (hours)	Alkali	Time of fixation (hours)	Colour Strength
1	NaSCN	1	Na_2CO_3	2	153.13
2	NaSCN	1	Alkaflo	1	93.56
3	NaSCN	1	Alkaflo	2	111.21

3.7 Dyeing studies on differential-dyeing cotton

3.7.1 Determination of the stoichiometry of the reaction

In order to determine the stoichiometry of the reaction between anionic dyes containing sulphonic acid groups and differential-dyeing cotton containing positive quaternary ammonium sites, two different classes of anionic dye were selected for use in the investigation; one generally associated with the dyeing of cotton and one not normally used on cellulose.

The direct dyes form the largest and one of the most important classes of dyes used on cellulosic fibres. Generally speaking they consist of large, planar molecules which are anionic in character and are strongly substantive towards cellulose (see section 1.2.1). Acid dyes, on the other hand, are small by comparison and consequently show little, if any, substantivity for unmodified cellulose. They are usually associated with the dyeing of nylon and wool, substrates which, under acidic conditions, contain positive quaternary ammonium groups which are capable of acting as sites for anionic dyes.

In the case of differential-dyeing cotton, however, acid dyes were observed to have a considerable affinity for the modified fibres, due to the presence of the positive sites which had been permanently incorporated into the substrate. Since acid dyes show little affinity for unmodified cellulose the contribution to the overall dye uptake of dye adsorbed diffusely was expected to be negligible. This was not, however, expected to be the case with direct dyes which are strongly substantive towards cellulose and hence it was considered of interest to compare the results obtained with each of the two dye classes in the subsequent investigation.

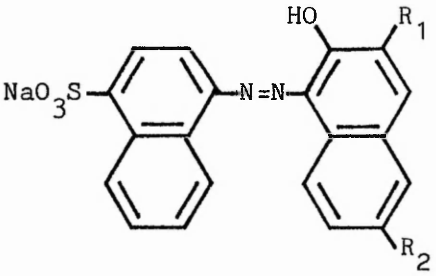
3.7.1.1 The interaction with acid dyes

In order to determine the stoichiometry of the reaction three acid dyes were selected having similar structures which differ only in the number of sulphonic acid groups they contain. The structures which were chosen are illustrated in Figure 53 and the number and position of sulphonic acid groups for each dye indicated. Commercial samples of the dyes were examined in order to determine the percentage of dye they contained and the λmax and extinction coefficient, ε, for each dye were obtained from the literature[209] (see Table 27).

Table 27. Data required for the determination of the stoichiometry of the reaction between acid dyes and cotton containing cationic sites.

Dye	C.I. No.	M.W.	No. of SO_3^- groups	Structure	λmax (nm)	εmax	% Purity
AR88	15620	400	1	(i)	505	20,350	58.82
AR13	16045	502	2	(ii)	506	24,100	67.96
AR27	16185	604	3	(iii)	522	26,200	67.14
AO7	15510	350	1	*	486	22,500	65.35

* For the structure of C.I. Acid Orange 7 see Figure 26, p.113.



Structure	R_1	R_2
(i)	H	H
(ii)	H	SO_3Na
(iii)	SO_3Na	SO_3Na

Figure 53. General structure for the series of acid dyes used in determining the stoichiometry of the reaction.

Six 2 g ($\pm$0.01 g) hanks of cotton treated to a site content (C1) were dyed to equilibrium in baths containing 0.2-2.5 x 10^{-3} molsdm^{-3} of the three acid dyes selected. Values of $[Df]_\infty$ and $[Ds]_\infty$ were then determined (see Table 28) and equilibrium isotherms drawn up.

As can be seen from Figure 54 the molar saturation values for the three dyes decreased with increasing number of sulphonic acid groups on the dye, that is in the order:

AR88 > AR13 > AR27

This was taken as an indication that a 1:1 relationship did not exist between cationic sites and dye molecules but rather that the stoichiometry of the reaction between sites and individual dyes was dependant on the number of sulphonic acid groups on the dye.

In the case of AR88 the evidence pointed to the occurrence of two separate processes namely site adsorption and diffuse adsorption and in fact the experimental data obtained for this dye was observed to fit the Freundlich equation which is generally used to describe diffuse adsorption

$$[Df]_\infty = K[Ds]_\infty^x \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where $[Df]_\infty$ and $[Ds]_\infty$ are the equilibrium concentrations of dye in the fibre and in solution respectively, K is a constant, and x is a fractional power. By taking the logarithm of both sides to obtain equation (2) it can be seen that a linear relationship should be obtained by plotting $\log[Df]_\infty$ versus $\log[Ds]_\infty$, which in fact for Acid Red 88 proved to be the case (see Figure 55).

$$\log[Df]_\infty = \log K + x\log[Ds]_\infty \ldots\ldots\ldots\ldots(2)$$

Table 28. Equilibrium adsorption measurements for the series of acid dyes on treated cotton (C1).

Dye sample No.		$[Ds]_o$ molsdm^{-3}x10^{4}	Aλmax	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^{4}	$[Df]_\infty$ mmolsKg^{-1}
AR88	1	2.12	0.160	10	0.786	6.67
	2	5.31	0.672	10	3.30	10.04
	3	10.61	0.667	25	8.19	12.08
	4	15.92	0.542	50	13.32	13.02
	5	21.23	0.374	100	18.38	14.26
	6	26.53	0.384	125	23.59	14.71
AR13	1	1.93	0.330	10	1.37	2.80
	2	4.82	0.977	10	4.05	3.83
	3	9.65	0.842	25	8.73	4.58
	4	14.47	0.660	50	13.69	3.89
	5	19.29	0.449	100	18.63	3.30
	6	24.12	0.455	125	23.60	2.60
AR27	1	1.98	0.417	10	1.59	1.94
	2	4.95	0.239	50	4.56	1.94
	3	9.91	0.994	25	9.48	2.10
	4	14.86	0.756	50	14.40	2.16
	5	19.81	0.508	100	19.39	2.10
	6	24.76	0.510	125	24.33	2.14

Figure 54. Equilibrium absorption isotherms for C.I. Acid Reds 88, 13 and 27.

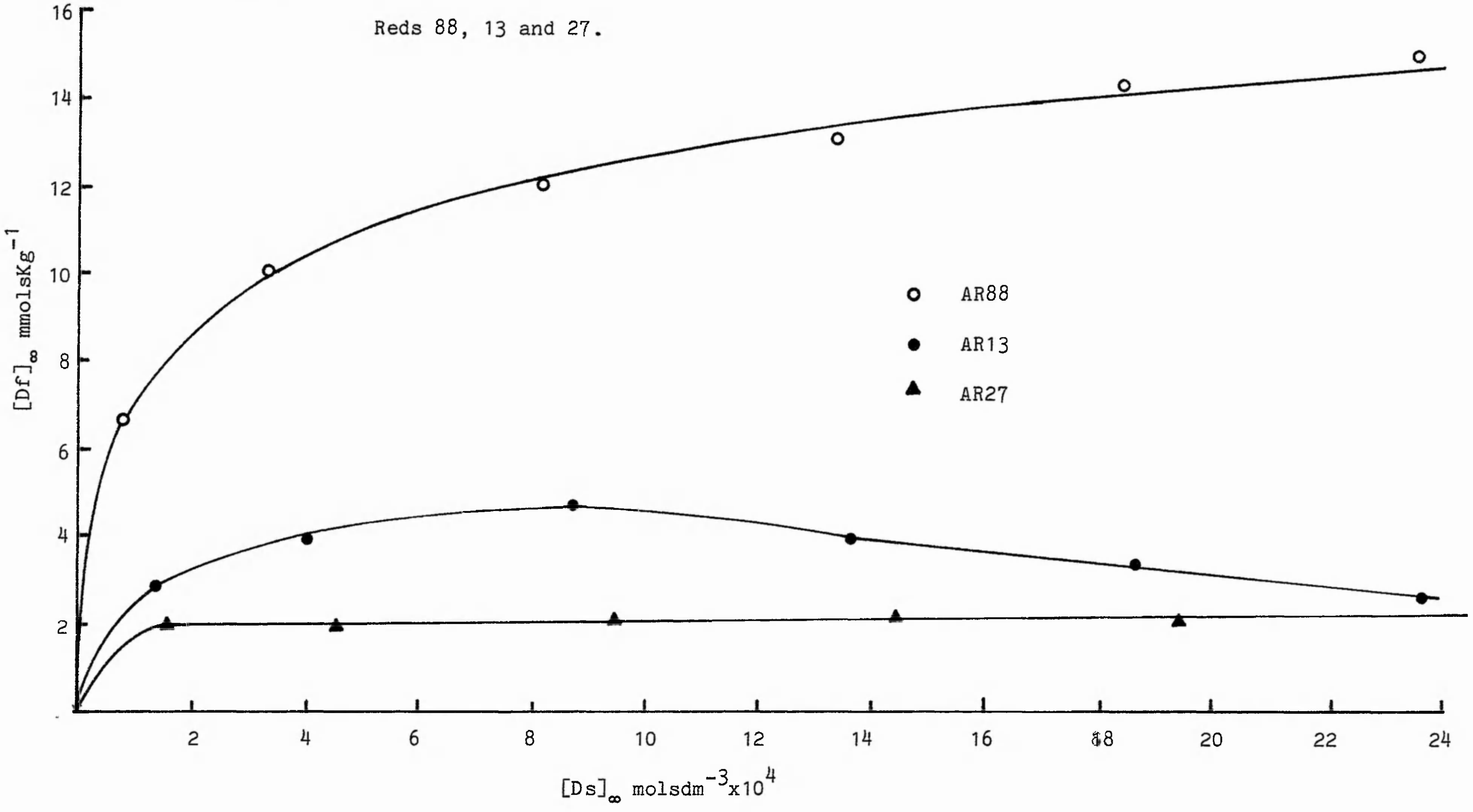


Table 29. Logarithmic plots of the equilibrium adsorption data obtained for the series of acid dyes on treated cotton (C1).

Dye	log[Ds]$_\infty$ molsdm^{-3}	log[Df]$_\infty$ molsKg^{-1}	Regression analysis
AR88	-4.10	-2.18	Intercept.... -1.21
	-3.48	-2.00	Slope..........0.234
	-3.09	-1.92	Correlation
	-2.88	-1.89	coefficient....0.995
	-2.74	-1.85	
	-2.63	-1.83	
AR13	-3.86	-2.55	Intercept.....-1.53
	-3.39	-2.42	Slope..........0.264
	-3.06	-2.34	Correlation
	-2.86	-2.41	coefficient....0.999
	-2.73	-2.48	
	-2.63	-2.58	
AR27	-3.80	-2.71	Intercept.....-2.57
	-3.34	-2.71	Slope..........0.038
	-3.02	-2.68	Correlation
	-2.84	-2.67	coefficient....0.902
	-2.71	-2.68	
	-2.61	-2.67	

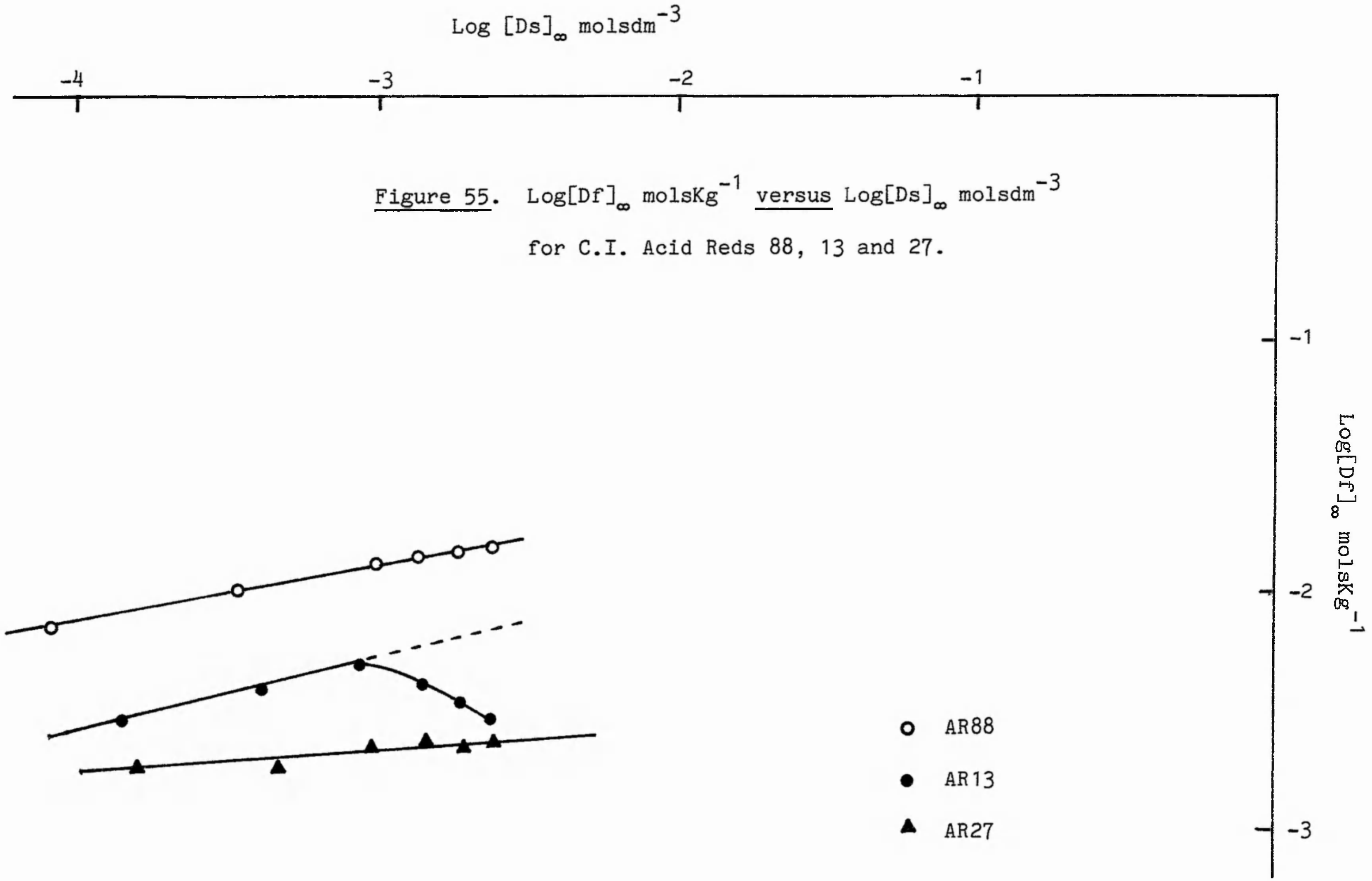


Figure 55. Log$[Df]_\infty$ molsKg^{-1} versus Log$[Ds]_\infty$ molsdm^{-3} for C.I. Acid Reds 88, 13 and 27.

A linear logarithmic relationship was also observed with C.I. Acid Red 27 (containing three sulphonic acid groups) although this was to be expected since the original adsorption isotherm indicated that a saturation level of 2.1 mmolsKg^{-1} had been reached even at the lowest concentration of dye applied.

In the case of C.I. Acid Red 13 the concentration of dye on the fibre appeared to approach a saturation level of 4.2 mmolsKg^{-1} and then unexpectedly began to decrease again. This anomaly was reflected in the logarithmic plot for this particular dye which was at first linear indicating the occurrence of diffuse adsorption, but which then began to fall away from a linear extrapolation of the graph. Colour Strength measurements of the dyed samples; taken against undyed 5% o.w.f. treated cotton (C1) as standard, confirmed that the concentration of the dye in the fibre had decreased with increasing dye in solution although the magnitude of the effect in this case was less than expected (see Table 30).

The greatest degree of diffuse adsorption occurred with C.I. Acid Red 88 presumably as a result of its greater hydrophobic character due to the fact that it contained only one sulphonic acid group, compared to the two and three present in C.I. Acid Reds 13 and 27 respectively. As a result of this, the actual levelling off point of the graph was difficult to establish and hence it was resolved to obtain a different measure of the amount of monosulphonated dye which could be taken up by the modified yarn this time using C.I. Acid Orange 7, a very small acid dye which, though related structurally to C.I. Acid Red 88, had been shown earlier (in section 3.3.3.3) to

Table 30. Colour Strength measurements for the series of acid dyes on treated cotton (C1).

Sample	Colour Strength		
	AR88	AR13	AR27
1	75.97	45.45	32.56
2	102.26	49.96	37.09
3	106.04	55.72	37.22
4	109.40	52.96	40.87
5	115.95	50.90	42.72
6	123.27	50.15	43.94

have very little affinity for untreated cellulose with the result that less diffuse adsorption occurred.

An equilibrium adsorption isotherm had previously been obtained for C.I. Acid Orange 7 using the same batch of modified cotton (C1); in this case a much lower levelling off point was obtained corresponding to a saturation value of 7.1 mmolsKg^{-1} (obtained by extrapolation).

A new ratio of molar saturation values, incorporating the earlier results for C.I. Acid Orange 7, may now be given as 7.1:4.2:2.1 for the series of acid dyes containing 1, 2 and 3 sulphonic acid groups respectively, which can be seen to fit fairly closely to the theoretical ratio of 6:3:2 (or 7.1:3.6:2.4) which would be expected for a 1:1 relationship between cationic quaternary ammonium sites in the substrate and sulphonic acid groups on the dye. The results for C.I. Acid Red 13 are however higher than expected (4.2 instead of 3.6) attributable perhaps to the presence of contaminating C.I. Acid Red 88 in the commercial dye sample which according to Nursten and Williams[209] would not be unexpected since the subsiduary dye could easily arise on coupling naphthionic acid to an insufficiently sulphonated 2-naphthol.

The increased substantivity of C.I. Acid Red 88 for the treated cellulose over that of C.I. Acid Red 13 (due to its greater hydrophobic character) may also explain why the molar saturation value was observed to increase rapidly to 4.2 mmolsKg^{-1} and then gradually decrease as the higher concentration of dye in solution meant that more C.I. Acid Red 13 was available to occupy sites in preference to the monosulphonic acid dye (one C.I. Acid Red 13 molecule occupying two sites as opposed to one in the case of C.I. Acid Red 88) so reducing the actual number of moles of dye adsorbed on the treated fibre.

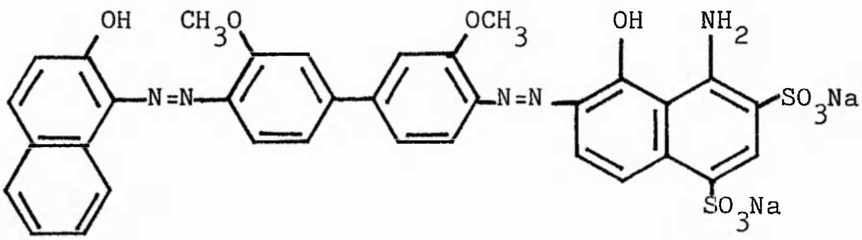
3.7.1.2 The interaction with direct dyes

The stoichiometry of the reaction between cotton containing cationic sites and direct dyes was determined employing three direct dyes, C.I. Direct Blues 1 and 22 and C.I. Direct Yellow 12, containing 4, 2 and 2 sulphonic acid groups repectively and whose structures are illustrated below in Figure 56. Commercial samples of the dyes were purified in order to ascertain the percentage of dye they contained and the λmax and extinction coefficients were determined for each dye using the purified material (Table 31).

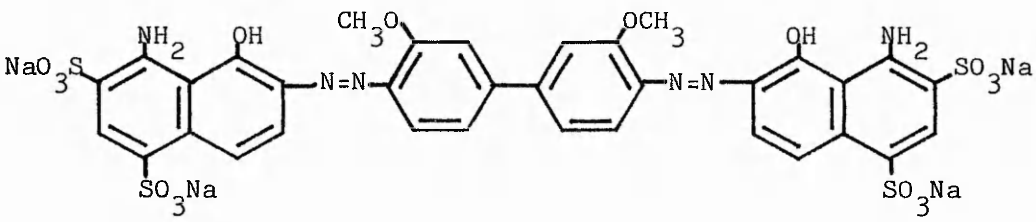
Six 2 g hanks of cotton treated to a site content (C1) were dyed to equilibrium in baths containing 0.2-2.5 x 10^{-3} molsdm^{-3} of C.I. Direct Blues 1 and 22 and 0.4-4.0 x 10^{-4} molsdm^{-3} of C.I. Direct Yellow 12. Values of $[Df]_\infty$ and $[Ds]_\infty$ were then determined and equilibrium isotherms drawn up (Figures 57, 58 and 59).

Table 31. Data required for the determination of the stoichiometry of the reaction between direct dyes and cotton containing cationic sites.

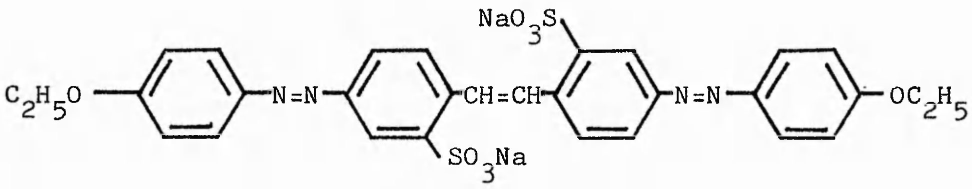
Dye	C.I. No.	MW	No. of SO_3^-	λmax	ε x10^4	% Purity
DB1	24410	992	4	621	6.58	20.87
DB22	24280	773	2	575	6.04	19.84
DY12	24895	680	2	393	5.00	30.34



C.I. Direct Blue 22



C.I. Direct Blue 1



C.I. Direct Yellow 12

Figure 56. Molecular structures for the series of direct dyes used in determining the stoichiometry of the reaction.

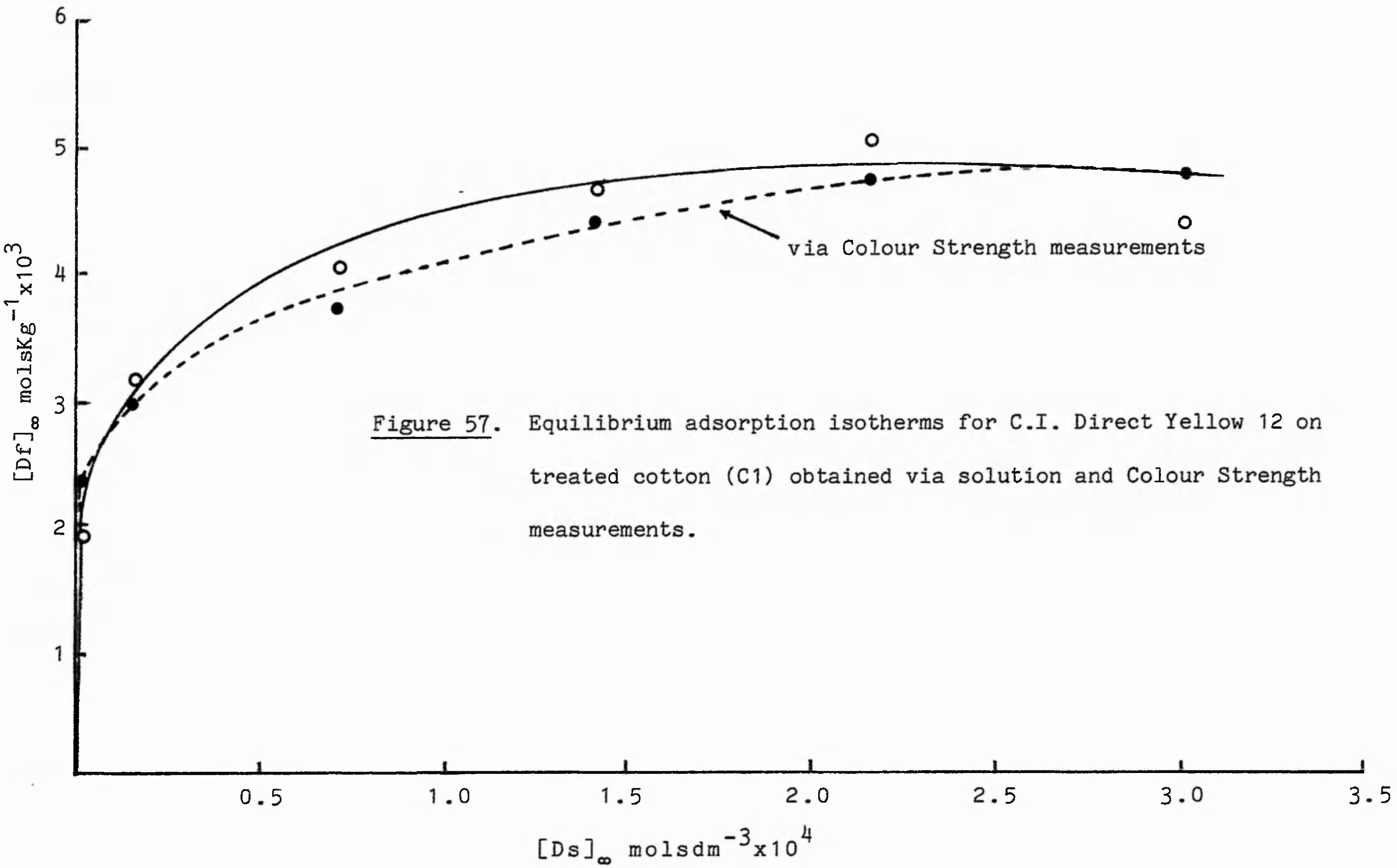
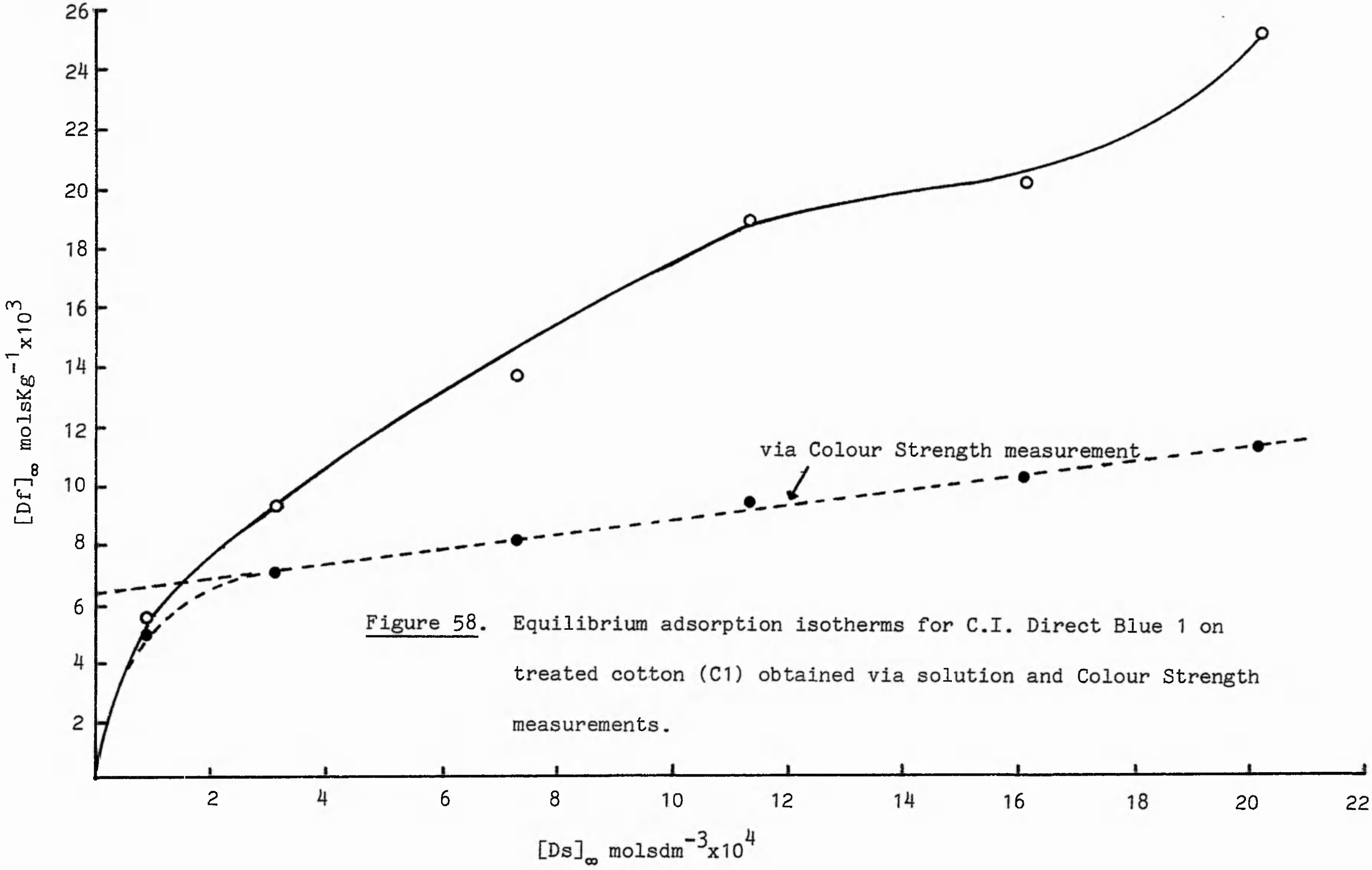


Figure 57. Equilibrium adsorption isotherms for C.I. Direct Yellow 12 on treated cotton (C1) obtained via solution and Colour Strength measurements.



<u>Figure 58</u>. Equilibrium adsorption isotherms for C.I. Direct Blue 1 on treated cotton (C1) obtained via solution and Colour Strength measurements.

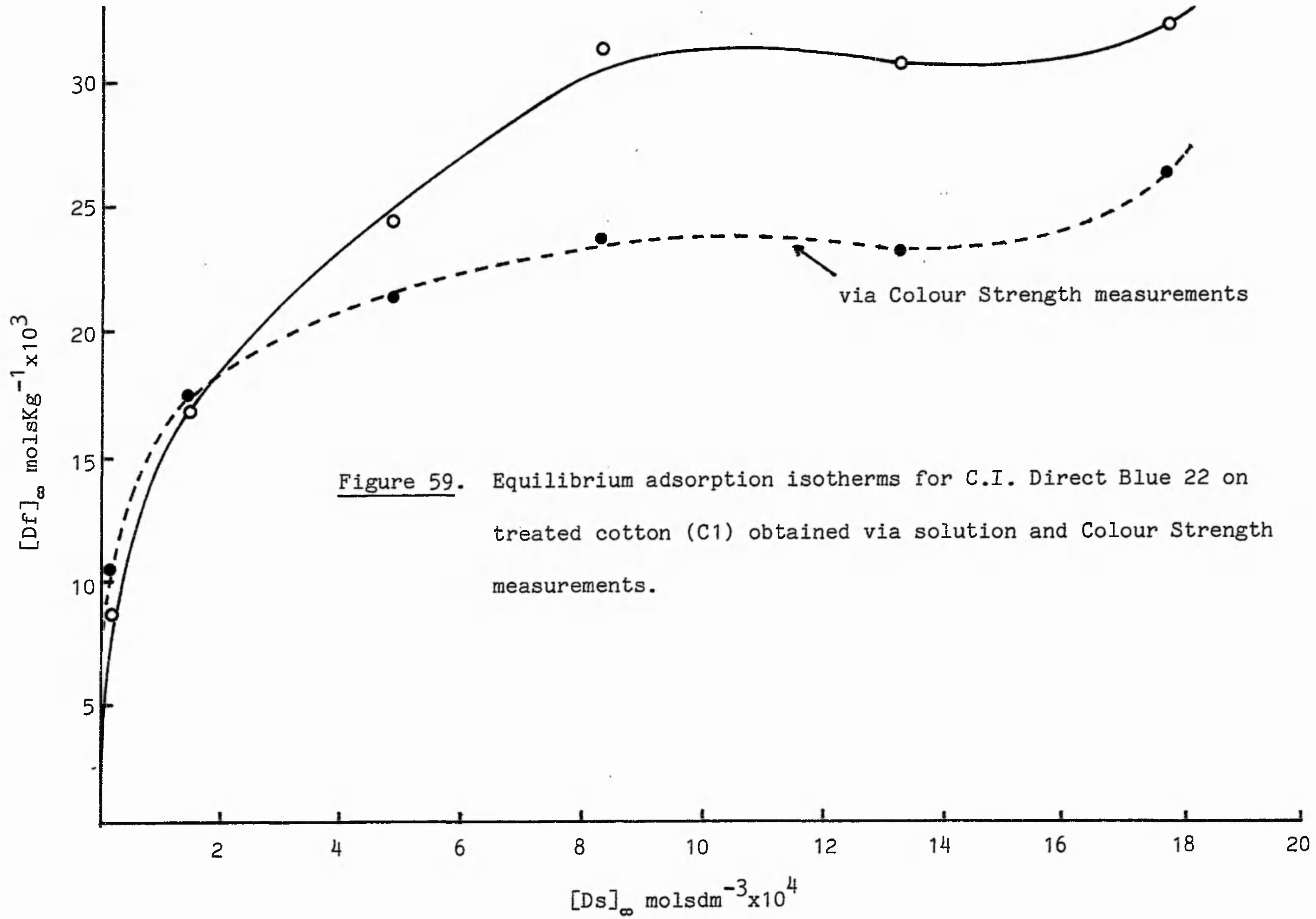


Figure 59. Equilibrium adsorption isotherms for C.I. Direct Blue 22 on treated cotton (C1) obtained via solution and Colour Strength measurements.

Since a considerable degree of diffuse adsorption was expected to occur in the case of the direct dyes, owing to their greater inherent substantivity for cellulose, Colour Strength versus $[Df]_{\infty}$ calibration graphs were drawn up for each of the dyes in question (see p.129 and Appendix III) employing relatively low concentrations of dye in solution so as to minimise the quantity of dye adsorbed diffusely. After soaping the dyed hanks in a non-ionic detergent, Colour Strength measurements were taken using an undyed sample of treated cotton (C1) as standard.

By comparing the Colour Strength obtained with the appropriate calibration graph, C.I. Direct Yellow 12 was observed to have a saturation value of 4.7 mmolsKg^{-1} which was in the same region as that obtained for C.I. Acid Red 13 (which also contained two sulphonic acid groups). In fact, very little diffuse adsorption occurred in the case of this particular direct dye (see graph in Appendix III) which is described in the Colour Index as a 'class A' direct dye (with good levelling or migration properties) and is, according to the technical literature, often used as an acid dye.

In contrast, a much larger degree of diffuse adsorption occurred with C.I. Direct Blue 1 and particularly with C.I. Direct Blue 22 (Appendix III). These dyes are described in the Colour Index as 'class B' and 'C' direct dyes respectively with progressively worsening migration properties which, no doubt, come about as a result of their increased substantivity for cellulose.

C.I. Direct Blue 22, which contained the same number of sulphonic acid groups as C.I. Direct Yellow 12, had a much greater saturation value of 23.4 mmolsKg^{-1} after soaping compared to the value of 4.7 mmolsKg^{-1} obtained for the class A dye. C.I. Direct Blue 1 on the other hand, containing four sulphonic acid groups, would have been expected to reach a saturation value of <2.4 mmolsKg^{-1} in the absence of diffusely adsorbed dye whereas a value of 6.4 mmolsKg^{-1} was actually obtained by extrapolation.

Clearly, therefore,the 1:1 relationship which existed between cationic sites in the fibre and sulphonic acid groups in the dye for the series of acid dyes was far less readily observed in the case of the direct dyes where the inherent substantivity of an individual direct dye for cellulose had a far greater influence on the number of moles of that dye taken up by the treated cotton than the number of sulphonic acid groups it contained.

Returning to the original equilibrium adsorption isotherms obtained for C.I. Direct Blues 1 and 22, similar types of adsorption isotherms were obatined by Iyer et al.[215] who carried out a detailed study of the saturation of the cellulose surface using C.I. Direct Blue 1 on viscose rayon. The plateau regions of the isotherms they obtained occurred at similar $[Ds]_\infty$ concentrations as observed in Figure 58 with treated cotton (C1) and were taken to represent saturation of the adsorbing surface[216]. At the higher values of $[Df]_\infty$ obtained it was suggested that the characteristic interaction taking place was multi-layer ie. between dye molecules rather than a dye-cellulose interaction.

Equilibrium adsorption isotherms for the series of direct dyes were also drawn up using samples of more highly modified cotton (C2), treated in bulk with 10% o.w.f. of the cationic reagent I.

Dyeing trials were carried out employing 2.25×10^{-4} - 2.5×10^{-3} molsdm^{-3} of C.I. Direct Blues 1 and 22 and 2.4×10^{-4} - 1.2×10^{-3} molsdm^{-3} of C.I. Direct Yellow 12 and the results are given in Figures 60, 61 and 62 (and in Appendix III). The equilibrium adsorption isotherm of C.I. Direct Blue 22 on untreated cotton was also determined to establish the extent of diffuse adsorption occurring in the absence of sites under identical conditions and over a similar range of dyebath concentrations.

As can be seen from Figure 60 in the case of C.I. Direct Yellow 12 the saturation value of 4.7 mmolsKg^{-1} obtained with C1 increased to 10.8 mmolsKg^{-1} for C2, after diffusely adsorbed dye had been removed. It would appear that saturation of the available sites did not take place in this instance, possibly as a result of the low dyebath concentrations employed, since the site content of 35.5 mmolsKg^{-1} previously determined for C2 (Table 2, p112) would suggest that at least 17.75 mmolsKg^{-1} of a disulphonated dye should have been capable of being adsorbed.

For C.I. Direct Blue 1 (Figure 61), increasing the site content increased the saturation value from 6.4-13.2 mmolsKg^{-1} whilst in the case of C.I. Direct Blue 22, containing the same number of sulphonic acid groups as C.I. Direct Yellow 12, a much larger amount of this class C dye was taken up by the treated fibre (C2) than had been observed with the class A dye (32 mmolsKg^{-1} as opposed to 10.8 mmolsKg^{-1}). The results for the untreated cotton confirm that this is largely due to the class C dyes inherent substantivity for cellulose since even in the absence of sites a saturation value of 15.4 mmolsKg^{-1} would have been expected at the dye concentrations employed.

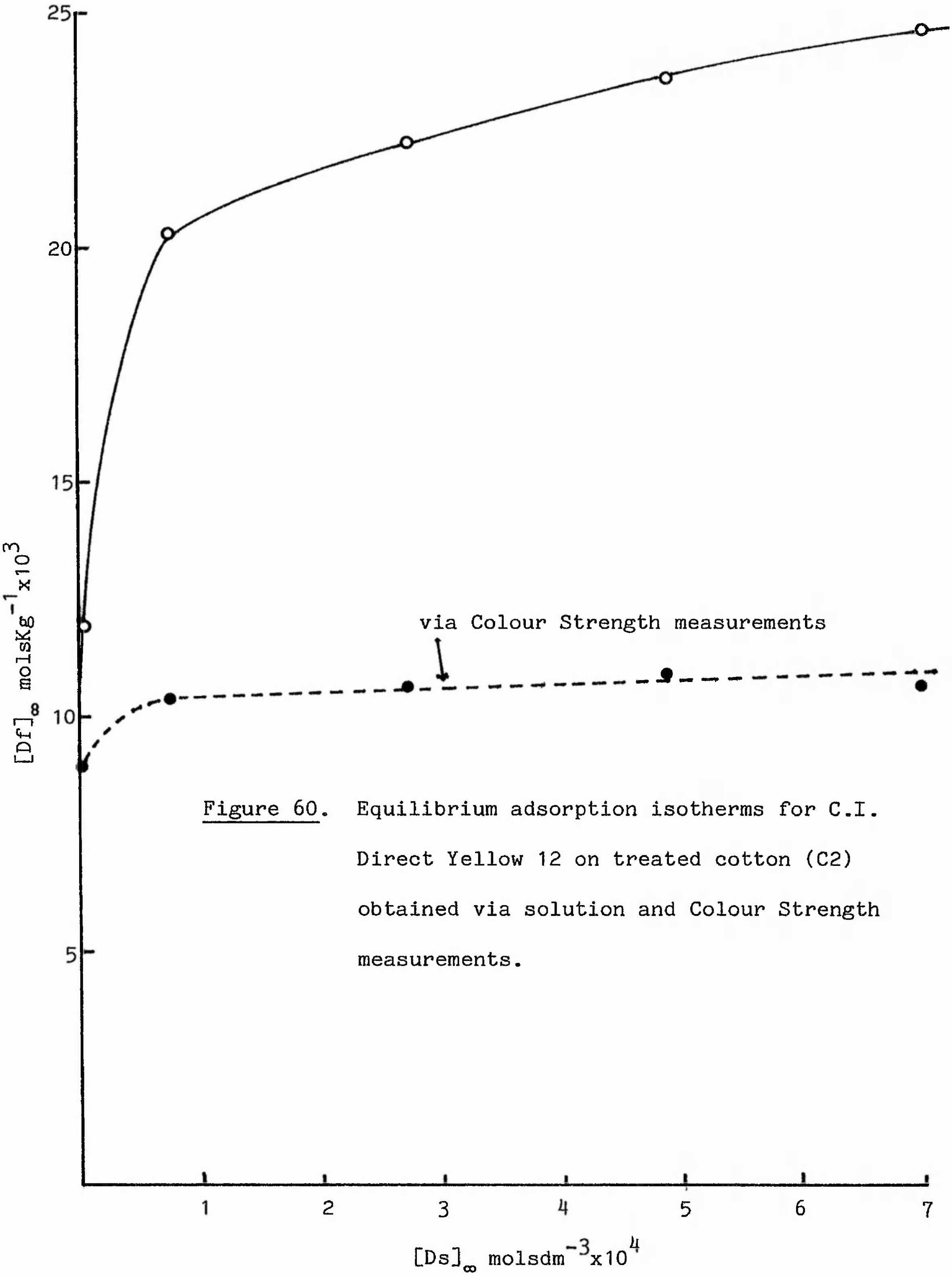


Figure 60. Equilibrium adsorption isotherms for C.I. Direct Yellow 12 on treated cotton (C2) obtained via solution and Colour Strength measurements.

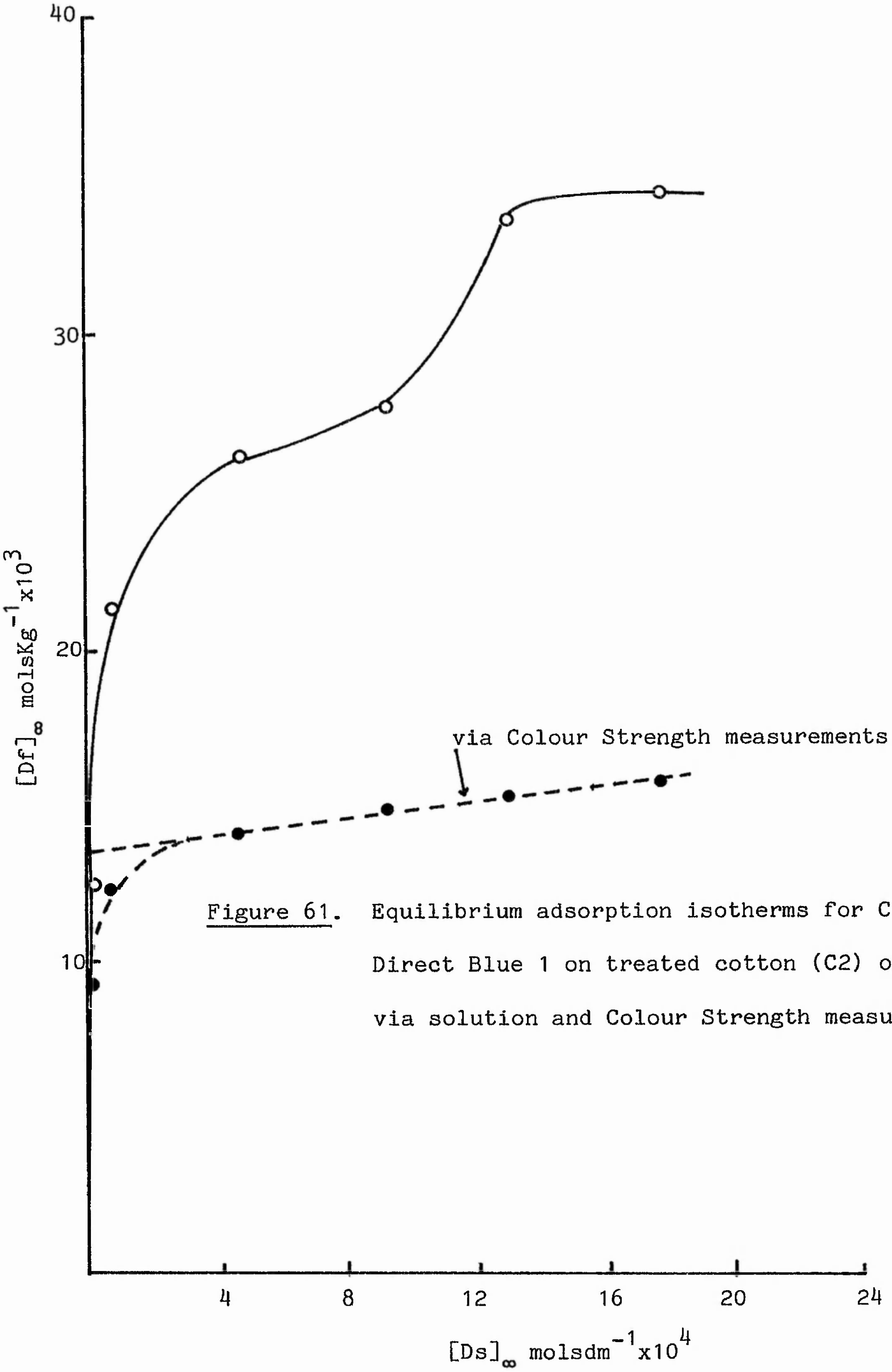


Figure 61. Equilibrium adsorption isotherms for C.I. Direct Blue 1 on treated cotton (C2) obtained via solution and Colour Strength measurements.

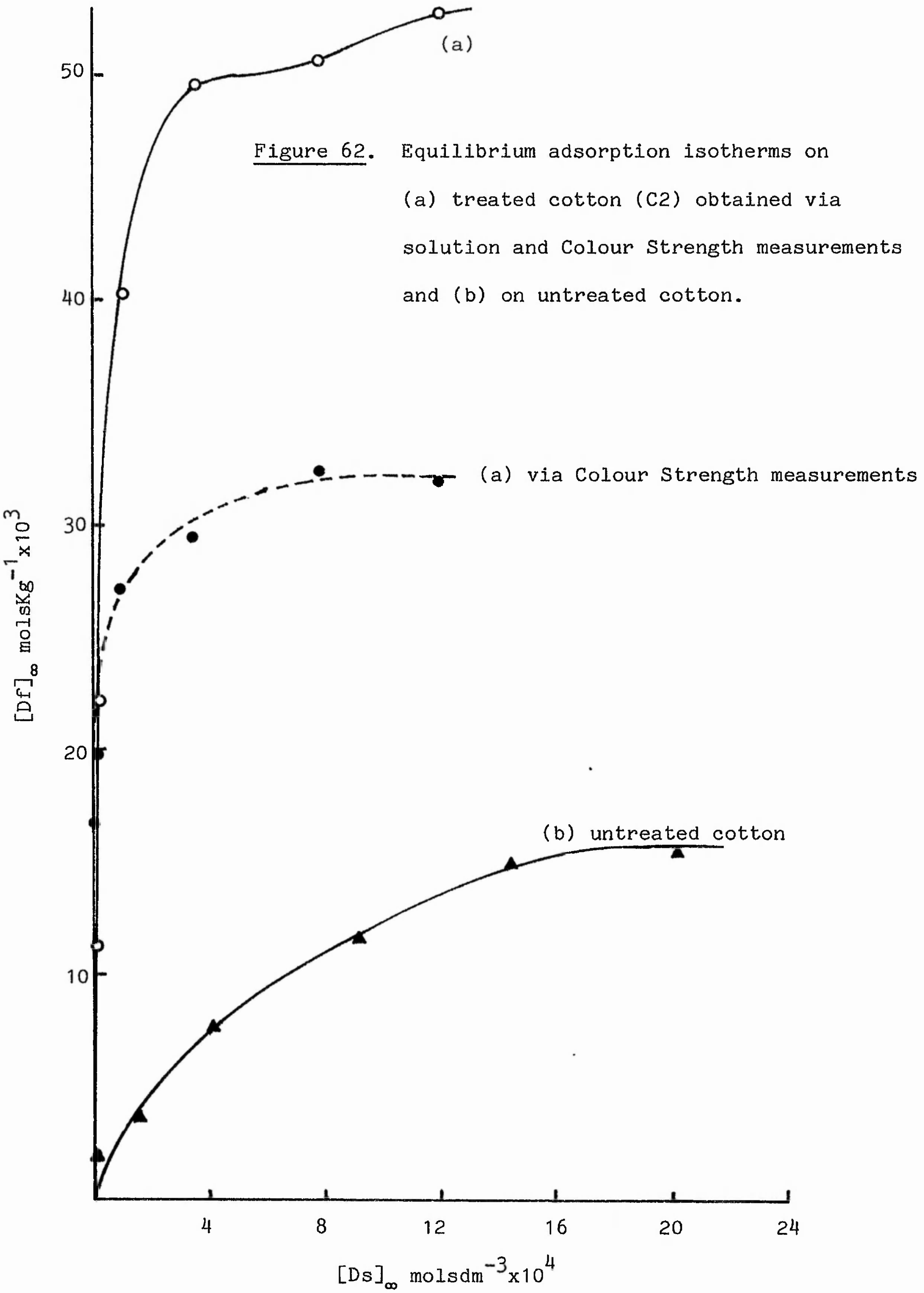


Figure 62. Equilibrium adsorption isotherms on (a) treated cotton (C2) obtained via solution and Colour Strength measurements and (b) on untreated cotton.

In conclusion, the shifts in λmax which were noted in very dilute solutions of the three direct dyes employed are thought to be attributable to complex formation between the anionic dyes and minute quantities of the cationic reagent I which which must have hydrolysed as a result of refluxing the highly treated (C2) cotton in aqueous solution for 6 hours, and thus was no longer covalently bound to the fibre. A similar phenomenon was noted in the case of an aqueous solution of C.I. Direct Blue 1 to which was added another quaternary ammonium compound 'CTAB', cetyl trimethylammonium bromide, λmax again being shifted hypsochromically as a result, it is suggested, of complex formation[217] (CTAB is generally used as aftertreatment agent to improve the wet fastness of direct dyes, the resulting insoluble dye/agent complex formed being faster to wet treatments than the uncomplexed dye).

3.7.2 Factors influencing the differential dye uptake obtained with direct dyes

3.7.2.1 Influence of the counter-ion

In industry anionic levelling agents are used to control the rate of dyeing of wool fibres with acid dyes enabling level dyeings of good penetration to be obtained in large scale processing. They operate by replacing a small counter-ion with a larger (often organic) anion which has a higher affinity for the dye sites and is thus less readily replaced by the dye anions, slowing down the dyeing process.

Obviously an analogous system, involving differential-dyeing cotton as the cationic substrate and similar anionic levelling agents to those used with wool, should therefore be possible and could be of interest, particularly since at the lower liquor to goods ratios often employed in large scale processing greater control of the rate of dyeing would be desirable especially with those dyes, such as directs, which are inherently substantive towards cellulose even in the absence of sites.

The effect of various counter-ions on the rate of dyeing of cotton treated with the cationic reagent I was therefore examined together with their influence on the equilibrium dye uptake. First to be studied were a series of inorganic anions increasing in size according to the series:

$$F^- < Cl^- < Br^- < I^- < SCN^-$$

A preliminary investigation indicated that very little difference in the rate of dyeing and equilibrium dye uptake was observed with these relatively small anions, however, by carrying out a competitive dyeing in which five similarly treated cotton samples, each containing a different counter-ion, were dyed in the same dyebath it was hoped that any slight differences in the equilibrium dye uptake would be accentuated.

Five solutions containing a large excess of the sodium salt of each anion under investigation were prepared and to each was added an equal weight of treated cotton (C1). After steeping the samples for several hours they were rinsed well in distilled water and dyed together in a bath containing 2% o.w.f. C.I. Direct Blue 1 (L.R. 50:1).

Colour Strength measurements were taken for each of the treated samples against an undyed sample of treated cotton (C1) as standard and the results are given in Table 32. As can be seen the equilibrium dye uptake increased according to the order:

$$Br^- < F^- < I^- < Cl^- < SCN^-$$

Table 32. Colour Strength measurements for the competitive dyeing of five treated cotton (C1) samples containing different inorganic counter-ions of increasing size and dyed in a single bath containing 2% o.w.f. C.I. Direct Blue 1.

Anion	Colour Strength
F^-	95.53
Cl^-	99.12
Br^-	91.88
I^-	97.36
SCN^-	100.90

The above results suggest that a number of factors, including the size of the counter-ion, are responsible for determining the ease with which it is replaced by dye anions in the dyeing process such as, for example, the affinity of the anion and its solubility.

In order to determine whether the use of larger anions as counter-ions would bring about a more pronounced effect on the rate of dyeing and equilibrium dye uptake three large organic anions, whose structures are given below in Figure 63, were selected for use in a further dyeing trial.

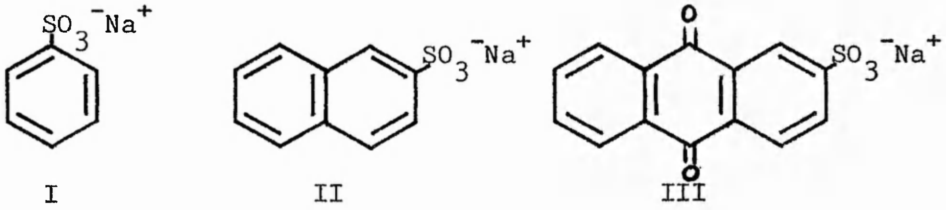


Figure 63.

I Benzene sulphonic acid (sodium salt)

II Naphthalene-2-sulphonic acid (sodium salt)

III Anthraquninone-2-sulphonic acid (sodium salt)

Saturated solutions of the sodium salt of each anion were prepared and to each was added five 1 g samples of treated cotton (C1). After allowing the samples to come to equilibrium over several hours they were rinsed well and each set containing a different counter-ion was dyed for 2 hours in a single dyebath containing 2% o.w.f. C.I. Direct Blue 1, removing samples at 15 minute intervals over the first hour.

After soaping, Colour Strength measurements were carried out on all the samples against undyed treated cotton (C1) as standard, and the results are given in Table 33 alongside those for the chloride ion which had been determined earlier. As can be seen in Figure 64 the size of the counter-ion does not appear to have significantly affected the rate of dye uptake, in fact samples in which naphthalene-2-sulphonic acid was the counter-ion were observed to have the slowest rate of dyeing which might possibly be attributed to the strong affinity of this anion for the positive sites incorporated into the fibre by this particular reagent, since it had earlier been prepared by quaternisation of the free base with 1-chloromethyl naphthalene.

Table 33. Colour Strength measurements, for four sets of treated cotton (C1) samples, each containing different counter-ions and dyed in a single dyebath containing 2% o.w.f. C.I. Direct Blue 1.

Time (minutes)		Colour Strength Counter-ion		
	chloride	I	II	III
15	52.58	52.43	46.34	51.58
30	63.70	67.57	59.42	65.94
45	73.85	76.02	73.69	77.72
60	72.73	76.87	77.78	75.77
120	96.78	91.96	91.73	91.51

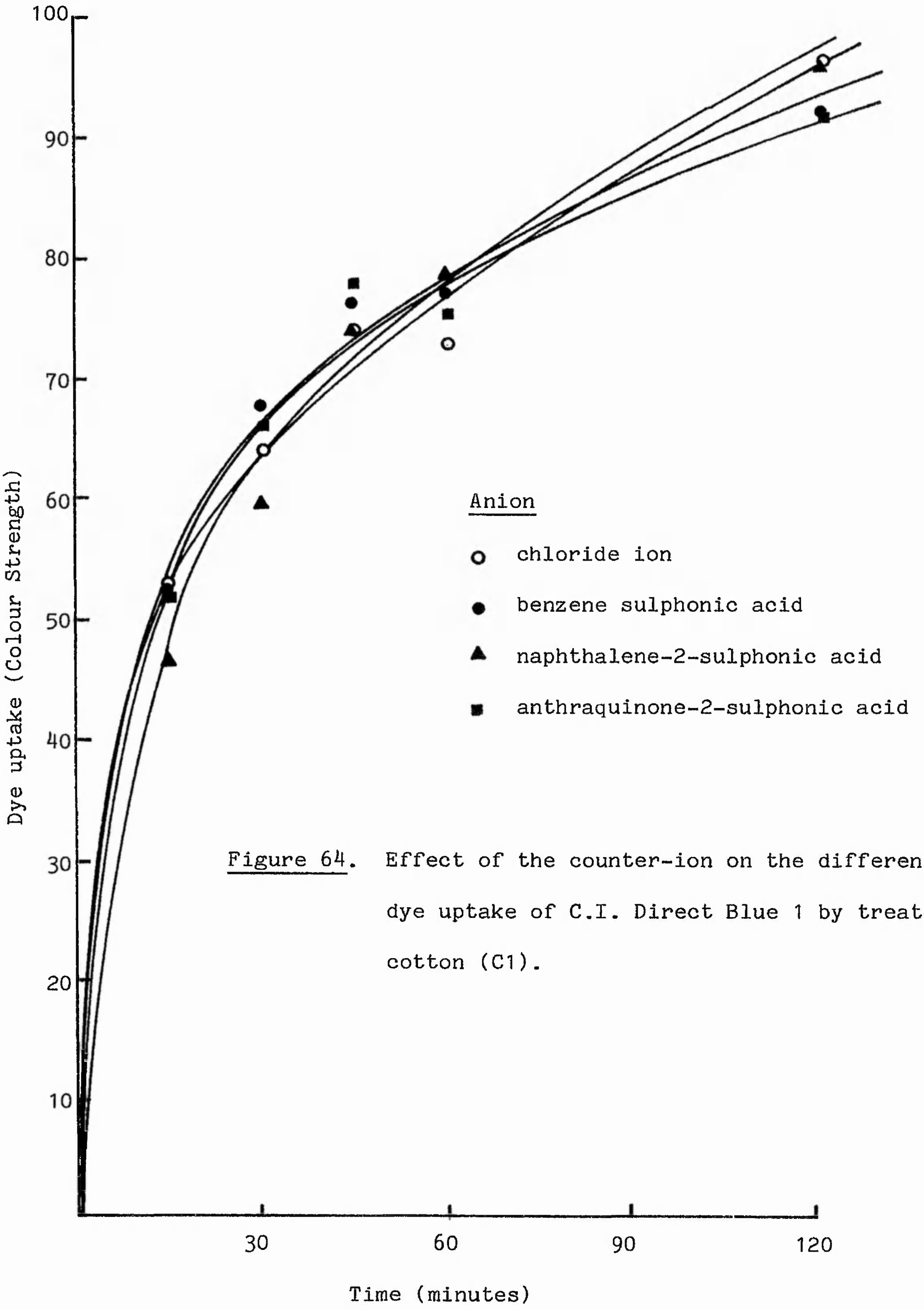


Figure 64. Effect of the counter-ion on the differential dye uptake of C.I. Direct Blue 1 by treated cotton (C1).

This could point the way to how choice of a suitable reagent combined with a particular anionic levelling agent may be used to lower the rate of dye uptake although, in so far as the size of the quaternising agent is concerned, there are limitations which may have to be taken into account such as, for example, whether the time required for quaternisation (which increases as the size of the quaternising agent increases) may preclude the use of a particular reagent or whether, in fact, steric factors may even prevent quaternisation occurring altogether.

The equilibrium dye uptake was observed to increase with decreasing size of the counter-ion, as expected, although the difference between the small inorganic chloride ion and the three larger organic anions was of much greater significance than the difference between the individual organic anions:

III < II < I << chloride ion

Possibly the use of a small acid dye of low affinity for native cellulose, such as C.I. Acid Orange 7, may have highlighted the differences between the counter-ions more successfully than the use of C.I. Direct Blue 1 (a class B dye) with its high intrinsic substantivity for cellulose.

3.7.2.2 Effects of ancillary treatments

The effects of ancillary treatments, such as bleaching and mercerisation of pretreated cotton (C2) were examined in order to determine at which stage in the large scale processing of cotton treatment with the reagent would best be carried out so as not to adversely effect the degree of differential dye uptake obtained.

Since treatment with the reagents tends to cause a slight yellowing of the fibres it would be advantageous if bleaching, for example, could be carried out on cotton already treated with the reagent so improving shade reproducibility on dyeing the treated material particularly where extremely bright pale shades are required, when a slight discolouration of the substrate can significantly affect the final results obtained.

Five 1 g samples of the treated cotton (C2) were therefore prepared, one of which was mercerised under tension according to a standard technique employing 52°Tw (24%) sodium hydroxide, three were bleached with sodium hypochlorite, hydrogen peroxide and sodium chlorite respectively, and one was retained without any further treatment as a standard. (For further details of the treatments see section 5.13).

After soaping, they were each added to one of five dyebaths containing 3% o.w.f. C.I. Direct Blue 1 (L.R. 50:1) and dyed for 1 hour at 96°C in the presence of an equal weight of untreated cotton. They were then resoaped individually and Colour Strength measurements were taken for the treated samples. The results are given in Table 34. 'Load at break' measurements of the variously treated samples were also carried out using an Instron 1122 Tensile Tester (scale 0-50N).

As can be seen from Table 35, treatment with the cationic reagent I, particularly at the 10% o.w.f. (C2) level, was shown to actually increase the breaking strength of the treated yarn over that of untreated cotton. (However, since no account was taken of any change in the thickness of the treated yarns it cannot be said whether this represents a real increase in their tensile strengths, normally measured in $Kgmm^{-2}$).

Table 34. Colour Strength measurements to illustrate the effects of bleaching and mercerisation on the differential dye uptake of modified cotton (C2).

Sample	Treatment	Colour Strength
1	-	266.81
2	mercerised	454.54
3	bleached (NaOCl)	269.69
4	bleached (H_2O_2)	125.14
5	bleached ($NaClO_2$)	200.28

Table 35. Load at break (N) and Tenacity ($Ntex^{-1}$) measurements to illustrate the effect of various bleaching and mercerisation treatments on the breaking strength of modified cotton (C2).

Cotton sample	Load at Break (N)	Tenacity ($Ntex^{-1}$) tex = 220/3	% change in tenacity from standard (1)
Untreated	30.0	0.14	
2.5% reagent treated	31.6	0.14	
10.0% reagent treated	37.2	0.17	
1	37.8	0.17	—
2	47.0	0.21	+23.5
3	37.8	0.17	0
4	10.0	0.05	-70.6
5	33.6	0.15	-11.8
4a)	25.4	0.12	-29.4

See Appendix V for photographs of test samples.

Mercerisation of the treated yarn was observed to further increase the tenacity by 23.5% from that of the standard sample (1), whilst dyeing of the mercerised sample with C.I. Direct Blue 1 resulted in a 70% increase in the Colour Strength compared to that obtained on the dyed standard.

Bleaching of the treated samples with sodium hypochlorite had no significant effect on either the Colour Strength or the tenacity and at the same time a softer handle was conferred on the dyed yarn.

In contrast, a very significant loss in Colour Strength (by 53%) and tenacity (by 71%) was observed when bleaching was carried out in hydrogen peroxide solution. This very severe degree of tenderisation was later found to be due to the use of distilled water as opposed to ordinary hard water. Sodium silicate, which is generally used to stabilise hydrogen peroxide solutions was found to only do so in the presence of alkaline earth ions, that is in hard water; in soft water it was found to actually activate the hydrogen peroxide because its solution had an alkaline reaction[218].

However, even when bleaching of the treated sample was carried out using a solution of hydrogen peroxide in hard water (4a), although the Colour Strength was much improved (198.46) and quaternary dye sites less affected, the loss in tenacity of 29% compared with the standard dyeing (1) still left much to be desired. On the other hand a bleaching treatment employing sodium chlorite was shown to have the opposite effect in that a greater loss in Colour Strength, and hence in the availability of dye sites, was accompanied by a much less severe degree of tenderisation (only 12%).

From the above results it may be concluded that bleaching of cotton already treated with the cationic reagent I can successfully be carried out without affecting the positive sites incorporated into the fibre or tendering of the fibres using sodium hypochlorite as the bleaching agent. This result confirms that the present treatment has certain advantages over earlier attempts to prepare cellulosic fibres of modified dyeability.

Ward and Hill[161], for example, who prepared the acid-dyeable 'DD' viscose fibres using a cellulose derivative containing basic groups linked directly to cellulose itself (possibly diethylaminoethylcellulose) found that when treating them with sodium hypochlorite, sodium chlorite or hydrogen peroxide at the strengths necessary for cotton bleaching, the DD fibres suffered irreversible loss in dyeability.

Treatment of cotton with the cationic reagent I was also shown to be fast to mercerisation and as a consequence, not suprisingly, mercerisation of the treated yarn prior to dyeing was observed to have considerable advantages, improving the breaking strength properties of the yarn and increasing the Colour Strength obtained on the treated fibre for a given dye content, so reducing dye consumption (see Appendix V-4).

3.7.2.3 Effect of electrolyte concentration

The effect of electrolyte concentration on the degree of contrast obtained between treated and untreated cotton dyed in the same bath was examined by dyeing six 1 g hanks of treated cotton (C2) for 1 hour at 96°C in baths containing 3% o.w.f. C.I. Direct Blue 1 and a range of sodium chloride concentrations (from 0-40% o.w.f.) in the presence of an equal weight of untreated cotton.

Colour Strength measurements were than taken (against an undyed portion of C2 or an untreated cotton sample as standard as appropriate) and the degree of contrast obtained between treated and untreated samples expressed as the ratio of their Colour Strengths, Colour Strength (treated)/Colour Strength (untreated).

The contrast between treated and untreated hanks can be seen (in Figure 65) to increase with decreasing concentration of electrolyte in the dyebath although in both cases more direct dye was actually going onto the fibres. These increases in dye uptake with increasing ionic strength of the dyebath may be attributed to the increased chemical potential of the dye in the solution and to screening of the negative surface charge which native cellulose acquires in solution, allowing dye anions to approach more closely before electrical repulsion becomes evident (so lowering the activation energy of the dyeing process). In the particular case of diffusely adsorbed dye the electrical repulsion between dye anions adsorbed on the cellulose surface will also be reduced in the presence of higher concentrations of electrolyte.

Table 36. Effect of electrolyte concentration on the contrast obtained between treated (C2) and untreated cotton dyed together with C.I. Direct Blue 1.

[NaCl] % o.w.f.	Colour Strength 10%	0%	Ratio of Colour Strengths 10%/0%
0	229.91	24.84	9.26
5	256.60	36.74	6.98
10	268.18	42.90	6.25
20	279.74	54.33	5.15
30	287.65	60.30	4.77
40	287.37	68.49	4.20

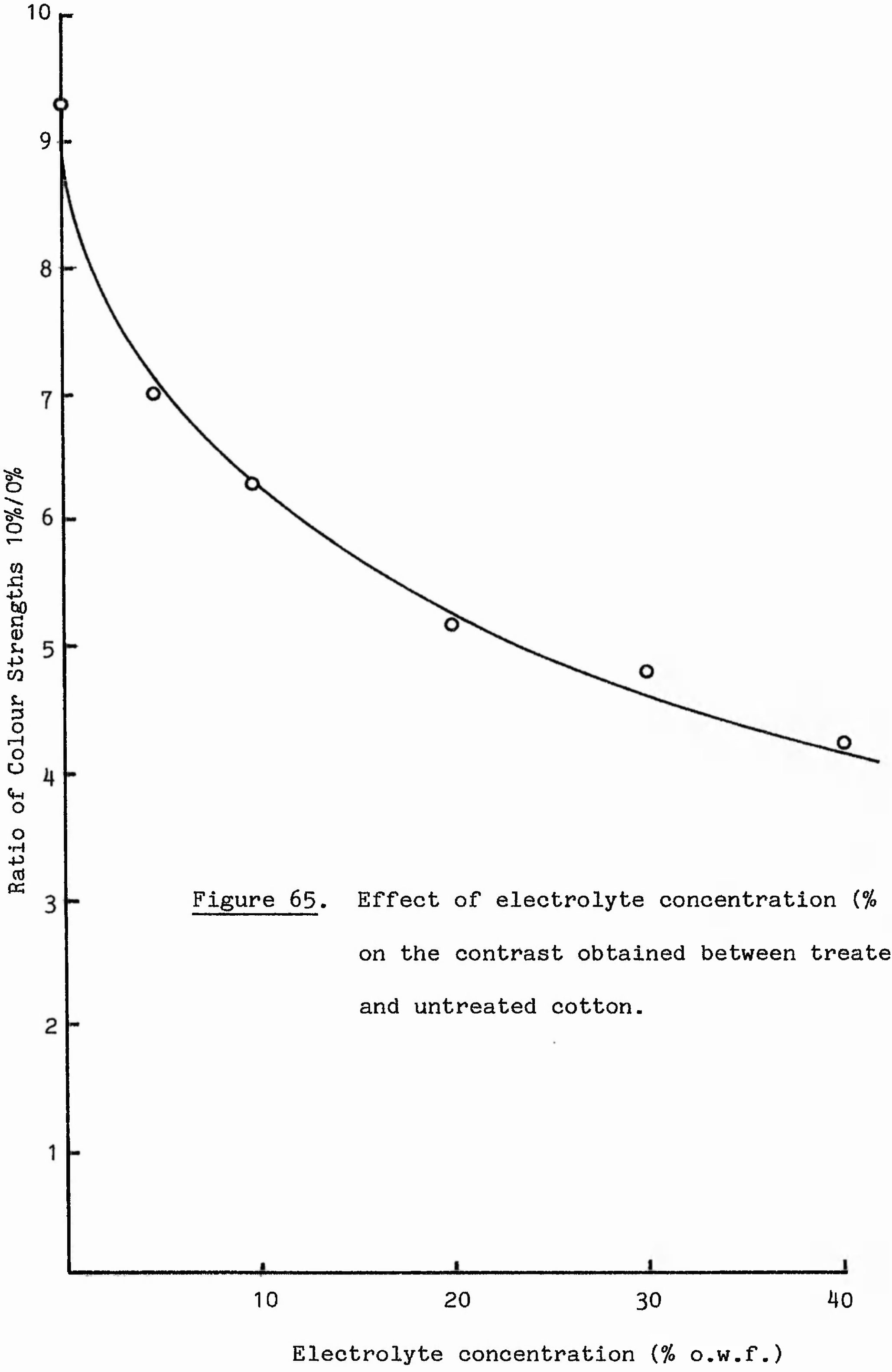


Figure 65. Effect of electrolyte concentration (% o.w.f.) on the contrast obtained between treated (C2) and untreated cotton.

In terms of their effect on the degree of contrast, however, small increases in the amount of dye taken up by the untreated sample are of far greater importance than similar amounts taken up by the treated portion. The maximum degree of contrast was thus obtained in the complete absence of additional electrolyte when the concentration of dye taken up by the untreated sample was at a minimum.

In fact, since a commercial dye sample was used in the study and was known to contain only 21% dye a small quantity of sodium chloride (<5% o.w.f.) was probably already present in the dyebath as an impurity in the dye prior to any further additions so that if pure dye was used it is possible that an even greater degree of contrast might be obtained.

3.7.2.4 Effect of liquor ratio

The study of the effect of liquor ratio on the contrast obtained between treated and untreated cotton was carried out by the same procedure as described in section 3.7.2.3 excepting that in this case all the dyeings were carried out for 1 hour at 96°C in the absence of added electrolyte and over a range of liquor ratios from 50-20:1 (o.w.f.).

As can be seen in Figure 66 the maximum contrast was achieved at the longest liquor ratio employed (50:1) probably due to the reduction in diffuse adsorption occurring as a result of the decrease in dyebath concentration. At even longer liquor ratios greater contrasts might be expected although from a commercial standpoint it is unlikely that they would be employed, especially since short liquor ratios are more economically viable and even at 20:1 - the shortest liquor ratio employed - very good contrast between treated and untreated cotton was obtained.

Table 37. Effect of liquor ratio on the contrast obtained between treated (C2) and untreated cotton dyed together with C.I. Direct Blue 1.

L.R. (o.w.f.)	Colour Strength 10%	 0%	Ratio of Colour Strengths 10%/0%
20:1	262.00	31.73	8.26
30:1	254.82	31.05	8.21
40:1	245.01	28.15	8.70
50:1	229.91	24.84	9.26

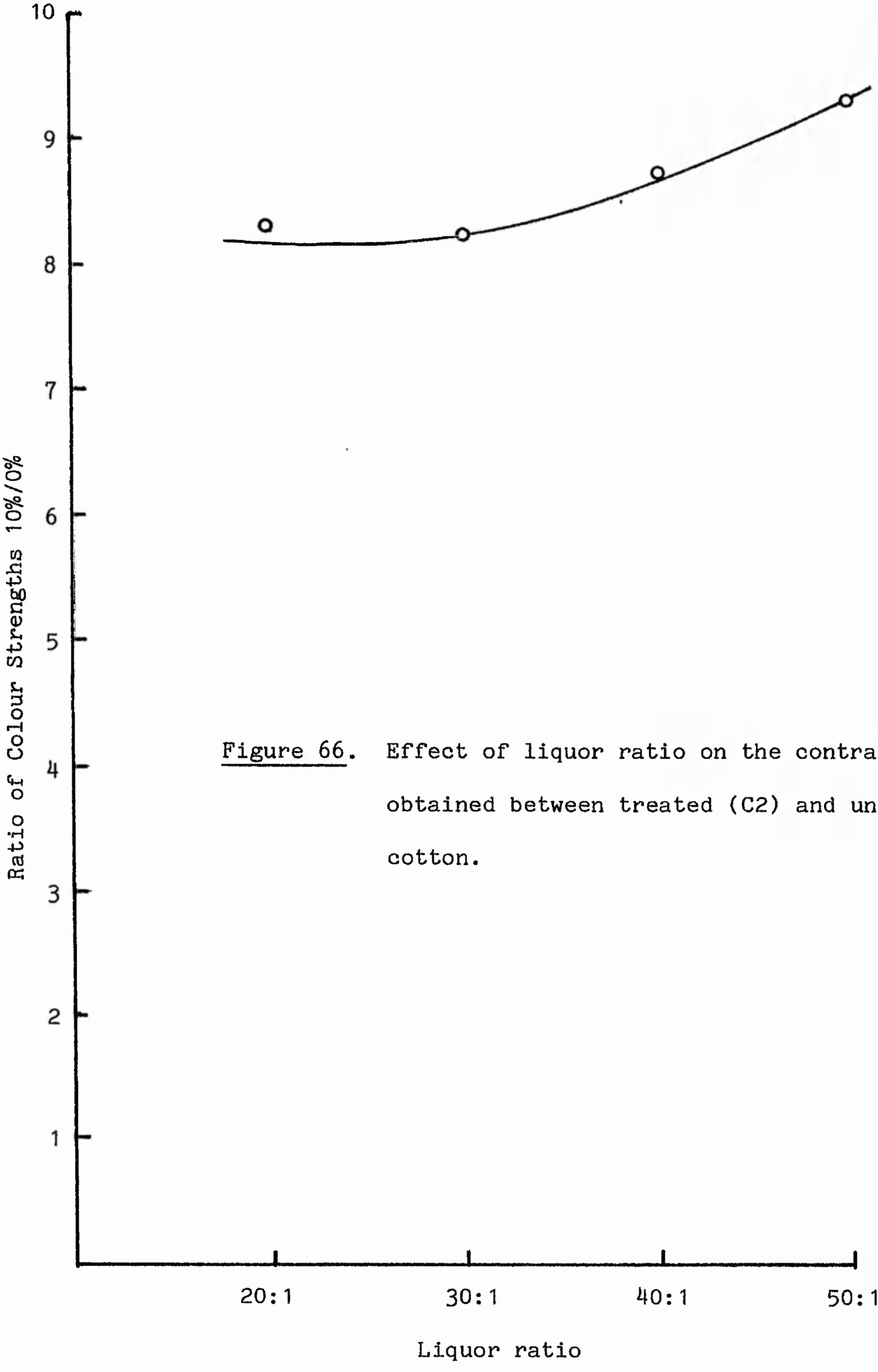


Figure 66. Effect of liquor ratio on the contrast obtained between treated (C2) and untreated cotton.

3.7.2.5 Effect of dyeing time

The effect of the time of dyeing on the contrast obtained between treated and untreated cotton was investigated according to the procedure outlined in section 3.7.2.3, excepting that in this case dyeing was carried out at 80°C in the absence of added electrolyte and at a L.R. of 50:1 for 1-4 hours. The results are given in Table 38 and are illustrated in Figure 67.

As can be seen the contrast was observed to improve significantly with time particularly as the time of dyeing was extended over >2 hours when dye was observed to desorb from the untreated cotton whereas the amount adsorbed on the treated cotton increased.

In practice, however, dyeing for this length of time would be uneconomical and a far better way of improving contrast might be to carry out the dyeing for only 1 hour at a higher temperature since greater contrasts seemed to be achieved when dyeing was carried out at 96°C.

Table 38. Effect of dyeing time on the contrast obtained between treated (C2) and untreated cotton dyed together with C.I. Direct Blue 1.

Time	Colour Strength		Ratio of Colour
(hours)	10%	0%	Strengths 10%/0%
1	199.99	35.94	5.56
2	228.70	38.33	5.97
3	249.55	36.58	6.82
4	258.29	32.03	8.06

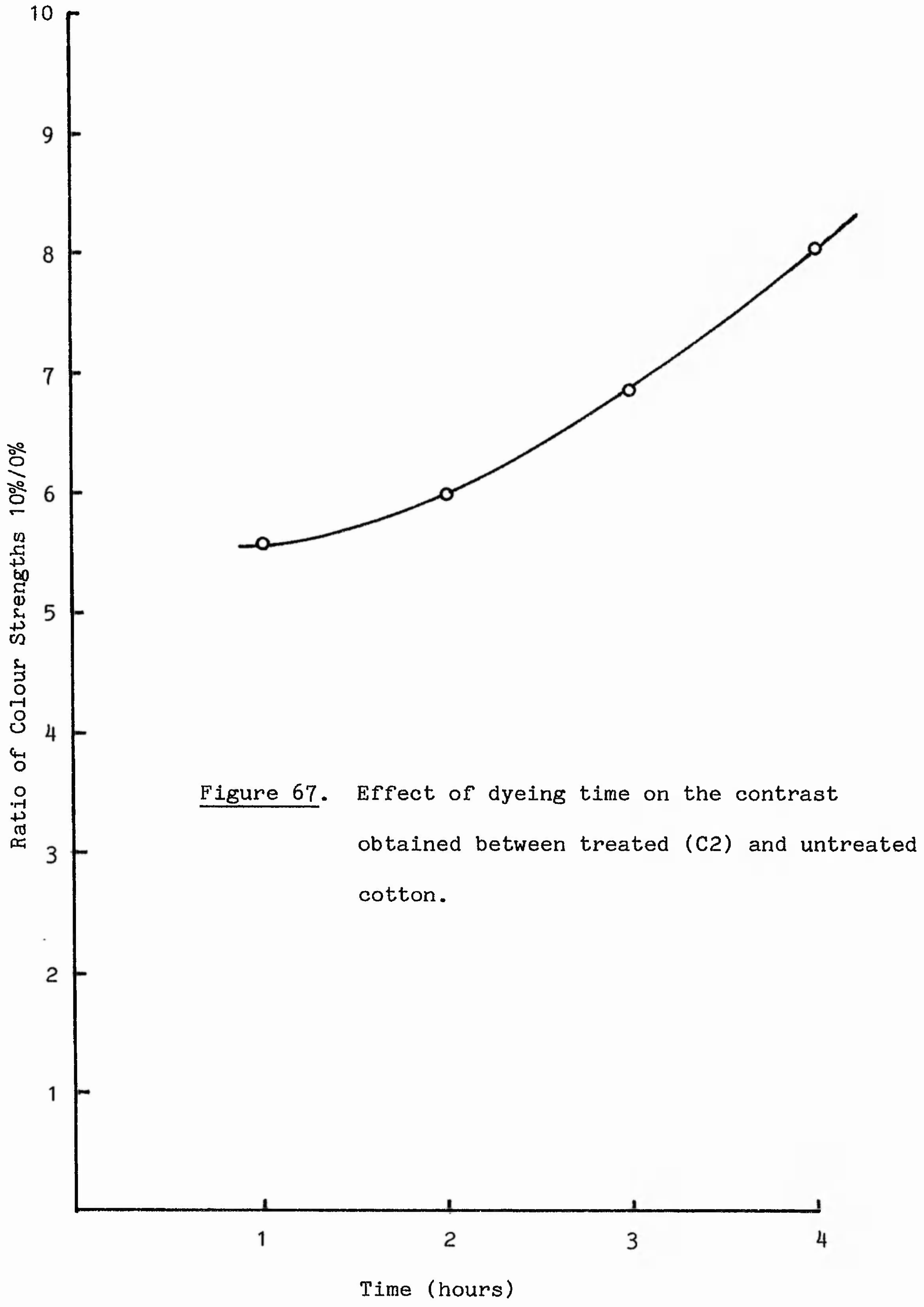


Figure 67. Effect of dyeing time on the contrast obtained between treated (C2) and untreated cotton.

3.7.2.6 Effect of dyeing temperature

In order to determine whether the greatest contrast between treated and untreated cotton was achieved by dyeing samples at 96°C or at a slightly lower temperature, the effect of temperature was examined according to the procedure outlined in section 3.7.2.3 excepting that in this case dyeing was carried out for 1 hour in the absence of added electrolyte (L.R. 50:1) over a temperature range of 70-96°C.

The contrast was observed to be greatest at the highest temperature employed where the degree of diffuse adsorption occurring was probably the least. Unexpectedly, however, by far the greatest increase in contrast was observed over the range 80-90°C so that from a commercial standpoint it would appear that the optimum contrast between treated and untreated cotton would be achieved by carrying out the dyeing for 1 hour at 90°C in the absence of electrolyte and at as high a liquor ratio as economically practical.

Table 39. Effect of temperature on the contrast obtained between treated (C2) and untreated cotton samples dyed together with C.I. Direct Blue 1.

Temperature (°C)	Colour Strength 10%	Colour Strength 0%	Ratio of Colour Strengths 10%/0%
70	196.34	44.39	4.42
80	199.99	35.94	5.56
90	244.04	27.49	8.88
100	229.91	24.84	9.26

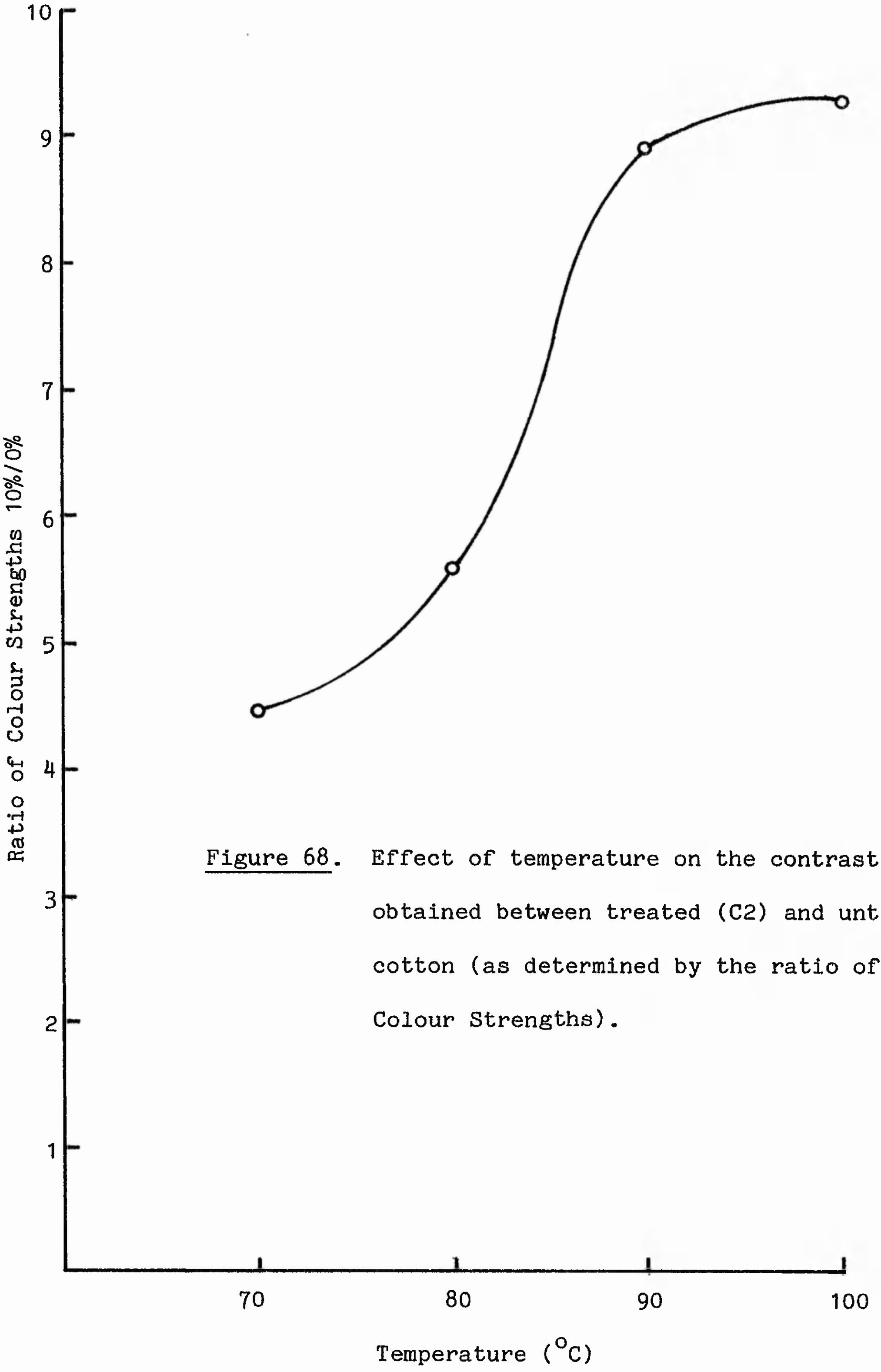


Figure 68. Effect of temperature on the contrast obtained between treated (C2) and untreated cotton (as determined by the ratio of their Colour Strengths).

3.7.3 The adsorption of mixtures of anionic dyes by differential-dyeing cotton

3.7.3.1 Stoichiometry of the adsorption process

In practical dyeing, mixtures are far more frequently used than single dyes to produce a desired shade. In the dyeing of nylon with acid dyes, for example, mixtures of yellow and blue dyes are often used to obtain green, provided that the dyes have been shown to be compatible, ie. that preferential uptake of one dye to the exclusion of the other (leading to what is known as a 'blocking-off' effect) does not occur. In fact two dyes which are known to produce a blocking-off effect on nylon, C.I. Acid Yellow 17, containing two sulphonic acid groups, and C.I. Acid Blue 47[219], containing one sulphonic acid group, were also shown to produce a similar effect on differential-dyeing cotton since both substrates have a limited number of available cationic sites for uptake of anionic dyes (see section 5.10.1). At depths of shade where the total amount of dye present initially was more than that required to saturate the fibre the blue component of the mixture, containing only one sulphonic acid group, was found to be more substantive toward cellulose than the yellow component and was also capable of a better build-up on the modified cotton resulting in a 1:1 (% o.w.f.) mixture of the two dyes producing a dyeing which was much bluer than expected.

The structures of C.I. Acid Yellow 17 and C.I. Acid Blue 47 are given below in Figures 69 and 70.

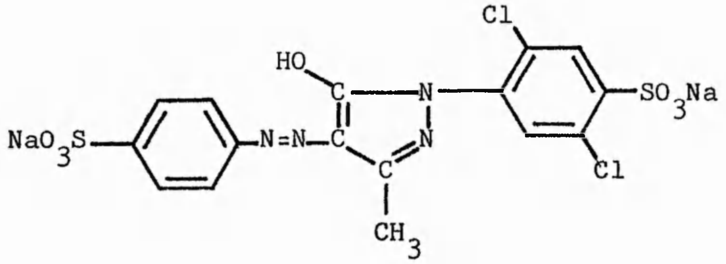


Figure 69. Molecular structure of C.I. Acid Yellow 17; C.I. 18965.

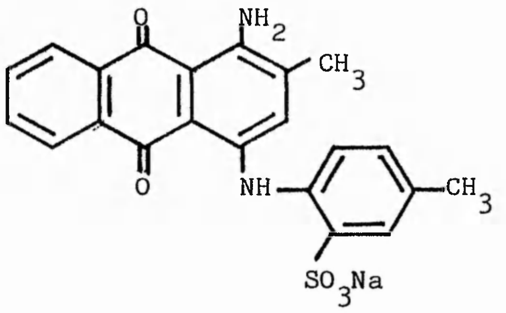


Figure 70. Molecular structure of C.I. Acid Blue 47; C.I. 62085.

It was therefore decided to examine the adsorption of two binary dye mixtures on the modified cotton (C1); (1) containing a 1:1 equimolar mixture of C.I. Direct Yellow 12 and C.I. Direct Blue 22 (both having the same degree of sulphonation) and (2) consisting of a 1:1 equimolar mixture of C.I. Direct Yellow 12 and C.I. Direct Blue 1 containing two and four sulphonic acid groups respectively.

Equimolar 1:1 binary mixtures of the appropriate purified dyes were therefore made up and diluted appropriately so as to give concentrations in the range $5 \times 10^{-5} - 2.0 \times 10^{-3}$ $\mathrm{molsdm^{-3}}$ total dye. These concentrations were chosen so as to be able to examine a potential blocking-off effect before and after saturation of the fibre. (C.I. Direct Yellow 12 had previously been shown to saturate similarly treated cotton at an initial concentration of 4×10^{-4} molsdm^{-3} in the absence of another dye).

For each binary mixture an equal weight of treated cotton (C1) was added to each dyebath at 60°C and dyeing was carried out for 1 hour at 96°C in the absence of additional electrolyte (L.R. 50:1). The hanks were than soaped at 60°C in 2% o.w.f. of a non-ionic detergent and the amount of each dye on the individual samples determined by a colorimetric method outlined below.

Using the relationship Kc = F(R) and the Kubelka-Munk reflectance function described in section 3.3.4 it may be seen that by determining the reflectance of a mixture dyeing and of individually dyed samples for each dye at their respective λmax's the concentration of each dye on the fibre, CB and CY, may be calculated (provided the absorption coefficients KB and KY are known) using the relationships expressed below in equations (1) and (2) below. (The values of λmax given are those for C.I. Direct Blue 22 and C.I. Direct Yellow 12 respectively).

$$F(R)_{600} = KY_{(600)}CY + KB_{(600)}CB \ldots\ldots\ldots\ldots\ldots (1)$$

$$F(R)_{420} = KY_{(420)}CY + KB_{(420)}CB \ldots\ldots\ldots\ldots\ldots (2)$$

The absorption coefficients K, for each dye at each wavelength were first determined using calibration samples for the two dyes in question and for which the individual concentrations of $[Df]_\infty$ were already known. Reflectance measurements were carried out on each dyed sample at each wavelength enabling K to be calculated. Inserting the respective K values, equations (1) and (2) could then be solved to give CB and CY. The results are given in Tables 41 and 43 for mixtures (1) and (2) respectively. Ratios of CB/CY are also shown to illustrate the stoichiometry of the relationship between the two dyes in question and Colour Strength measurements were taken to indicate increasing or decreasing total concentrations of dye on the fibre.

As can be seen in Figure 71 for mixture (1), in which both dyes contained two sulphonic acid groups, at low $[Ds]_o$ the stoichiometry of their relationship was 1:1 (CB/CY = 1.01) as equal concentration of the two dyes were adsorbed on the positive sites incorporated into the fibre. As $[Ds]_o$ increased and saturation of the available sites occurred the concentration of C.I. Direct Blue 22 on the fibre increased relative to that of C.I. Direct Yellow 12 (CB/CY increased) probably on account of its much greater substantivity towards cellulose and hence the greater degree of diffuse adsorption it exhibited as a result.

At the higher values of $[Ds]_o$, however, the concentration of C.I. Direct Yellow 12 on the fibre also began to increase due to diffuse adsorption and CB/CY gradually decreased to a point where it eventually levelled off (CB/CY = 1.79), both dyes being diffusely adsorbed at their own individual rates, the blue class C dye adsorbing at a faster rate than the yellow class A dye as might be expected from their respective substantivities for cellulose.

In the case of mixture (2) the stoichiometry at low $[Ds]_o$ was found to be 1.11 - saturation of the available sites being expected to occur at a lower concentration in the presence of a tetrasulphonated dye. However, as $[Ds]_o$ increased it can be seen that CB levelled off

Table 40. Reflectance measurements on the individual calibration dyeings of known concentration for the calculation of K values.

Standard	Reflectance		Kc =	C	Adsorption
sample	λ_1 = 420 nm	λ_2 = 600 nm	$(1-R)^2/2R$	mmolsKg^{-1}	coefficients, K
DY12	0.1963	0.8330	1.6453 0.0167	0.773	KY_{420} = 2.1284 KY_{600} = 0.0217
DB22	0.3023	0.0971	0.8051 4.1979	1.890	KB_{420} = 0.4260 KB_{600} = 2.2211

Table 41. Reflectance measurements on treated cotton (C1) dyed with mixture (1) for the determination of the concentration of each dye on the fibre.

$[Ds]_o$	Colour	Reflectance		Kc =	CB	CY	CB/CY
molsdm^{-3} x10^{3}	Strength	λ_1 = 420 nm	λ_2 = 600 nm	$(1-R)^2/2R$			
0.125	119.66	0.098	0.1086	4.1510 3.6584	1.63	1.62	1.01
0.25	186.69	0.0805	0.0668	5.2514 6.5184	2.92	1.88	1.55
0.50	201.97	0.0822	0.0590	5.1238 7.5041	3.36	1.73	1.94
0.75	243.43	0.0703	0.0502	6.1475 8.9853	4.03	2.08	1.93
1.00	241.51	0.0701	0.0511	6.1677 8.8103	3.95	2.11	1.87
1.50	249.62	0.0671	0.0506	6.4851 8.9067	3.99	2.25	1.77
2.00	243.53	0.0688	0.0516	6.3018 8.7157	3.90	2.18	1.79

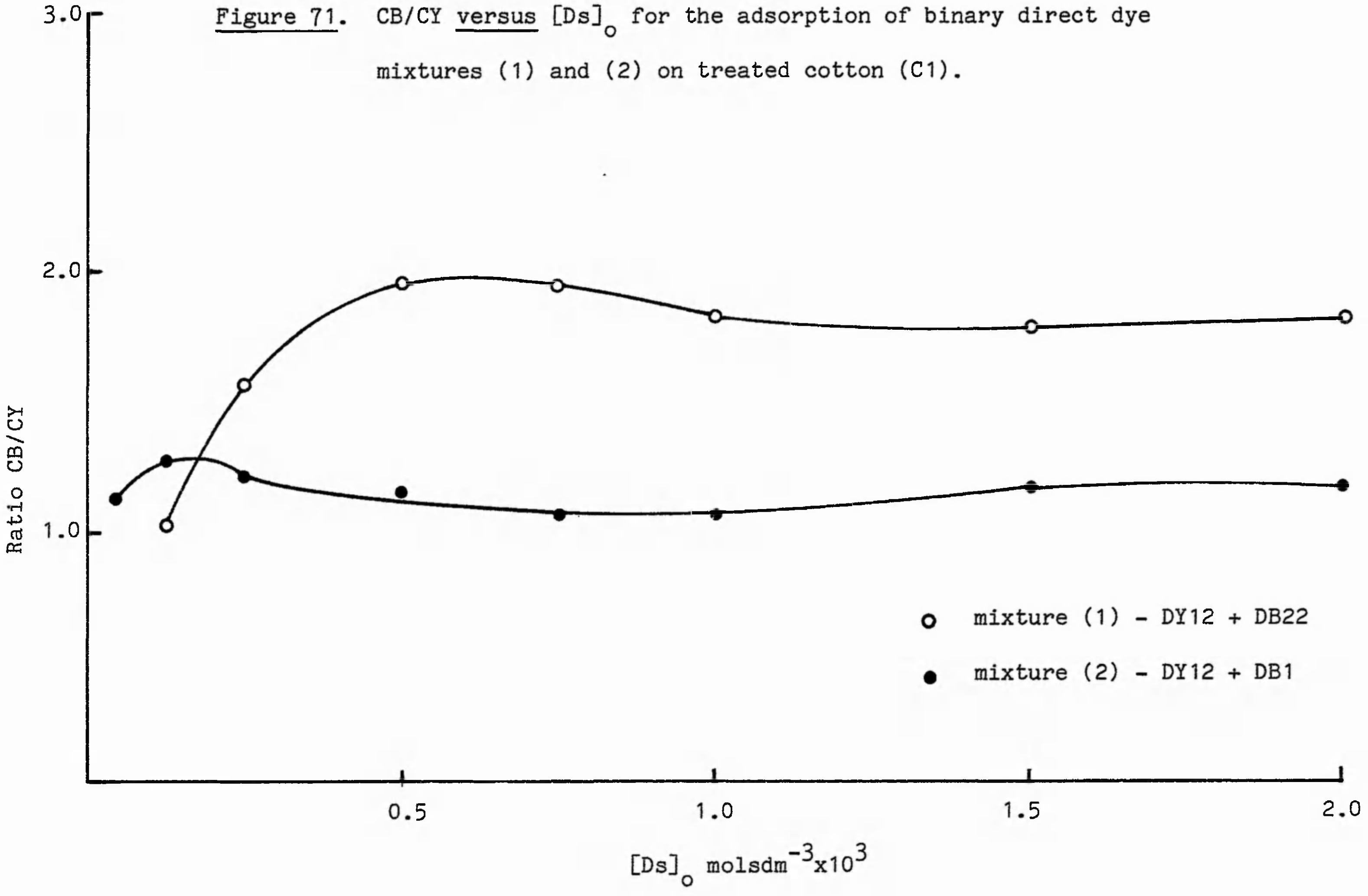
Table 42. Reflectance measurements on the individual calibration dyeings of known concentration for the calculation of K values.

Standard sample	Reflectance$_{(0-1)}$ λ_1 = 420 nm	λ_2 = 620 nm	Kc = $(1-R)^2/2R$	C mmolsKg^{-1}	Adsorption coefficients, K
DY12	0.1926		1.6924	0.773	KY_{420} = 2.1894
		0.8371	0.0159		KY_{620} = 0.0206
DB1	0.3667		0.5469	1.578	KB_{420} = 0.3466
		0.1254	3.0499		KB_{620} = 1.9328

Table 43. Reflectance measurements on treated cotton (C1) dyed with mixture (2) for the determination of the concentration of each dye on the fibre.

$[Ds]_o$ molsdm^{-3} x10^3	Colour Strength	Reflectance λ_1 = 420 nm	λ_2 = 620 nm	Kc = $(1-R)^2/2R$	CB	CY	CB/CY
0.05	58.29	0.1462		2.4931	1.08	0.97	1.11
			0.1653	2.1075			
0.125	93.93	0.1052		3.8055	1.83	1.45	1.26
			0.1110	3.5600			
0.25	97.31	0.1002		4.0401	1.85	1.55	1.19
			0.1097	3.6127			
0.50	98.37	0.969		4.2084	1.84	1.63	1.13
			0.1104	3.5842			
0.75	112.45	0.0847		4.9455	2.02	1.94	1.04
			0.1020	3.9530			
1.00	106.40	0.0878		4.7387	1.93	1.86	1.04
			0.1059	3.7744			
1.50	121.45	0.0826		5.0946	2.29	1.96	1.17
			0.0923	4.4633			
2.00	125.94	0.0801		5.2822	2.38	2.04	1.17
			0.0892	4.6500			

Figure 71. CB/CY *versus* $[Ds]_o$ for the adsorption of binary direct dye mixtures (1) and (2) on treated cotton (C1).



at 1.84 mmolsKg^{-1} which is far in excess of the expected saturation value for this dye in the presence of a disulphonated dye (CB = 1.29) although, interestingly, very close to that which would have been expected if C.I. Direct Blue 1 had been used to dye the treated cotton alone, assuming a 1:1 stoichiometry between sulphonic acid groups on the dye and positive sites in the modified fibre (known to have a site concentration of approximately 7.1 mmolsKg^{-1}).

However the treated fibre was observed to contain a significant concentration of C.I. Direct Yellow 12 which increased as $[Ds]_o$ increased without any change in CB so that CB/CY gradually fell to 1.04 and the molar ratio of dye on the fibre approached 1:1.

Factors which might be expected to affect the adsorption of dye mixtures on the modified cellulose include competition between the different dye anions for the available sites and cellulose surface, the contribution each different diffusely adsorbed dye anion makes to the surface charge and its sodium ion concentration, and lastly interactions between dyes in solution.

In fact, another investigation into the behaviour of mixtures of C.I. Direct Blue 1 and C.I. Direct Yellow 12, this time on unmodified cotton, led to the conclusion that an interaction occurs between these two dyes in solution even at 90°C with the formation of a 1:1 complex[220].

This could then explain why a 1:1 relationship existed between the same two dyes on the modified cotton whilst, at the same time, far more total dye was adsorbed by the fibre than theoretically possible taking into account the sulphonic acid groups on the dyes and the number of positive sites available.

It would appear then that as $[Ds]_o$ increased sites that were originally occupied by a mixture of the C.I. Direct Blue 1/C.I. Direct Yellow 12 complex and uncomplexed C.I. Direct Blue 1 (hence CB/CY >1) became increasingly occupied by the direct dye complex and hence CB/CY tended towards 1. This could come about if, for example, site adsorption of C.I. Direct Blue 1 originally proceeded at a faster rate than complex formation with C.I. Direct Yellow 12 but that as $[Ds]_o$ increased the rate of complex formation was also increased, so that more dye complex was available to be taken up by the fibre.

Eventually, however, CB/CY increased again to 1.17, the two dyes being adsorbed diffusely at their own rates (the blue class B more quickly than the yellow class A), CB/CY eventually becoming constant.

3.7.3.2 Selection of compatible dyes

In so far as the investigation of a blocking-off effect was concerned, the selection of C.I. Direct Blue 1 and C.I. Direct Yellow 12 may therefore have been fortuitous since, in the absence of an interaction such as 1:1 complex formation described earlier, blocking-off effects may still be envisaged as a result of binary mixtures of anionic dyes in which there are differences in the degree of sulphonation and hence more than likely in the extent to which the individual dyes are capable of being adsorbed by the modified cotton.

When dyeing differential-dyeing cotton with mixtures of direct dyes the use of dyes possessing a similar degree of sulphonation is therefore to be recommended and particularly where heavier shades are required (ie. where the available sites are to be saturated) it would also be advisable to take into account the classes of the direct dyes chosen and to match them, eg. a class C with a class C, wherever possible.

At pale to medium depths where the site concentration is not to be exceeded the results for mixture (1) indicated that when both dyes contain the same number of sulphonic acid groups the rate of site adsorption is equal and is thus independent of the class of the dyes, emphasising the fact that the forces operating in this instance are long range and electrostatic in nature rather than the short range attractive forces which are more generally associated with the application of direct dyes to unmodified cotton, and which it is their ability to maximise which normally confers substantivity for cellulose in the absence of specific dye sites.

3.7.4 Investigation of the differential dye uptake obtained with various types of cotton dye

As was previously mentioned in section 1.2 there are several dye classes which are commonly used with cellulose and it was therefore decided that an investigation into whether or not they all showed a good degree of preferential dye uptake on the modified fibres would be appropriate. In order to determine under what conditions the best contrast between treated and untreated yarns was obtained a brief discussion of each dye's normal method of application to native cellulose was therefore unavoidable but, for a more detailed description, the reader is referred to section 1.2.

Colour Strength measurements were carried out on both treated and untreated samples against the appropriate standard after dyeing with representatives of the various dye classes and the degree of contrast obtained expressed as the ratio of their Colour Strengths.

3.7.4.1 Application of vat dyes

Three vat dyes were first selected as important representatives of their class; the classic C.I. Vat Blue 1 (indigo), C.I. Vat Yellow 3 (from the acylaminoanthraquinone class) and C.I. Vat Green 1 (a violanthrone derivative); see Figure 6 (section 1.2.2) and Figures 72 and 73 below for their respective structures.

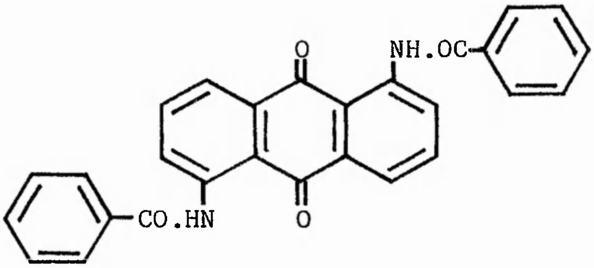


Figure 72. Molecular structure of C.I. Vat Yellow 3; C.I. 61725.

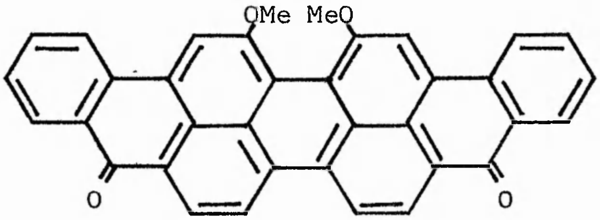


Figure 73. Molecular structure of C.I. Vat Green 1; C.I. 59825.

Each of the three dyes was applied to treated cotton (C2) at a depth of 2% o.w.f. in the presence of an equal weight of untreated cotton, according to the method outlined in section 5.9.3. More specific details of the various dyeing trials carried out are summarised in Table 44. The hanks were then soap-boiled for 30 minutes in 2% o.w.f. of a non-ionic detergent to develop their hue and fastness properties.

In trial 1 it can be seen that prior to oxidation the hanks were soaped at 60°C for 20 minutes in a weak solution of sodium hydroxide and sodium dithionite containing 2% o.w.f. of a non-ionic detergent in order to remove reduced dye adsorbed on the cellulose surface rather than on the cationic sites in the treated fibre.

In this way it was hoped to maximise the contrast obtained between treated and untreated fibres and so increase the differential dye uptake achieved when they were dyed together in one bath. From the results given in Table 44 it can be seen that this generally proved to be the case since for all three dyes the contrast between treated and untreated cotton was observed to decrease in trial 2, in which no sodium hydroxide/ dithionite soap was carried out prior to oxidation.

In the case of C.I. Vat Blue 1 the fact that much more dye was taken up by both treated and untreated fibres was probably the result of lowering the dyeing temperature to 25°C since in trial 1, carried out at 50°C, the dyeing obtained was pale green due to the presence of yellow decomposition products. It would also seem likely that, provided satisfactory levelness could be achieved, much heavier depths of C.I. Vat Blue 1 could conveniently be obtained on the modified yarn using higher dye concentrations without having to revert to the cumbersome 'successive dipping' technique, followed by repeated oxidations, which

Table 44. Summary of dyeing trials carried out with vat dyes to investigate their differential dye uptake on modified cotton (C2).

Dye	Trial	Dyeing temp. °C/oxidation method	Colour Strength 10%	Colour Strength 0%	Ratio of Colour Strengths
VY3	1	50/air	16.48	2.59	6.36
	2	25/air	19.80	3.32	5.96
VB1	1	50/air	35.93	9.84	3.65
	2	25/air	123.44	47.06	2.62
	4a	25/air	93.35	42.73	2.18
VG1	1	50/air	230.91	71.98	3.21
	2*	50/air	152.65	68.65	2.22
	3*	50/sodium hypochlorite	51.05	9.79	5.21
	4*a	50/sodium perborate/ bicarbonate	148.64	67.26	2.21
	b		147.67	74.59	1.98
	5*a	50/sodium perborate/ bicarbonate	215.63	145.44	1.48

Key to vat dyeing trials

1 Sodium hydroxide/dithionite soap prior to oxidation.

2 No sodium hydroxide/dithionite soap.

3 Use of a non-ionic levelling agent, a) 5%, b) 2%, then as 1.

4 Use of an anionic retarding agent, a) 2%, b) 5%, then as 2.

5 Abbot/Cox prepigmentation process with a levelling agent, then as 2.

* 2% o.w.f. Sandozin NI employed.

(see Appendix V for photographs of test samples).

is currently employed to obtain deep dyeings with this particular, very popular, dye[221].

For the blue and green vat dyes in particular the increase in contrast due to the sodium hydroxide/dithionite soap was, however, accompanied by a certain amount of unlevelness in the case of both the treated and untreated samples which became evident once oxidation was complete. The effect was particularly noticeable in the case of C.I. Vat Green 1 and it was therefore determined that in all future trials involving this dye at least 2% o.w.f. of a non-ionic levelling agent, Sandozin NI (Sandoz), should be introduced into the dyebath to assist levelling by a retarding process.

In fact, when vat dyes are applied normally, that is to unmodified cellulose, vat retardants such as Sandozin NI are extremely important dyebath assistants without which certain vat dyestuffs, including C.I. Vat Green 1 (Caledon Jade Green XN) which have extremely high rates of dyeing and which show very little tendency to level once they are on the fibre, are virtually impossible to dye levelly[222].

Their retarding action is proportional to their concentration in the dyebath and besides reducing the rate of dyeing they also decrease the final degree of exhaustion. Only very low concentrations are required (0.1-0.2 g/l) - the use of excess, in the case of C.I. Vat Green 1, being known to suppress its affinity for cotton almost completely[222].

Thus in trial 2 it can be seen that, in addition to the large amount of dye remaining on the untreated fibre in the absence of a sodium hydroxide/dithionite soap, much less dye was adsorbed by the treated cotton further reducing the contrast obtained. The levelness of the untreated sample was, however, much improved although that of the modified cotton was still unsatisfactory, the jade green dyeing containing tiny specks of blue which suggested that it had only been partially oxidised. Since in commercial practice air oxidation is often too slow, besides tending to cause uneveness it was therefore decided to use chemical methods of oxidation in all future trials involving the green vat dye.

Consequently in trial 3, in which treated and untreated cotton were dyed with C.I. Vat Green 1 in a bath containing 5% o.w.f. of the non-ionic levelling agent, hypochlorite was used to oxidise the dyed sample after a sodium hydroxide/dithionite soaping had been carried out. As might be expected, in the presence of such a large quantity of Sandozin NI, the rate of dyeing was so reduced and the final degree of exhaustion so lowered in the case of both treated and untreated samples that very low Colour Strengths were obtained, particularly in the case of the untreated sample for which the affinity of the dye had been almost completely suppressed. This had the effect of increasing the contrast obtained between treated and untreated cotton to its highest level yet, although once again the treated sample appeared to be only partially oxidised whilst the untreated sample was dyed satisfactorily to a uniform, level, albeit pale shade.

In terms of the degree of contrast obtained, however, it would appear that with vat dyes, as with directs, the best degree of differential dye uptake is achieved under conditions where the affinity of the dye for native cellulose is usually at a minimum but where, being anionic in its application stage, it is still capable of showing affinity for the cationic sites in the modified fibres. However, when using non-ionic levelling agents (or vat retardants) such as Sandozin NI it is obvious that a balance would need to be preserved between the desire for level results and a high degree of contrast between treated and untreated samples on the one hand and achieving economical dyebath exhaustion on the other.

In trials 4a) and 4b) it was therefore decided to examine the effect of a different type of proprietary levelling agent - an anionic retarding agent - namely Matexil DA-AC (ICI) which was applied as a pretreatment at two different levels (2% and 5% o.w.f. respectively) in order to see whether similarly high degrees of contrast were obtained between treated and untreated samples. Described in the Textile Auxiliary Index as the disodium salt of methylene dinaphthalene sulphonic acid, the structure of Matexil DA-AC is illustrated below in Figure 75.

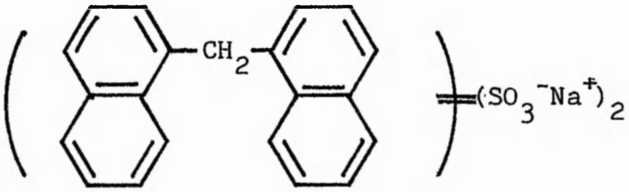


Figure 75. General structure of Matexil DA-AC (ICI).

In this particular trial a sodium hydroxide/dithionite soaping was not carried out and the oxidation was performed using a mixture of sodium perborate and sodium bicarbonate which is recommended for C.I. Vat Green 1 in industrial applications.

Unfortunately the treated samples were still observed to be only partially oxidised, even after prolonged exposure to the oxidising agent. Also as can be seen from Table 44, the degrees of contrast obtained were not nearly as high as in trial 3, although the levels of exhaustion were much higher. In fact the results for 4a) and 4b) (which were also carried out in the presence of 2% o.w.f. Sandozin NI) were so similar to those of 2) that it would appear that the presence of Matexil DA-AC had very little effect on the rate at which dye was taken up by the treated cotton. This would seem to support the results obtained earlier in which the use of large organic anions as counter-ions for the cationic sites in the modified fibres was shown to have very little effect on the rate at which dye was taken up by the fibres or on substrates. Reduction to the anionic leuco form takes place rapidly allowing very little time for redistribution of the dye between treated and untreated fibres and once adsorbed by cotton fibres C.I. Vat Green 1 generally shows very little tendency to level.

Once again the treated cotton dyeing appeared to be only partially oxidised and in this and earlier trials it was considered that this non-uniformity of hue which was obtained was due to the electrostatic interaction between the dye in its anionic leuco form and the cationic sites in the modified fibres.

This interaction, which is assumed to be responsible for the increased affinity of the dye for the treated fibres and thus the differential dye uptake observed between treated and untreated cotton, would also appear to be preventing the oxidation of the dye back to its insoluble form so hindering the regeneration of its true colour. Dye which is adsorbed by the treated fibre on the cellulose surfaces as opposed to on sites is unaffected and therefore oxidises normally giving rise to dyeings which are green overall but which contain small blue 'flecks' of unoxidised dye in its anionic leuco form.

Alternatively the presence of a hydrolysed dye-reagent complex which is substantive towards cellulose and resistant to the oxidising treatments employed might also give rise to the blue flecks observed on the fibre. (Addition of a solution of unhydrolysed reagent I to a portion of the vatting solution containing C.I. Vat Green 1 in its leuco form resulted in the formation of a blue complex which was, however, capable of being oxidised back to a green precipitate with a strong solution of hydrogen peroxide).

It would seem then that by using a stronger oxidising system the anionic leuco form of the dye may be completely reoxidised back to the insoluble pigment (whether or not it is still adsorbed on sites in the treated fibres or in the form of a hydrolysed dye-reagent complex) in order to regenerate the true colour of the dyeing.

3.7.4.2 Application of sulphur dyes

Very little information is currently available concerning the structure of many of the dyes in this class, apart from the fact that they are characterised by the presence of sulphur-sulphur linkages. Nevertheless, two were selected about which some structural details were known; C.I. Solubilised Sulphur Violet 1 (C.I. 53411), the thiosulphonic acid derivative of C.I. Leuco Sulphur Violet 1 (C.I. 53410) illustrated below in Figure 76 and C.I. Solubilised Sulphur Black 1 (C.I. 53185) based on 2,4-dinitrophenol.

Like vat dyes solubilised sulphur dyes are non-substantive to cellulose but are converted into the substantive leuco form by a reducing

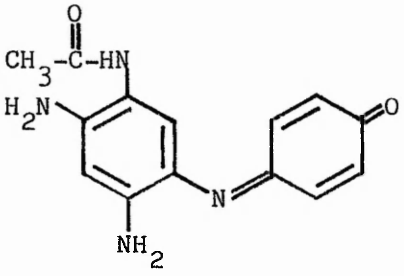


Figure 76. Molecular structure of C.I. Leuco Sulphur Violet 1 - an indophenol based intermediate which when heated with sodium polysulphide and oxidised produces a violet dye of unknown chemical constitution.

agent. After dyeing they are converted into the insoluble polydisulphides inside the fibre by oxidation in the usual manner.

Two dyebaths were made up for each dye containing 2.5% and 15% o.w.f. dye for the violet and black dye respectively and an equal weight of treated (C2) and untreated cotton was added to each in the cold. The temperature of each bath was then raised to the boil and after 10 minutes sodium chloride, 20% o.w.f. for the violet dye and 45% o.w.f. for the black dye, was added to one of the two baths made up for each dye.

Dyeing was then continued at the boil for 40 minutes as described in section 5.9.4, after which time the samples were squeezed to remove excess dye liquor and allowed to oxidise in air for 10 minutes. They were then soaped for 20 minutes at 50°C in the presence of a non-ionic detergent, rinsed and dried.

In order to avoid the weakening of cellulsic fibres which is sometimes observed with heavily dyed black materials and is caused by decomposition of the dye with the formation of sulphuric acid, the black dyeings were also given a final rinse in 1% w/v sodium carbonate and dried without washing off.

Colour Strength measurements were then taken for each dyed sample against the appropriate standard and the results are given in Table 45. As can be seen, a good degree of differential dye uptake was observed for each dye and good level dyeings were obtained in each case. In the presence of sodium chloride more dye was adsorbed by both treated and untreated samples due to suppression of the repulsive forces operating between the cellulose surfaces in the absence of sites and the sulphur dyes in their substantive anionic leuco forms but, as might be expected, the overall contrast between the treated and untreated dyed substrates actually decreased.

Interestingly, in the case of sulphur dyes, no difficulty was experienced in oxidising the leuco form of the dye back to its original insoluble form.

Table 45. Dyeing trials carried out with sulphur dyes to investigate their differential dye uptake on modified cotton (C2).

Dye	% o.w.f. applied	[NaCl] % o.w.f.	Colour Strength 10%	Colour Strength 0%	Ratio of Colour Strengths
SSV1	2.5	-	71.50	7.96	8.98
		20	96.22	11.47	8.39
SSB11	15	-	212.74	28.93	7.35
		45	237.42	39.16	6.06

(see Appendix V for photographs of test samples).

3.7.4.3 Application of azoic dyes

As mentioned earlier, in section 1.2.4, azoic dyes are formed in the fibre by coupling of two relatively colourless soluble components, a coupling component and a diazo component, to form a larger water-insoluble coloured molecule.

Three combinations of coupling components and stabilised diazo salts were therefore selected using the manufacturers' recommendations and are listed below in Table 46; their respective structures are given in Figures 77 to 81.

Table 46. Azoic combinations employed.

Combination	C.I. Azoic Coupling Component	C.I. Azoic Diazo Component	Colour
1	5	5	Orange
2	34	8	Bordeaux
3	15	8	Brown

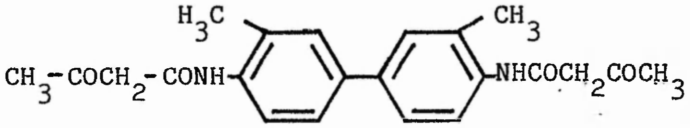


Figure 77. Azoic Coupling Component 5; C.I. 37610.

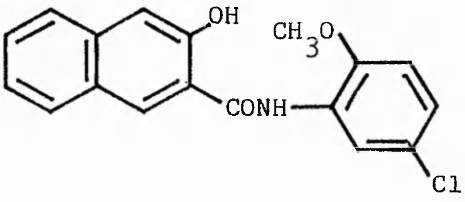


Figure 78. C.I. Azoic Coupling Component 34; C.I. 37531.

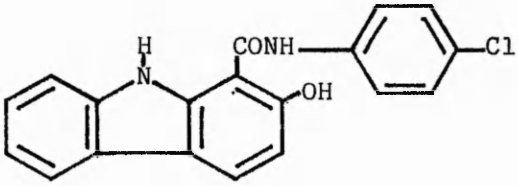


Figure 79. C.I. Azoic Coupling Component 15; C.I. 37600.

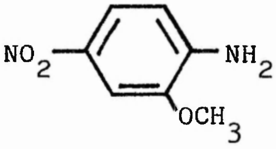


Figure 80. C.I. Azoic Diazo Component 5 (as the free base); C.I. 37125.

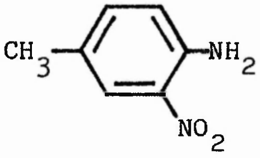


Figure 81. C.I. Azoic Diazo Component 8 (as the free base); C.I. 37110.

In trial 1 manufacturers' recommended application levels were employed for each component in the various combinations chosen and the effect of sodium chloride on the coupling reactions occurring, and ultimately on the differential dye uptake obtained, was examined. The initial naphtholation procedure was carried out in the absence of sodium chloride to maximise the differential dye uptake observed.

The azoic coupling component solutions were made up as described in section 5.9.5 and to each was added two treated cotton (C2) samples and an equal weight of untreated cotton. After working the samples in the solutions for 20 minutes at room temperature they were squeezed well without rinsing and divided between two similar diazo solutions (prepared from stabilised Fast Salts), one of which contained 50 g/l sodium chloride, and worked for a further 15 minutes. They were then rinsed well and soaped at the boil in a solution of a non-ionic detergent containing sodium carbonate.

After drying the samples Colour Strength measurements taken against the appropriate standard revealed that, although the contrast was in general slightly improved by carrying out the coupling reaction in the absence of sodium chloride, overall, at these application levels (which were very high in terms of % o.w.f.), very little differential dye uptake occurred. Dyeings carried out in the absence of sodium chloride were also observed to produce brighter shades and in a second trial it was therefore decided to omit sodium chloride from the Fast Salt bath and halve the concentration of azoic coupling component employed. (See Table 47).

The results for trial 2 showed a significant increase in the

Table 47. Dyeing trials carried out with azoic dyes to investigate their differential dye uptake on modified cotton (C2).

Trial	Azoic combination	NaCl	Colour Strength 10%	Colour Strength 0%	Ratio of Colour Strengths
1	1	-	273.82	240.32	1.14
		50	289.24	273.01	1.06
	2	-	400.07	283.44	1.41
		50	396.52	295.83	1.34
	3	-	529.11	580.19	0.91
		50	528.70	578.19	0.91
2	1	-	161.69	30.02	5.39
	2	-	226.42	54.03	4.19
	3	-	328.58	164.06	2.00

Key to azoic dyeing trials

1 Manufacturers' recommended application levels employed.

2 Concentration of azoic coupling component halved - sodium chloride omitted from the Fast Salt bath.

(see Appendix V for photographs of test samples).

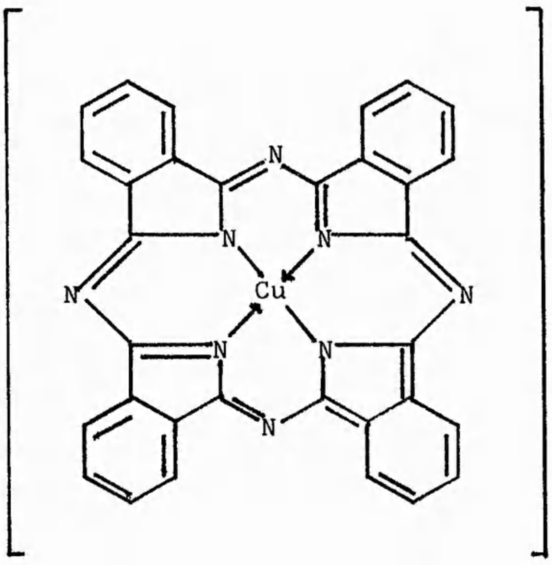
degree of differential dye uptake occurring for each azoic dye combination, particularly in the case of combinations 1 and 2. These dyes are formed from azoic coupling components which are generally applied to cellulose in the presence of sodium chloride so that in the absence of added electrolyte very little affinity was shown for the untreated cotton.

Interestingly, however, C.I. Azoic Coupling Component 15, used in combination 3, is generally recommended to be applied in the absence of sodium chloride, an indication that it probably has an unusually high affinity for native cellulose. This could explain why such a high Colour Strength was observed for the untreated cotton compared to that obtained on untreated cotton with the other dyes and hence the relatively low degree of contrast obtained as a result.

3.7.4.4 Application of reactive dyes

Four reactive dyes were selected as being typical of the class; C.I. Reactive Blue 7, C.I. 74460; C.I. Reactive Blue 19, C.I. 61200; C.I. Reactive Red 8. C.I. 17908; and C.I. Reactive Blue 5, C.I. 61210. Their structures are illustrated below in Figures 82 to 85.

Three different reactive systems are represented; the monochlorotriazine group (C.I. Reactive Blues 5 and 7), the dichlorotriazine group (C.I. Reactive Red 8), and the vinylsulphone group (C.I. Reactive Blue 19), each of which is capable of reacting with hydroxyl groups in the cellulose molecule under alkaline conditions to form a covalent bond between the dye and the fibre. The four dyes also contain varying numbers of sulphonic acid groups which impart water solubility and should ensure that the dyes have affinity for the cationic sites in



Copper phthalocyanine

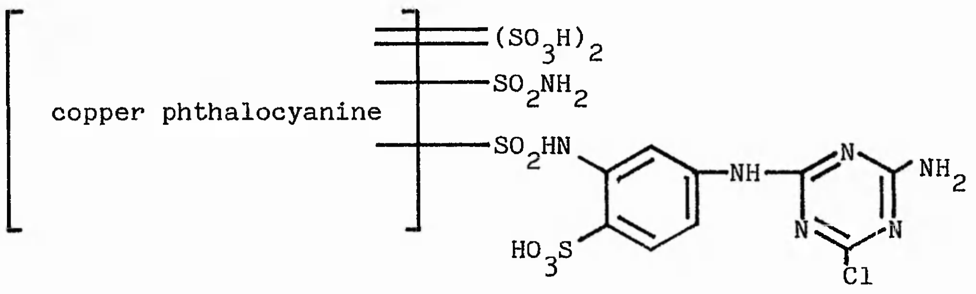


Figure 82. Molecular structure of C.I. Reactive Blue 7; C.I. 74460.

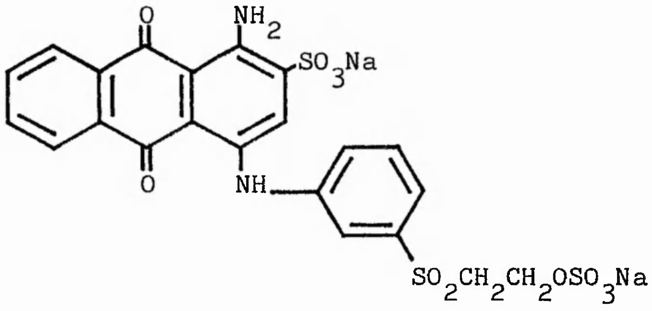


Figure 83. Molecular structure of C.I. Reactive Blue 19; C.I. 61200.

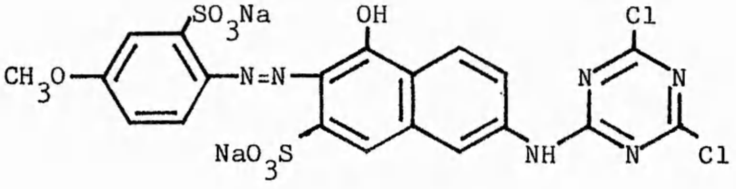


Figure 84. Molecular structure of C.I. Reactive Red 8; C.I. 17908.

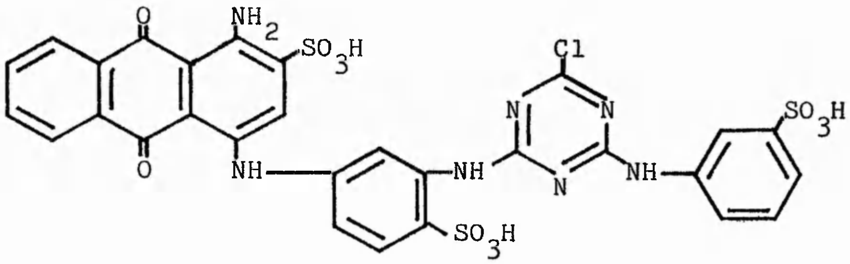


Figure 85. Molecular structure of C.I. Reactive Blue 5; C.I. 61210.

the modified fibres, even in the absence of alkali. It was therefore decided to apply all four dyes both in the presence and absence of sodium carbonate to examine the influence of alkali on firstly, the contrast obtained between treated and untreated cotton and secondly, the wet fastness properties of the resultant dyeings.

Generally the reactive dyes have lower substantivity for cellulose than the directs and so higher concentrations of sodium chloride are employed to bring about adequate exhaustion prior to fixation. However, as with the other dye classes examined the use of sodium chloride was observed to decrease the contrast obtained between treated and untreated cotton with the result that it was excluded from the four reactive dyeings described below.

The three different types of reactive dye have different reactivities and therefore required different methods of application. The monochlorotriazinyl dyes, for example, are hot dyeing reactives and were applied by making up two 2% o.w.f. dyebaths at 50°C for each dye, adding an equal weight of treated (C2) and untreated cotton and, after running them both for 15 minutes, adding 100% o.w.f. sodium carbonate to one of the baths. Dyeing was then carried out at the boil for 45 minutes after which time the samples were rinsed and soaped in a non-ionic detergent.

Dichlorotriazinyl dyes, such as C.I. Reactive Red 8, have higher reactivities than the monochlorotriazine derivatives and so require less alkali and lower dyeing temperatures for fixation. Two dyebaths were therefore prepared containing 2% o.w.f. C.I. Reactive Red 8 and an equal weight of treated (C2) and untreated cotton, to one of which was added sodium carbonate (40% o.w.f.). Dyeing was carried out at 40°C for 30 minutes after which time the samples were rinsed and soaped in a non-ionic detergent.

C.I. Reactive Blue 19 is a vinylsulphone dye and is recommended to be applied by a pad-batch heat fixation technique. This involves impregnating the material in a solution of the dye in the presence of alkali, drying, and then heating to promote dye-fibre reaction. However, in this case alkali was omitted since in the previous reactive dyeings it was observed to cause a marked reduction in the degree of contrast obtained between treated and untreated cotton.

Heating to promote fixation was therefore also unnecessary since in the absence of alkali the main interaction occurring between the dye and the fibre was expected to be electrostatic, that is between the cationic sites in the fibre and the negatively charged sulphonic acid groups on the dye.

An equal weight of treated (C2) and untreated cotton was therefore immersed for 30 minutes in two solutions containing 1% w/v of C.I. Reactive Blue 19, to one of which was added 10 g of urea per 100 cm^3 of padding liquor. Urea is known to promote dye fixation by increasing the solubility of the dye in the padding liquor but in this case its effect on the contrast obtained between treated and untreated cotton was to be examined. Excess liquor was then squeezed out and the samples rinsed and soaped well in a non-ionic detergent.

All the samples were then dried and Colour Strength measurements taken against the appropriate standard. Good level dyeings were obtained in all cases but, as can be seen from the results in Table 48, the contrast obtained between treated and untreated cotton varied according to the nature of the dye and the conditions under which dyeing took place. In the absence of alkali the contrast was invariably greater, but no reaction between the dye and the fibre with the formation of a covalent bond can have occurred with the result that under certain conditions the wet fastness properties of the dyes may have suffered. (This question is examined in more detail later).

Table 48. Dyeing trials carried out with reactive dyes to investigate their differential dye uptake on modified cotton (C2).

Dye	Reactive system	Na_2CO_3	Urea	Colour Strength		Ratio of Colour
		% o.w.f.	g/l	10%	0%	Strengths
RB7	Monochlorotriazinyl	-	-	79.50	1.82	43.68
		100	-	159.47	14.35	11.11
RB19	Vinylsulphonyl	-	-	153.22	1.95	78.57
		-	100	175.56	3.02	58.13
RR8	Dichlorotriazinyl	-	-	154.82	1.78	86.98
		40	-	184.01	54.41	3.38
RB5	Monochlortriazinyl	-	-	94.79	1.49	63.62
		100	-	107.88	5.04	21.40

(see Appendix V for photographs of test samples).

The results for C.I. Reactive Blue 19 confirmed that the greatest degrees of contrast were obtained without alkali, the presence of urea also serving to decrease the contrast obtained, presumably its action of increasing the dielectric constant of the solution tending to suppress the repulsive forces operating between the unmodified cellulose surfaces and the anionic reactive dyes in solution.

Where reaction between the dye and the fibre took place (that is, where dyeing was carried out under alkaline conditions) the hot dyeing monochlorotriazine dye, C.I. Reactive Blue 5, gave one of the best degrees of contrast yet obtained with a typical cellulose dye. The contrast obtained with the other monochlorotriazine dye, C.I. Reactive Blue 7, was somewhat less, nevertheless, both hot-dyeing reactive dyes gave considerably better contrasts than the cold-dyeing, dichlorotriazine dye C.I. Reactive Red 8, in spite of the fact that less alkali was employed with the latter dye, presumably because at higher temperatures the amount of dye exhausting onto the untreated cellulose was considerably reduced decreasing the likelihood of it reacting with the fibre.

However, in the complete absence of alkali the reverse was the case; C.I. Reactive Red 8 was observed to give a greater degree of contrast between treated and untreated fibres than either of the two monochlorotriazine dyes possibly because, possessing fewer sulphonic acid groups (two instead of the three contained by each of the two blue dyes mentioned earlier), a greater build-up of dye could take place on the modified cotton (assuming that in this case the main interaction occurring would be electrostatic).

A further study was carried out to compare the wet fastness properties of the treated samples dyed with C.I. Reactive Blue 5 in the presence and absence of alkali. A standard reactive dyeing of untreated cellulose was carried out as a reference using the same dye under normal conditions, exhausting the dye at 60°C in the presence of sodium chloride and then fixing in the presence of alkali.

After soaping the reference dyeing in a non-ionic detergent Colour Strength measurements were taken of the dried sample after which all three samples were removed from their mountings and refluxed for 2 hours in a 10% solution of Atexal DA-BD - a large anionic agent (more usually employed in maintaining the dispersion stability of disperse dyebaths[223]). The results are given in Table 49 and reveal that, as expected, virtually all of the reactive dye taken up by the reference sample (98%) was covalently bound to the fibre whereas for

Table 49. Colour Strength measurements taken for C.I. Reactive Blue 5 before and after refluxing with Atexal DA-BD.

% Treatment	NaCl	Na_2CO_3	Colour Strength		% Dye fixed
	% o.w.f.	% o.w.f.	Before	After	
10	-	-	94.79	16.74	17.66
10	-	100	107.88	68.57	63.56
0 (ref)	400	100	60.66	59.30	97.76

the modified cotton dyed with the same dye in the presence and absence of alkali the percentage of dye fixed (or at least incapable of being removed by a process of anion exchange) was 64% and 18% respectively.

Clearly in the case of dye taken up by the treated sample in the absence of alkali very little reaction with the fibre had occurred whereas, of the dye applied in the presence of alkali, 36% was found not to be covalently bound to the fibre. It would appear then that in the presence of a non-ionic detergent this hydrolysed dye was more difficult to remove from the treated fibres than the same hydrolysed dye adsorbed on untreated cellulose, presumably due to its affinity for the cationic sites in the modified cotton. This could perhaps result in some loss in the normally excellent wet fastness properties exhibited by reactive dyes on cellulose unless, e.g., an anionic detergent was used in the washing-off stage, which would facilitate the removal of hydrolysed dye adsorbed on sites by a process of anion exchange.

In the light of the results obtained earlier it is also to be recommended that only the minimum quantity of alkali be employed in the dyebath, sufficient to bring about adequate fixation, since the presence of excess will serve only to increase unnecessarily the loss in differential dye uptake obtained between treated and untreated cotton.

Alternatively a sequence involving dyeing followed by soaping off prior to fixation should enable maximum fixation of reactive dye on the treated fibres to be achieved, whilst at the same time ensuring a contrast equal to that obtained in the absence of a fixation step.

3.7.5 Cross-dyeing of differential-dyeing cotton

3.7.5.1 Introduction

In 1973[224] the Terms and Definitions Committee of the J.S.D.C. defined cross-dyeing as "the dyeing of one component of a mixture of fibres of which at least one is already dyed". However, in this context the term 'cross-dyeing' has been used to describe the dyeing of two types of modified cotton fibre in a single dyebath, one containing cationic quaternary ammonium groups and the other anionic sulphonic acid groups which are capable of acting as sites for anionic and cationic dyes respectively.

Fabrics woven from the two types of modified yarn could therefore be dyed two colours from a single dyebath containing an anionic and a cationic dye enabling producers of coloured cotton goods to retain large quantities of a fabric with a popular weave which could then be quickly dyed without having to revert to the package dyer or the weaver once the market had been tested and the most popular colours ascertained.

In theory, at least, it should also be possible to obtain a cross-dyeable fabric by weaving together two cotton yarns, one of which was modified with an anionic reagent whilst the other remained untreated. In this case treated and untreated fibres woven into a fabric could be dyed two colours from a single dyebath containing, for example, a basic and a direct dye. However, in practice it was found that, even when the affinity of the direct dyes for the untreated cotton was enhanced by incorporating cationic sites into the fibre, a considerable degree of cross-staining of the basic-dyeable cotton occurred as a result of the very great substantivity exhibited by direct dyes for cellulosic substrates.

In the absence of cotton containing cationic sites it may be assumed that this cross-staining effect would only be exaggerated and thus most of the cross-dyeing studies were carried out employing the two different types of differential-dyeing cotton referred to earlier with affinity for anionic and cationic dyes respectively.

3.7.5.2 Influence of dye structure on it's adsorption by cotton modified with an anionic reagent

In order to study the cross-dyeing behaviour of the two types of differential-dyeing yarn it first became necessary to examine the uptake of basic dyes by cotton modified with an anionic fibre-reactive reagent, in this case Sandospace R (see section 3.2.2), and the influence of dye structure on the degree of differential dye uptake observed between treated and untreated fibres. This was, however, complicated by the fact that very few of the basic dyes readily available had structures which were listed in the Colour Index.

Two basic dyes were nevertheless selected; C.I. Basic Red 18

(C.I. 11085), the structure of which is given below in Figure 86, and C.I. Basic Yellow 19 which is described as a monoazo dye although unfortunately no further information is available concerning its chemical constitution.

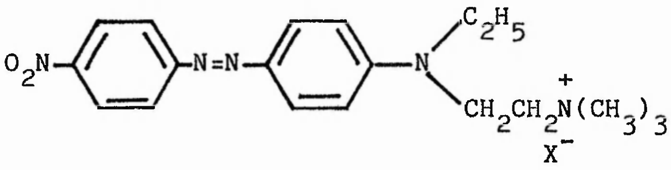


Figure 86. Molecular structure of C.I. Basic Red 18; C.I. 11085.

Cotton samples treated with the anionic reagent were then dyed with 1% o.w.f. of the two basic dyes in the presence of an equal weight of untreated cotton. Good differential dye uptake between treated and untreated samples was observed with C.I. Basic Red 18, however, this was not so in the case of C.I. Basic Yellow 19 for which there was virtually no difference in shade obtained between the two samples.

Since the two modified samples had been treated in the same batch the only factor which could be giving rise to differences in their differential-dyeing behaviour was assumed to be the structures of the individual dyes themselves. C.I. Basic Red 18 is a monoazo dye containing a pendant cation with a non-resonating or localised charge. Some basic dyes, however, contain a delocalised positive charge which, it was thought might reduce their affinity for the sulphonic acid sites incorporated into the cotton fibres as a result of treatment with an anionic reagent; an example of such a dye, C.I. Basic Yellow 28, is illustrated in Figure 87.

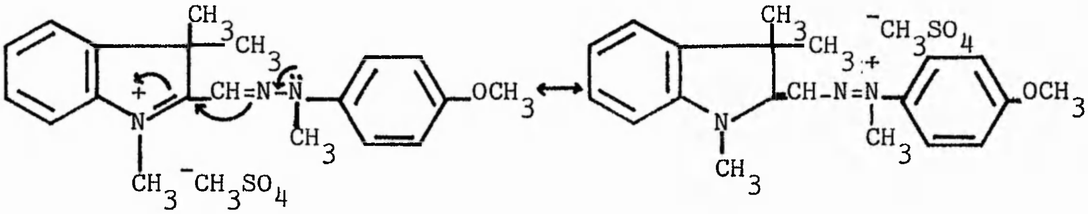


Figure 87. Molecular structure of C.I. Basic Yellow 28; C.I. 48054, showing its delocalised charge.

In order to examine this question further, two 1% o.w.f. dyebaths containing respectively C.I. Basic Yellow 28 and C.I. Basic Yellow 15 were made up and used to dye cotton samples previously treated in bulk with the anionic reagent derived from sulphanilic acid, reagent II (see Figure 98, p298), in the presence of equal weights of untreated cotton. In contrast to the former dye C.I. Basic Yellow 15 has a non-resonating, localised charge and thus was expected to show considerable affinity for the anionically modified cotton; its structure is given below in Figure 88.

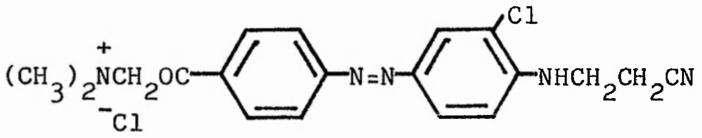


Figure 88. Molecular structure of C.I. Basic Yellow 15; C.I. 11087.

This, in fact, proved to be the case, good differential dye uptake being obtained with C.I. Basic Yellow 15, however, C.I. Basic Yellow 28 also showed good preferential uptake of dye on the treated cotton which suggests that a delocalised charge on a basic dye does not inhibit site adsorption on anionically modified cotton.

To confirm this proposal a further 1% o.w.f. dyeing of the anionically modified cotton was carried out using the classic, delocalised, basic dye Malachite Green (C.I. Basic Green 4; C.I. 42000) (see Figure 89) in the presence of an equal weight of untreated cotton. Good differential dye uptake between treated and untreated cotton was obtained confirming that a delocalised charge does not inhibit the adsorption of basic dyes on cotton modified so as to contain anionic sites.

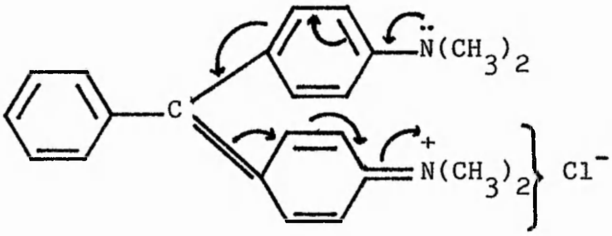


Figure 89. Molecular structure of Malachite Green; C.I. Basic Green 4, C.I. 42000.

3.7.5.3 Cross-dyeing studies

The first cross-dyeing study using the two types of differential-dyeing cotton having affinity for cationic and anionic dyes respectively was carried out using a basic and a direct dye. C.I. Basic Red 18 (Figure 86) containing a non-resonating localised charge, was selected as the basic component of the mixture having previously shown good preferential dye uptake on anionically modified cotton whilst C.I. Direct Blue 10 (C.I. 24340), whose structure is given in section 5.8.1, was found to show considerable substantivity for cotton treated with the cationic reagent I.

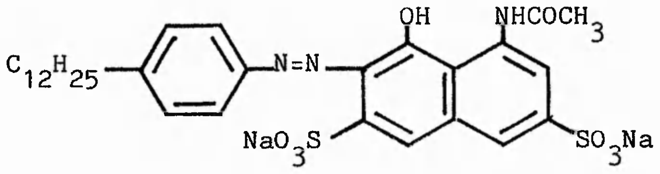
Individual 1% o.w.f. dyeings were carried out on two cotton samples treated with the oppositely-charged reagents V and IV (see section 5.4) employing C.I. Direct Blue 10 and C.I. Basic Red 18 respectively. A further pair of oppositely-charged, modified samples was then cross-dyed in a dyebath containing 0.5% o.w.f. each of the same two dyes for 45 minutes at 80°C.

After soaping and drying the samples a comparison of the two sets of dyeings indicated that considerable cross-staining of the basic red-dyed, anionically modified cotton had occurred, whilst the direct blue dyeing of the cationic treated cellulose exhibited only a slight loss in depth of shade in the crossed dyebath compared to that which had been obtained in the individual dyebath.

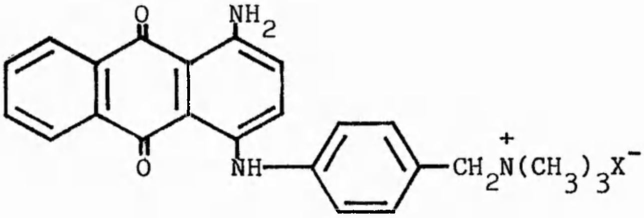
The basic-dyed sample was thus a much duller, bluer and considerably more unlevel shade of red than had been obtained in the individual dyebath no doubt as a result of a small amount of the direct dye becoming adsorbed on the anionically modified cotton, once the negative surface charge was neutralised,as a result of its inherent substantivity for native cellulose.

Interaction of the two oppositely charged dye ions in the absence of a dispersing agent resulting in the precipitation of an acid/base dye complex would also be expected to interfere with the production of good cross-dyeing effects by causing unlevel dyeings.

In the second cross-dyeing trial a milling acid dye, C.I. Acid Red 138, was employed as the anionic component of the dye mixture in order to try to prevent the cross-staining due to the cellulose-substantive direct dye. Its structure is given below together with that of C.I. Basic Blue 47 (Figure 90) which was selected as the cationic dye for this particular cross-dyeing mixture on account of its known chemical constitution.



C.I. Acid Red 138; C.I. 18073.



C.I. Basic Blue 47; C.I. 61111.

Figure 90. Molecular structures of the acid and basic dyes employed in the second cross-dyeing trial.

The resultant dyeings indicated that a considerable amount of cross-staining had again occurred although, in contrast to the results obtained earlier, it was due to basic dye being adsorbed by the cotton modified with the cationic reagent as opposed to the anionic dye adsorbing on the anionically modified fibres.

Interestingly, the order in which the two dyes were applied was observed to have a significant effect on the degree of cross-staining exhibited by the basic dye. In two separate dyeing trials in which the acid dye was added first, prior to the basic dye and then second, after the basic dye, the dyeings of the cationically modified fibres were found to be purple and pink respectively indicating a much greater degree of cross-staining by the blue basic dye having occurred when the red acid dye was applied first.

This perhaps suggests that acid dye when already adsorbed on cationic sites in the fibres reduces the electrical repulsion experienced by the basic dye due to the presence of the aforementioned sites resulting in a more favourable environment in which diffuse adsorption onto the modified cotton occurred more readily, especially in the case of this particular basic dye, whose anthraquinone-based structure appears to have conferred upon it a certain degree of substantivity for native cellulose, since it was observed to stain fairly heavily both cationically-modified and untreated cotton.

Alternatively, it has been suggested that the acid dye may be acting as a mordant for the basic dye presumably through one of its two sulphonic acid groups, although in this case this would imply that a good cross-dyeing could only be obtained with monovalent dye ions which was not in fact found to be the case (see later).

In order to prevent cross-staining by the basic dye another dye, C.I. Basic Yellow 15, was selected for a further cross-dyeing trial involving C.I. Acid Red 138. This particular dye, illustrated in Figure 90, had earlier been shown to give good differential dye uptake on anionically modified fibres whilst having very little substantivity for untreated cotton.

The results confirmed that the amount of cross-staining by the basic dye had been considerably reduced particularly when taking into consideration the fact that the acid dye was added to the dyebath first followed by the basic component of the mixture. However, cross-staining due to the acid dye on the anionically modified cotton now appeared to be more in evidence and in a final trial it was therefore decided to examine whether the use of smaller equalising acid dyes (which would tend to have less affinity for the positively charged substrate than the larger milling acid dye C.I. Acid Red 138) would reduce the degree of cross-staining and if, in fact, an acid dye containing only one sulphonic acid group (which would limit the possibility of interaction between the two oppositely charged dye ions) would show more or less cross-staining than a disulphonated dye which would tend to be less hydrophobic and therefore less substantive towards cellulose.

Two analogous acid dyes were therefore selected, C.I. Acid Red 88 and C.I. Acid Red 13, containing one and two sulphonic acid groups respectively (see section 3.7.1.1 for their structures). Cross-dyeing trials were carried out according to the method outlined in section 5.11 employing C.I. Basic Yellow 15 as the basic component of the mixture in each case and adding both dyes simultaneously at the beginning of dyeing in addition to 5% o.w.f. of a non-ionic dispersing agent to prevent precipitation of the acid/base complex.

The resultant dyeings revealed far more cross-staining of the anionically modified fibres on the part of C.I. Acid Red 88, the monosulphonic acid dye, indicating that at these dye concentrations an increase in hydrophobic character, and hence in the tendency of a dye to adsorb diffusely, increases the degree of cross-staining occurring when differential-dyeing yarns of opposite charge are cross-dyed two different colours from a single dyebath.

A very good cross-dyeing of the two types of differential-dyeing yarns was, however, obtained using C.I. Basic Yellow 15 and the less hydrophobic C.I. Acid Red 13 with minimal cross-staining on the part of both dyes (see Appendix V). In fact, since the dyes could be applied simultaneously to achieve this result, this process would appear to be far more convenient than normal cross-dyeing methods for the dyeing of fibre mixtures to achieve contrasting colours, in which it is recommended to allow sufficient time for the anionic dye to become appreciably exhausted before adding the cationic dye, and if necessary cooling the dyebath. Also since the two different types of differential-dyeing cotton are of the same generic class many of the drawbacks generally associated with the cross-dyeing of fibre mixtures, as a result of differences in their physical and mechanical properties, may be avoided.

3.7.6 Fastness properties of selected dyes on differential-dyeing cotton

3.7.6.1 Introduction

There are many different tests for determining the fastness of dyed textiles to agents such as bleaching solutions, acids and alkalis, gaseous impurities in the atmosphere and dry heat, as in ironing, however, in this instance, the relative fastness of treated and untreated cotton fabric dyed with typical cellulose dyes to washing and light were considered to be of the greatest technical importance and hence warranted investigation.

Two cellulose dyes were therefore selected, C.I. Direct Blue 1 and C.I. Reactive Blue 5, both of which were of known chemical constitution (see Figure 56 and 85) and had earlier been shown to give good differential dye uptake on treated and untreated cotton when dyed simultaneously in a single bath. Since the light and wash fastness properties of dyes are known to vary with the depth of shade, light fastness increasing with increasing depth of shade whilst wash fastness decreases as the concentration of dye on the fibre increases, samples of cotton fabric treated with 10% o.w.f. of the cationic reagent I and untreated cotton samples were dyed two standard depths, $^1/3$ and $^1/1$, for each dye, ensuring that for each dye at each depth the resultant dyeings on the treated and untreated cotton, although necessarily carried out in separate dyebaths, were reasonably well matched. Details of the treatment of fabric and of the dyeings carried out are given in section 5.14.

3.7.6.2 Wash fastness

The fastness to washing of the treated and untreated samples dyed with C.I. Direct Blue 1 and C.I. Reactive Blue 5 were examined under two different sets of conditions; the first being the recommended British Standard test applied to direct and reactive dyeings, namely ISO 3 and ISO 4 respectively, whilst the second more general test was applied to all the dyeings carried out regardless of dye class.

In principle both tests involved mechanically agitating a specimen of the dyed sample in contact with various specified adjacent fabrics (in this case bleached cotton and wool) under specified conditions of time and temperature in a solution of soap (or for the general test, non-ionic detergent) and sodium carbonate. All the samples were then rinsed and dried and the change in colour of the specimen and the staining of adjacent fabrics assessed using the two sets of Grey Scales[225] (see Table 50).

Further details of the preparation of composite specimens together with the exact conditions under which the tests were carried out may be found by referring to the ISO (International Organisation for Standardisation) recommendations (see BS 1006: 1978[225]).

As can be seen from Table 50, the results for the ISO 3 test involving C.I. Direct Blue 1 showed that at both depths of shade the wash fastness properties of the dyeings produced were considerably improved by pretreatment of the cotton fabric with reagent I to incorporate cationic dye sites. Comparison with the appropriate Grey Scale revealed that staining of adjacent cotton fabric was reduced by one step for both the $^1/3$ and $^1/1$ dyeings on modified cotton, whilst no staining of adjacent wool was observed for either the treated or the untreated sample.

As expected, the change in colour ratings revealed that the fastness of the untreated cotton to washing decreased as the depth of dyeing increased although interestingly, this was not the case with the treated fabric whose fastness seemed to be greater on the more heavily

Table 50. Wash fastness ratings for C.I. Direct Blue 1 and C.I. Reactive Blue 5 on treated and untreated cotton.

Test	Sample			Fastness rating		
	Dye	Depth	% Treated o.w.f.	Staining of adjacent fabric		Change in colour
				Cotton	Wool	
Non-ionic detergent 5 g/l + sodium carbonate 2 g/l (95°C)	DB1	1/3	10	5	5	5
			-	3	5	3
		1/1	10	4-5	5	5
			-	1-2	5	2
	RB5	1/3	10	5	3-4	5
			-	5	3	5
		1/1	10	5	3-4	5
			-	5	3	5
ISO 3 (60°C)	DB1	1/3	10	2-3	5	4
			-	1-2	5	3
		1/1	10	2	5	4-5
			-	1	5	2
ISO 4 (95°C)	RB5	1/3	10	5	-	4-5
			-	5	-	5
		1/1	10	4-5	-	4-5
			-	5	-	5

$^1/1$ dyed sample (4-5 as opposed to 4 for the $^1/3$ dyeing).

Overall much less staining of the adjacent cotton fabric was observed with the direct dye using a non-ionic detergent, as opposed to an anionic soap, particularly in the case of the treated cotton whose fastness rating improved by two and three steps for the $^1/3$ and $^1/1$ dyeings respectively. No change in colour was observed at either depth for the treated cotton (note the maximum fastness rating of 5), whereas use of the anionic soap in ISO test 3 appeared to facilitate removal of dye from the modified yarn resulting in losses in depth of the same dyeings corresponding to 4 and 4-5 for the $^1/3$ and $^1/1$ depths respectively, in spite of the lower washing off temperatures employed. Presumably this was due to competition between the anionic soap and the dye anions for the cationic sites in the modified cotton resulting in more dye being available to stain adjacent fibres.

Similarly with the reactive dye, no change in colour or staining of adjacent cotton was observed for the treated and untreated fabrics alike in the presence of the non-ionic detergent. The staining of adjacent wool which was noted was due to yellowing of the fibres rather than true staining and was probably the result of the high bath temperatures employed.

However, in ISO test 4 at both depths treatment with the reagent was observed to cause a slight reduction in the normally excellent fastness properties associated with reactive dyes, resulting in a change in colour of both dyed samples equivalent to 4-5 on the Grey Scale.

This is more than likely due to the presence of the quaternary ammonium groups in the fibre which although responsible for the differential-dyeing effect could also inhibit removal of hydrolysed reactive dye anions which, though incapable of reacting with the fibre, still have affinity for the cationic sites in the treated cotton, in much the same way as small acid dyes have been shown to have affinity for the modified yarn.

3.7.6.3 Light fastness

The fastness to light of the treated and untreated samples, dyed with C.I. Direct Blue 1 and C.I. Reactive Blue 5, was measured by exposing then to a xenon arclight in a fading lamp, alongside a set of standard patterns. These standards consist of eight wool fabrics dyed with different dyes, numbered 1 to 8 in order of increasing fastness (an increase in one grade, at least up to grade 6, represents roughly a doubling of the time required to cause fading). The fastness of the samples was thus assessed by comparing the change in colour of each specimen with that of the standards.

Further details of the preparation and arrangement of the samples under test may be found by referring to the ISO recommendations (see BS 1006: 1978[225]).

The results given in Table 51, indicate that pretreatment of cotton with the cationic reagent I brought about a loss in light fastness of the dyed samples equivalent to 0.5 and $\geq$1.5 points for C.I. Direct Blue 1 and C.I. Reactive Blue 5 respectively.

For C.I. Direct Blue 1, both the treated and the untreated cotton samples dyed the paler shade ($^1/3$ of the normal depth) showed a greater degree of fading than the samples dyed to the normal $^1/1$ depth. The loss in colour was, however, particularly noticeable in the case of

Table 51. Light fastness ratings for C.I. Direct Blue 1 and C.I. Reactive Blue 5 on treated and untreated cotton.

Dye	Depth	% Treatment o.w.f.	Light fastness rating
DB1	$^1/3$	10	1
		-	1-2
	$^1/1$	10	1-2
		-	2
RB5	$^1/3$	10	3-4
		-	≥ 5
	$^1/1$	10	3-4
		-	≥ 5

the treated, $^1/3$ dyed sample which had faded almost completely to a pale grey.

The cause of this loss in light fastness is thought to be due to changes in the nature of the dye-fibre interactions taking place on the modified cotton and the effect that this is likely to have on the ability of the dye to closely approach the fibre and hence to dissipate its adsorbed light energy throughout the entire dye-fibre system. Energy which is not dissipated results in some of the dye molecules being promoted to an excited state, in which condition they are more likely to react with surrounding materials such as oxygen in the air or even the fibre itself, hence decomposing and losing their colour.

The reaction sequence may be expressed as:

$$D \xrightarrow{\text{light}} D^* \xrightarrow{O_2} \text{oxidation products}$$

where D and D* represent the dye molecule in the ground and excited states respectively.

The presence of cationic sites in the modified yarn in the form of bulky quaternary ammonium groups and the formation of ionic links between these groups and the sulphonic acid groups of the direct dye may effectively prevent the close approach of the dye to the fibre, hindering the short range, non-polar, van der Waals forces of attraction from coming into play, the operation of which are considered to be of great importance in the dyeing of untreated cellulose.

Evidence in support of this proposal comes from a comparison of the reflectance spectra of treated and untreated cotton samples dyed to a similar depth with C.I. Direct Blue 1 (Figure 91). In aqueous solution C.I. Direct Blue 1 has λmax (ie minimum reflectance) at 620 nm (see Figure 92) known as the long-wave (x-) band, however, when applied to untreated cellulose this band can be seen to shift to longer wavelengths in the region of 640 nm which is taken to be an indication of the orientation of dye molecules along the cellulose surface[217]. When the same dye is applied to modified cellulose, however, this band is restored to its original position for water solution, presumably indicating a disorientation of dye molecules away from the cellulose, in much the same way as was shown to occur on addition of another quaternary ammonium compound, cetyltrimethylammonium bromide, 'CTAB', to untreated cellulose dyed with C.I. Direct Blue 1[217,226].

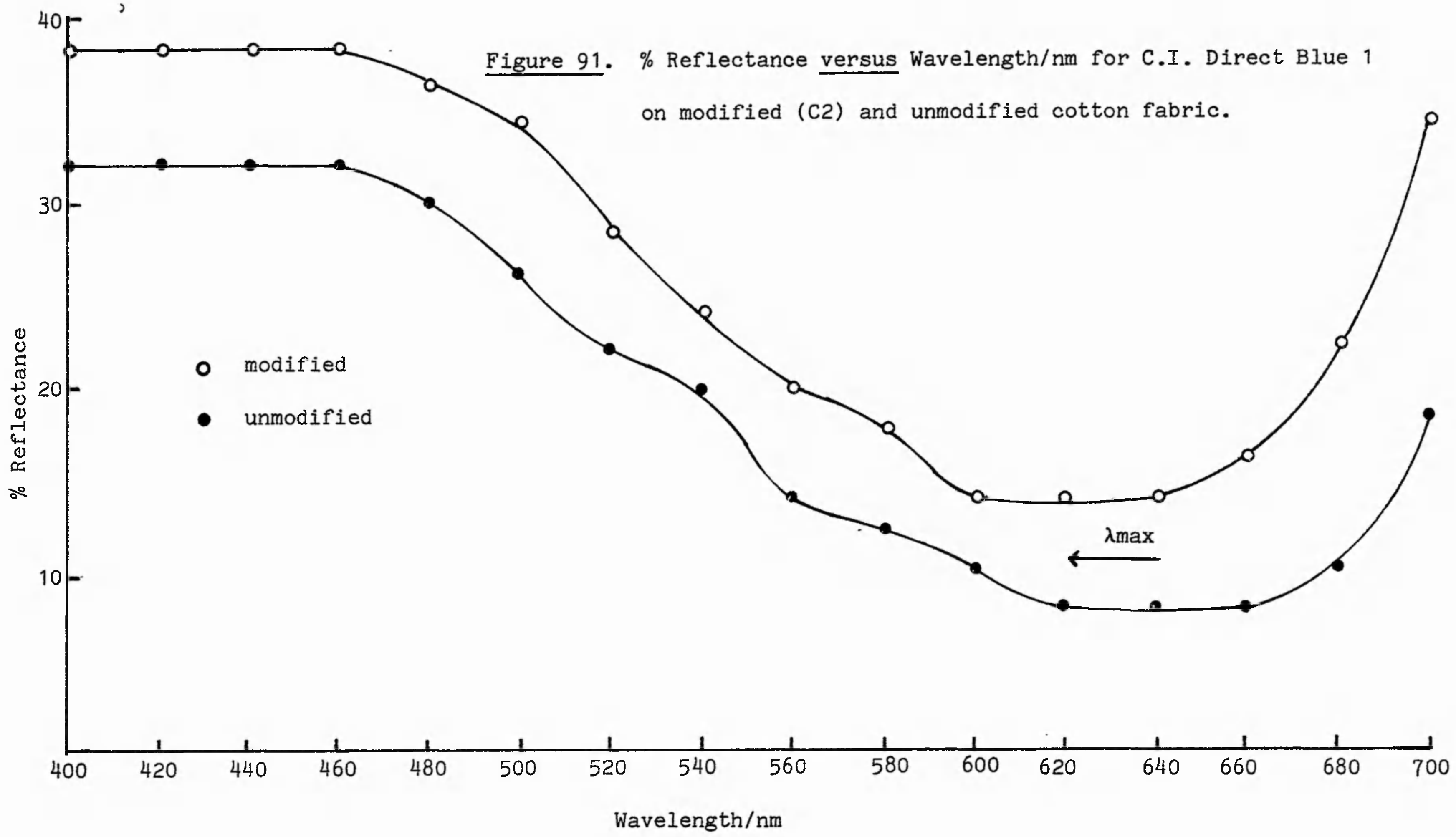
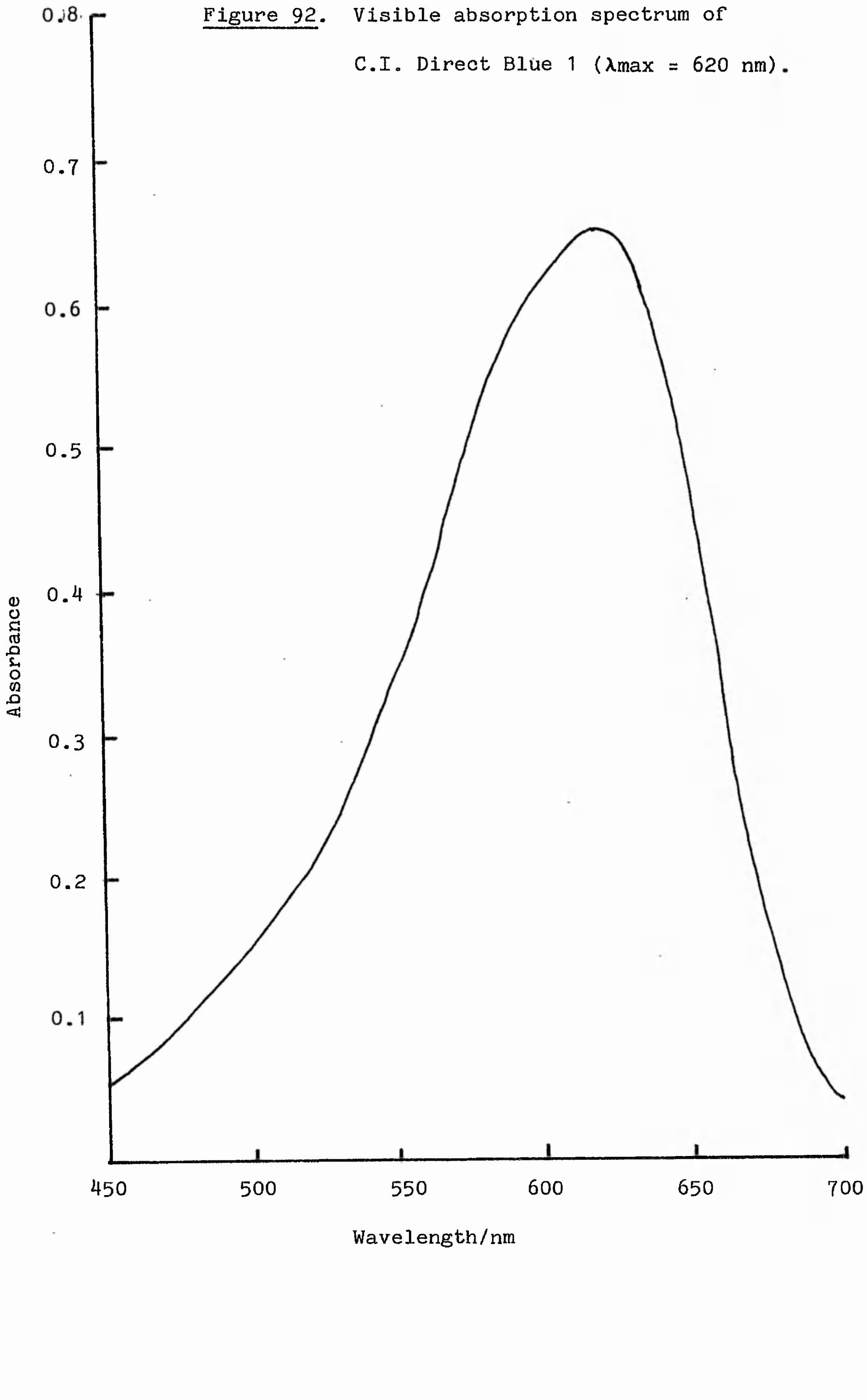


Figure 91. % Reflectance *versus* Wavelength/nm for C.I. Direct Blue 1 on modified (C2) and unmodified cotton fabric.

Figure 92. Visible absorption spectrum of C.I. Direct Blue 1 (λmax = 620 nm).



Non-reactive, surface active, cationic compounds such as CTAB are used as aftertreatment agents to improve the wet fastness of direct dyes on cellulosic fibres, however, many have been shown to bring about reductions in light fastness by varying extents. They operate by electrostatic association with sulphonic acid groups in the dye molecule forming an insoluble dye-agent complex which is readily retained by the fibre, greatly reducing staining. Dye molecules normally attached to the cellulose chains by van der Waals forces are thought to be dislodged from their orientated positions alongside the cellulose molecules losing their close bond with the fibre and hence becoming more susceptible to photo-degradation because they cannot pass on adsorbed light energy so readily to the cellulose in the form of heat. Also the mixed micelles formed as a result of dye-cationic agent association tend to be less stable to light than pure dye particles.

Interestingly, certain reactive dyes also suffer a decrease in light fastness on aftertreatment with cationic fixing agents and changes in hue or brightness can sometimes occur[227]. Such an effect was observed on comparing treated and untreated cotton dyed with C.I. Reactive Blue 5. At each depth of shade the light fastness was reduced by ≥ 1.5 points and, particularly at the paler depth a considerable difference in hue was observed, the treated sample appearing greener (yellower) than the untreated sample (ie. less red). The reflectance spectra for C.I. Reactive Blue 5 on modified and unmodified cotton are given in Figure 93.

It has been suggested that the very good light fastness properties of reactive dyes on cotton are due in part to the strong covalent bond formed between the dye and the fibre, which facilitates the transfer

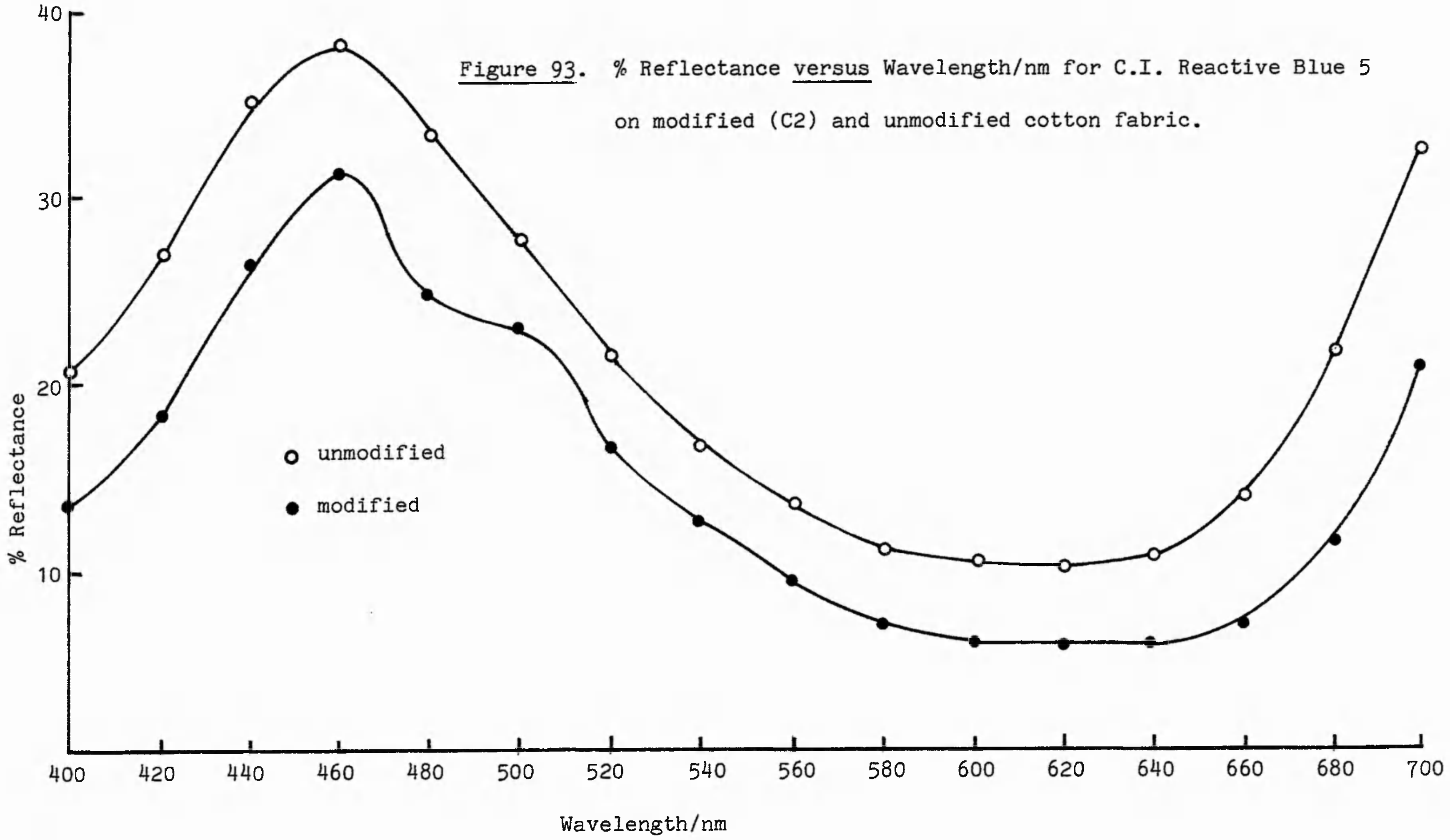


Figure 93. % Reflectance versus Wavelength/nm for C.I. Reactive Blue 5 on modified (C2) and unmodified cotton fabric.

of absorbed light energy to the substrate,diminishing the likelihood of the primary photolytic breakdown of the dye[217]. The fact that the light fastness gradings of reactive dyes are not markedly higher than those of other fast dyes on cellulose, and in some cases they are very low, implies, however, that there are other factors besides covalent bonding which must be responsible for the excellent light fastness properties exhibited by some reactive dyes.

An interaction, for example, between the sulphonic acid groups on the dye and the cationic sites in the fibre which reduces the degree of association of the dye with the fibre and so hinders energy transfer between the two, may therefore be expected to lower the light fastness of the dye on the modified cotton. The fact that the colour a dye exhibits on a particular substrate can also be influenced by the degree of association of the dye on that substrate may also explain why the same dye appeared much greener (yellower) on the modified cotton as compared to the colour obtained on untreated cotton.

The absorption spectra of most dyes show two broad overlapping wavebands, the x band representing monomeric dye, and the shorter wavelength y band representing the associated species[217]. The ratio of the y/x absorbances, a measure of association, rises with concentration when the dye is dissolved in an associating solvent or adsorbed on a solid substrate. This means that if the degree of association decreases and thus the proportion of unassociated dye increases, its absorbance and therefore x will increase, y/x will decrease and the hue of the dye will move towards the blue end of the spectrum (ie. appear greener or less red).

Alternatively, it could be the degree of dye-dye association in the fibre which is actually decreasing rather than the extent of dye-fibre association. This could result if, for example, the presence of the cationic reagent in the fibre restricts the growth of dye aggregates in the amorphous regions of the fibre (the size and form of which determines the exposed air-dye interface and hence the rate of photodegradation) as is thought to be the case with other treatments which involve incorporating foreign substances into cellulose such as delustrants and crease resist resins, and which also usually lower the light fastness.

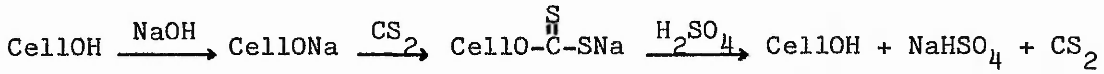
However, the fact that the greatest difference in hue between the C.I. Reactive Blue 5 dyeings on treated and untreated cotton appeared to be at the lower shade depth (of $^1/3$ normal depth) would seem to suggest that it is the dye-fibre interactions which are more important in this respect since at the lower shade depth the proportion of dye-fibre to dye-dye association would tend to be greatest.

3.8 Preparation and dyeing behaviour of differential-dyeing cellulosics other than cotton

3.8.1 Differential-dyeing viscose rayons

In industry much of the high grade cellulose required for viscose rayon is derived from wood pulp sheets which consist of 90-94% pure cellulose. Cotton also contains a high percentage of cellulose, typically 94%, and since yarns pretreated with the 10% o.w.f. of the reagents I and II were readily available these particular cellulose sources were utilised in the preparation of differential-dyeing viscose rayons with high affinity for acid and basic dyes respectively, using the method outlined in section 5.14.

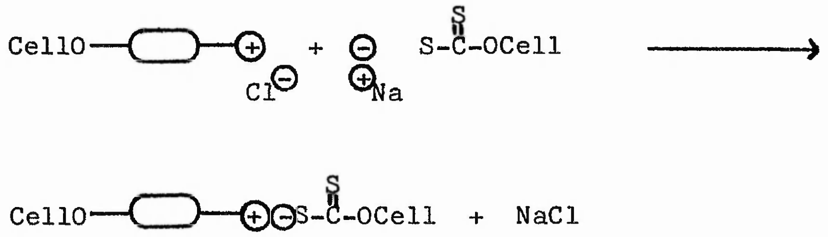
The reaction taking place may be given as:



$$\mathrm{CellOH} \xrightarrow{\mathrm{NaOH}} \mathrm{CellONa} \xrightarrow{\mathrm{CS_2}} \mathrm{CellO{-}}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{{-}SNa} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{CellOH} + \mathrm{NaHSO_4} + \mathrm{CS_2}$$

The process is thus essentially the same as that employed in the preparation of standard, untreated, viscose rayon in that it involves the formation of an orange cellulose xanthate intermediate, except that in this case the so-called orange 'crumbs' prepared from cellulose pretreated with the cationic reagent I were of a totally different consistency from those prepared from untreated cellulose, their being dryer and much more rubbery.

This was thought to be possibly due to the occurrence of a considerable degree of cross-linking resulting from salt formation between the cellulose xanthate anion and the cationic quaternary ammonium groups incorporated into the modified yarns:



where  = cationic reagent I.

The resulting viscose rayons prepared from cellulose pretreated with the cationic reagent I and viscose rayon fibres prepared from untreated cellulose were then refluxed for 2 hours in individual baths containing a known concentration of the monosulphonic acid dye C.I. Acid Red 88 whose structure is given in Figure 53, section 3.7.1.1.

The solutions were then filtered free of loose fibres and their absorbances read at λmax = 505 nm to give $[Df]_{\infty}$ values of 24 and 5.5 mmolsKg^{-1} for the treated and untreated samples respectively (see Table 52).

Table 52. Comparison of $[Df]_{\infty}$ values for viscose rayon prepared from treated and untreated cotton.

% Treatment of original cotton	Aλmax 505 nm	F	$[Ds]_{o}$ molsdm^{-3} x10 ^{4}	$[Ds]_{\infty}$ molsdm^{-3} x10 ^{4}	$[Df]_{\infty}$ mmolsKg^{-1}
10	0.164	x5	5.1966	0.4030	23.97
0	0.417	x20	5.1966	4.0983	5.49

It can be concluded therefore, that most, if not all, of the cationic sites incorporated into the differential-dyeing cotton have remained intact and unaffected by the severe conditions of the viscose process. Similarly viscose fibres prepared from cellulose pretreated with the anionic reagent II, possessed excellent affinity for basic dyes compared to that shown by regenerated cellulose prepared from untreated cotton fibres.

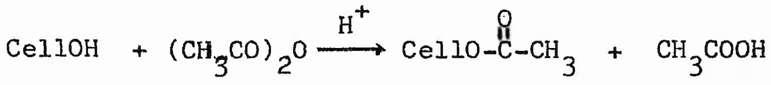
Thus new varieties of differential-dyeing viscose rayon fibres have been produced with potentially new and improved dyeing and bleaching characteristics akin to those of the differential-dyeing cotton from which it was prepared.

On an industrial scale it would therefore be possible to modify the native cellulose at a very early stage of the viscose process enabling differential-dyeing cellulose pulp sheets to be stored ready for use in much the same way as the unmodified cellulose is stored now.

3.8.2 Differential-dyeing cellulose triacetate

Cellulose triacetate production was reintroduced in the U.K. in the 1950's after dichloromethane had become commercially available as a cheaper and safer alternative to chloroform for use as a solvent from which filaments of the triacetate could be regenerated. On an industrial scale it is manufactured from the same high grade cellulose pulp sheets as used in the viscose process, however, in this particular preparation of differential-dyeing cellulose triacetates cotton yarns pretreated with 10% o.w.f. of reagents I and II were used as the cellulose sources according to the method outlined in section 5.15.

The reaction taking place may be given as:



$$\mathrm{CellOH} + (CH_3CO)_2O \xrightarrow{H^+} \mathrm{CellO}-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3COOH$$

The resulting triacetate fibres prepared from cellulose pretreated with the cationic reagent I showed high affinity for the equalising acid dye, C.I. Acid Orange 3, whilst triacetate fibres prepared from untreated cellulose were found to be only slightly stained with this particular dye.

The uv/visible spectrum of a film cast from a 10-15% solution of the cationically modified triacetate fibres dyed with another acid dye, C.I. Acid Red 13, is illustrated in Figure 94 and clearly shows the characteristic absorptions of the reagent at λmax = 223 and 270 nm. Inspection of the infrared spectrum of the film confirmed that almost

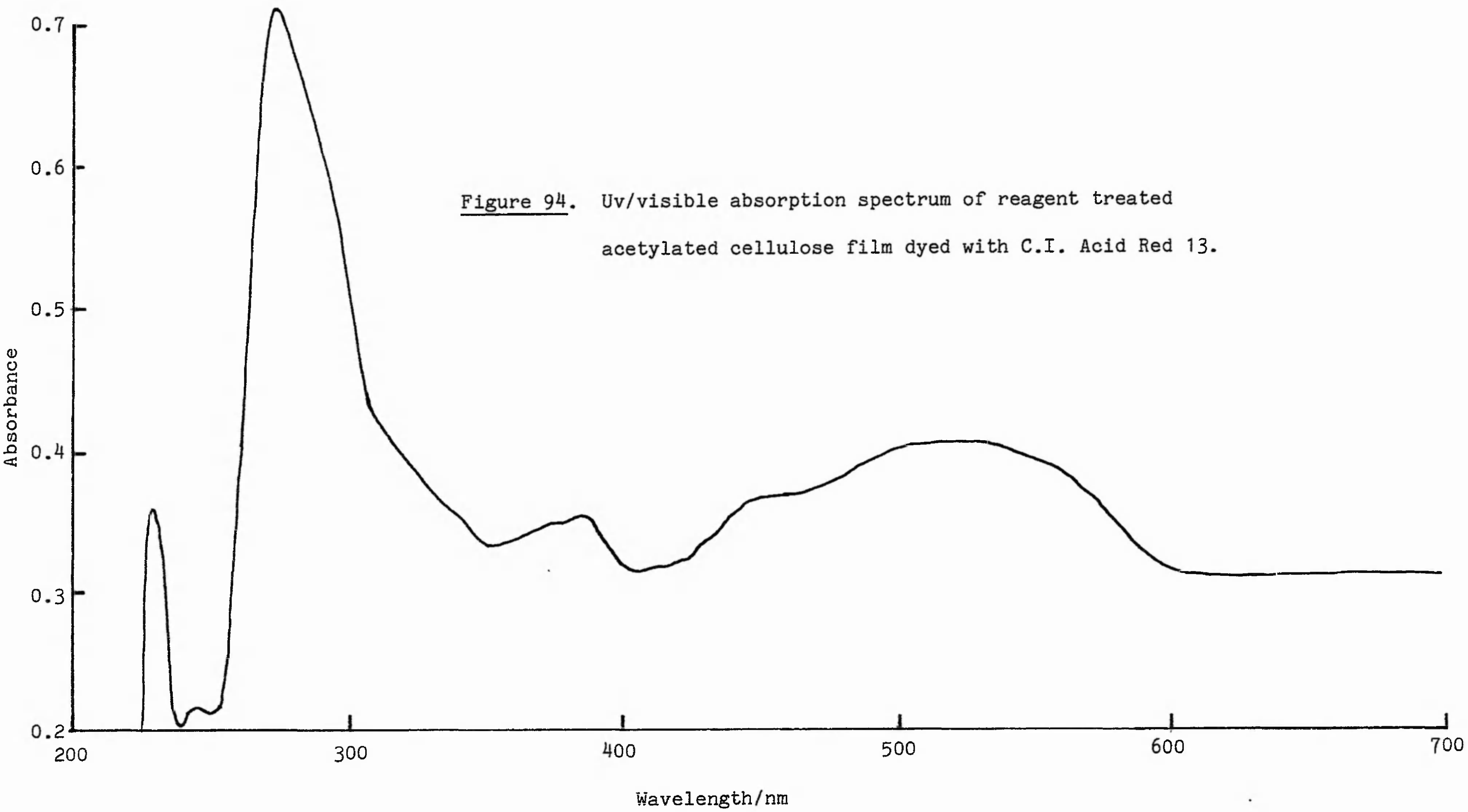


Figure 94. Uv/visible absorption spectrum of reagent treated acetylated cellulose film dyed with C.I. Acid Red 13.

complete acetylation of the hydroxyl groups had taken place (Figure 95).

Thus it would appear that the cationic sites incorporated into the modified yarn were completely unaffected by the concentrated acids employed in the acetylation process. Similarly, triacetate fibres prepared from cellulose pretreated with the anionic reagent II possessed excellent affinity for basic dyes compared to that shown by triacetate fibres prepared from untreated cotton.

3.9 Application of reagents I and II in printing

The series of haloheterocyclic fibre-reactive reagents prepared were also found to have application in the silk-screen printing of cotton fabrics. Print pastes were made up containing cationic reagent I and anionic reagent II and samples of cotton fabric were silk-screen printed using these pastes according to the method outlined in section 5.12.

The localised portions of fabric pretreated with the cationic reagent I showed high affinity for anionic dyes, such as C.I. Acid Red 138 and C.I. Direct Blue 10, when samples were dyed by the same method as described in 5.9 for yarn, whilst the untreated portions were merely stained giving attractive tone-on-tone patterns.

Similarly, localised portions of fabric pretreated with the anionic reagent II showed excellent affinity for basic dyes when dyed in a bath containing 1% o.w.f. C.I. Basic Yellow 15, according to the method outlined in section 5.12, compared to that shown by the untreated regions of the fabric - see Appendix V-8.

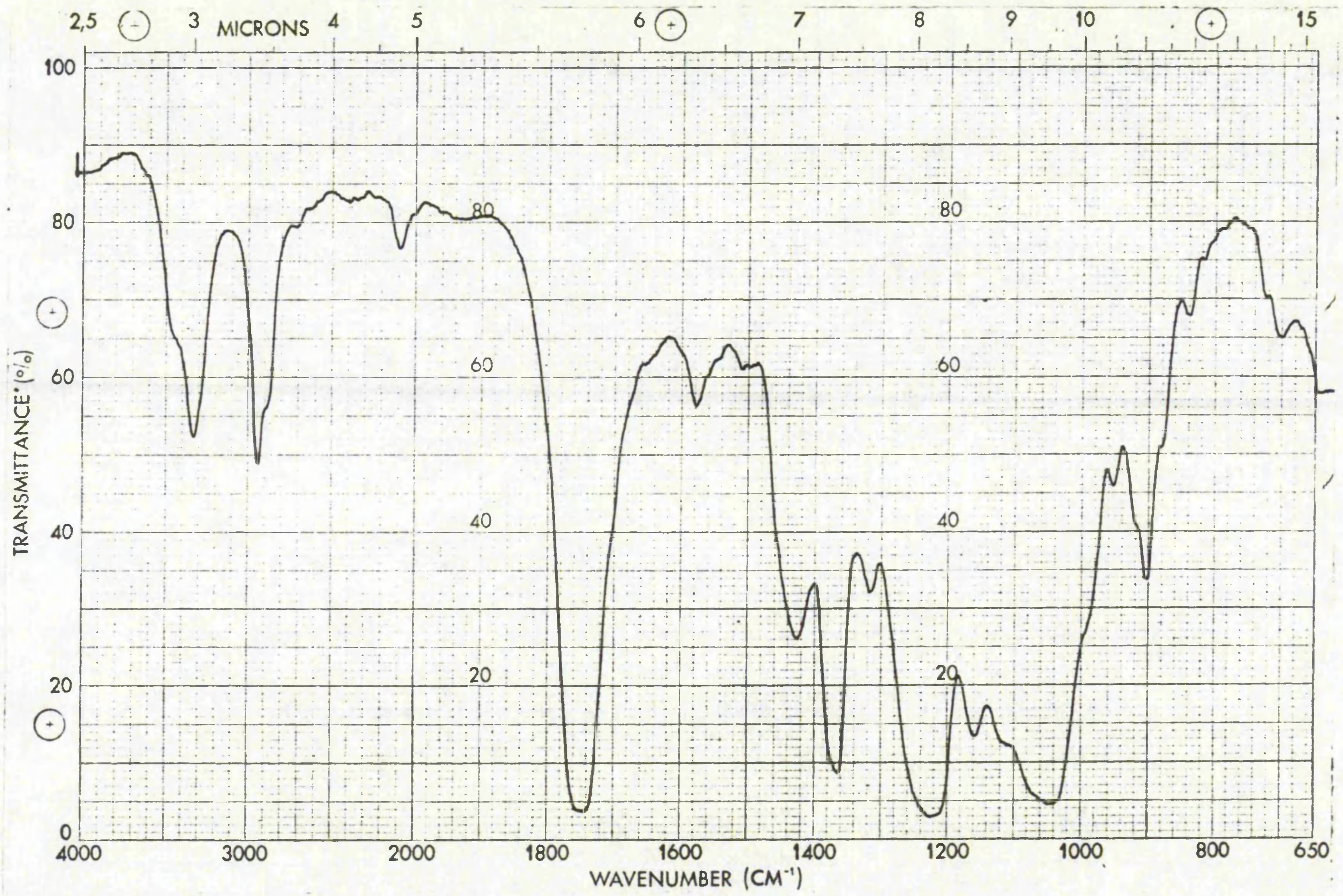
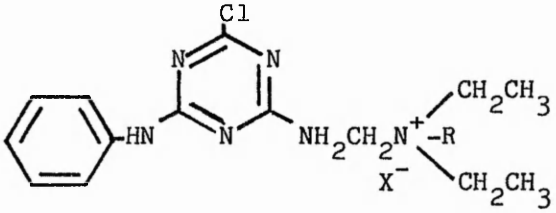


Figure 95. The i.r. spectrum of acetylated cellulose treated with reagent I and dyed with C.I. Acid Red 13.

CHAPTER 4

CONCLUSIONS

1. Treatment of cotton fibre or yarn with colourless, fibre-reactive cationic compounds having the general structure:



where R = alkyl or aryl group

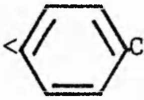
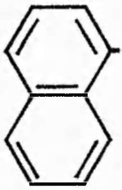
and X = Cl , Br , I or other simple anion.

introduced positively charged sites into the fibre which enhanced its affinity for anionic dyes and thus imparted differential-dyeing behaviour to the yarn when combined with untreated cotton. Previous use of dyeing auxiliaries to increase the degree of exhaustion of reactive dyes on cotton made no mention of the prior treatment of loose fibre or yarn to impart differential-dyeing characteristics.

2. The degree of differential dye uptake between treated and untreated cotton depended on the level of pre-treatment so that a range of yarns of differing dye capacities could be produced giving a variety of tone-on-tone effects. This treatment thus had advantages over the partial acetylation process used for the production of "Cotopa" yarns, with which tone-on-tone effects could not be obtained.

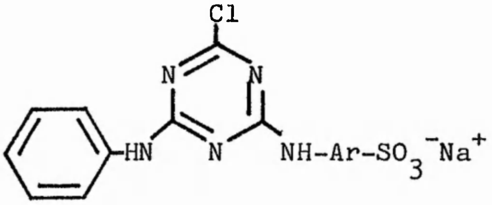
3. The affinity of the reagents for cellulose, and hence their effectiveness, depended on the nature of the group R, increasing with

increasing molecular weight according to the series:

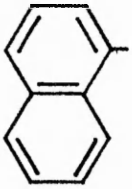
$CH_3 < CH_3CH_2 < CH_3(CH_2)_3 < CH_3(CH_2)_5 < CH_3(CH_2)_9 <$  $CH_2 <$  CH_2

Compounds containing non-planar R groups such as  or $(C_6H_5)_2CH-$ showed no appreciable adsorption confirming the importance of Van der Waals forces in conferring affinity for cellulose.

4. Treatment of cotton with colourless fibre-reactive anionic compounds having the structure



where Ar = C_6H_4 or $C_{10}H_6$, imparted enhanced affinity for cationic dyes. The presence of a delocalised positive charge on certain basic dyes did not affect their affinity for the anionic sites incorporated into the fibre.

5. The equilibrium exhaustion of a typical cationic reagent (R =  CH_2) as a function of sodium chloride concentration initially decreased in the range of 0-0.1 mols dm^{-3} and then increased again as the concentration of sodium chloride was gradually raised to 1.0 mols dm^{-3}. This behaviour was attributed to the operation of

two opposing effects; suppression of the negative surface charge on the cellulose, which reduced the electrostatic forces of attraction, and a gradual increase in the chemical potential of the reagent in solution, the former effect being dominant initially.

6. The nature of the anion of added neutral electrolyte was important in determining the equilibrium of the cationic reagent I, the degree of equilibrium exhaustion increasing according to the series:

$SO_4^{=} < F^- < Cl^- < Br^- < NO_3^- < I^- < SCN^-$

which is in fact the reverse of the lyotropic series of decreasing salting-out power. The effect of the cation was of much less significance, the exhaustion decreasing only slightly on going from Na^+ to Cs^+ in agreement with the lyotropic series.

Conversely, the nature of the cation of added electrolyte was far more important in determining the equilibrium exhaustion of an anionic reagent than was the nature of the anion. The order of effectiveness was again the reverse of the lyotropic series:

$Li^+ < Na^+ < K^+ < Cs^+$

The effects of different anions on the exhaustion of the cationic reagent, and of different cations on the exhaustion of the anionic reagent are in agreement with the theory of water-structure enforced ion-pair formation[212].

7. The level of fixation of the cationic reagent may be determined

by measurement of the saturation uptake of a low molecular weight mono-basic acid dye such as C.I. Acid Orange 7 or by using a previously constructed calibration plot relating Colour Strength, as measured by an ICS Micromatch, to dye uptake (alternatively it may be measured using an ion-exchange technique).

8. Yarns pretreated with cationic reagent I showed differential-dyeing behaviour when dyed in the presence of untreated cotton using all the normal cellulosic dyes; direct, reactive, vat, sulphur and azoics, as well as with acid dyes. As the dyesites are quaternary nitrogen groups they will be positively charged throughout the whole pH range which is a considerable advantage over the differential-dyeing DD viscose rayon fibres which could not be used with azoic, sulphur or vat dyes because it was necessary to dye at acid pH values to obtain the differential-dyeing effect.

9. Using three acid dyes, containing 1,2 and 3 sulphonic acid groups respectively, the stoichiometry of the interaction between the cationic dye sites on the treated cellulose and the sulphonic acid groups on the dye molecules was found to be 1:1. No such simple stoichiometry existed in the case of direct dyes where diffuse adsorption effects were far more pronounced.

10. The high diffusion rates of dyes could be controlled to a certain extent by the selection of a suitable counter-ion or the use of anionic levelling agents.

11. Maximum contrast between treated and untreated yarns was found under conditions where the substantivity of the dyestuffs for untreated cellulose was at a minimum. Thus the contrast between treated and

untreated yarns was generally observed to increase with decreasing concentration of added electrolyte, increasing temperature and increasing liquor ratio. Even with vat dyes of high affinity for untreated cotton, such as C.I. Vat Green 1, good contrast could still be obtained between treated and untreated yarns. In the case of azoic dyes, maximum contrast was obtained by applying only half the manufacturers recommended amount of coupling component in the absence of added electrolyte.

12. Bleaching of cotton fibres treated with reagent I could be carried out using sodium hypochlorite without adversely affecting the differential dye uptake exhibited by the modified cotton or tendering of the fibres. In contrast,Ward and Hill found that their acid-dyeable DD viscose fibres suffered irreversible loss in dyeability on treating with sodium hypochlorite, sodium chlorite and hydrogen peroxide at the strengths necessary for cotton bleaching.

13. The treatment was also fast to mercerisation, increasing the Colour Strength obtained on treated yarn by 24% (relative to unmercerised treated cotton) and thus enabling reductions to be made in dye consumption.

14. Treatment of cotton with reagent I considerably improved the wash fastness properties of direct dyes compared to those exhibited on untreated cotton although those of reactive dyes were slightly reduced by comparison with untreated yarn,probably as a result of hydrolysed dye still having affinity for the cationic sites in the modified cotton.

15. Light fastness ratings on treated yarn were slightly reduced

compared to those obtained on untreated cotton for the two dyes examined, particularly in the case of the reactive dye. This was thought to be due to changes in the nature of the dye-fibre interactions taking place in the modified yarn.

16. Combinations of cationic and anionic modified yarns can be cross-dyed two colours from a single dyebath containing anionic and cationic dyes in a one-step process. Cross-staining is minimised by selecting dyes having low substantivity for untreated cellulose, such as, for example, acid dyes and basic dyes not based on the anthraquinone ring system.

17. Both cationic and anionic differential-dyeing varieties of cellulose triacetate and viscose rayon have been prepared from celluloses pretreated with cationic and anionic reagents I and II respectively.

18. The above cationic and anionic reagents have also found application in the printing of cotton fabrics; fabrics treated in part being dyed with anionic and cationic dyes respectively to reveal the pattern or design.

CHAPTER 5

EXPERIMENTAL

5.1 Materials used

5.1.1 Cotton

The cotton yarn used was spun from high quality cotton fibres of the Sea Island variety, in the absence of spinning oils, to a resultant tex of 110/2 (spinning twist 334 turns per metre, doubling twist 250 turns per metre).

5.1.2 Chemicals

The chemicals and solvents used were of General Purpose Reagent grade. The dyes used were the commercial samples unless otherwise stated. The purification of commercial samples was carried out as necessary and is described in section 5.3. The water was singly distilled.

5.2 Spectroscopic methods

Infrared spectra were recorded on a Pye Unicam SP1000 infrared spectrophotometer. Reflectance and Colour Strength measurements were carried out on an ICS Micromatch abridged spectrophotometer, yarn samples being wound onto card to form 1" x 1" square samples prior to the measurements being taken. Uv and visible spectra and single wavelength measurements were obtained using a Perkin Elmer 551S spectrophotometer.

Proton magnetic resonance spectra were recorded on a Jeol FX60Q 60MHz spectrophotometer with tetramethylsilane as the internal standard.

5.3 Purification of dyes

The purification of direct dyes by recrystallisation was carried out using one or other of the standard methods outlined below for C.I. Direct Blue 1 and C.I. Direct Yellow 12.

5.3.1 Purification of C.I. Direct Blue 1

3 g of commercial (crude) C.I. Direct Blue 1 was dissolved as far as possible in 150 cm^3 of cold dimethyl formamide. The slurry was then filtered and the filtrate retained. This procedure was then repeated with two further portions of dimethyl formamide and the extracts combined to give a total volume of 400 cm^3. Sufficient acetone was then added to the solution to precipitate the dye. After leaving the solution to stand for 16 hours precipitation was complete and the pure solid was filtered off, collected on a sinter and dried for 16 hours at 60°C to yield 0.4 g of C.I. Direct Blue 1 - a brown solid with a coppery sheen.

5.3.2 Purification of C.I. Direct Yellow 12

A saturated solution of commercial (crude) C.I. Direct Yellow 12 was made up containing 4 g of dye in 150 cm^3 of boiling distilled water. The solution was filtered hot to free it if insoluble impurities and then allowed to cool. The pure dye which precipitated from solution was filtered off, washed with a small volume of cold water, and oven dried at 70°C for 16 hours. The remaining filtrate was concentrated and a second crop of the pure solid was observed to crystallise out slowly from solution in the form of fine orange needles. Total yield = 0.85 g.

5.4 Preparation of reagents

5.4.1 Cationic reagents

The synthesis of a series of reagents was based on the preparation of the following typical examples.

Reagent I.

A solution of cyanuric chloride (18.4 g) in acetone (50 cm^3) was added to a well stirred mixture of ice and water (50 g). A solution of aniline (9.3 cm^3) in acetone (50 cm^3) was run into the mixture and a 10% solution of sodium carbonate (60 cm^3) was added simultaneously so as to maintain a pH of 6.5-7.0. The temperature was kept at 0-5°C throughout. After stirring for 1 hour the colourless product was filtered off, washed with distilled water until free of chloride ion and dried overnight at <70°C. Recrystallisation from toluene yielded 18 g of 2-anilino-4,6--dichloro-1,3,5-triazine (Intermediate 1). Melting point = 138°C, yield = 75%.

N,N-Diethylethylene diamine (8.7 g) dissolved in acetone (30 cm^3) was carefully added to a solution of Intermediate 1 (18 g) in acetone (50 cm^3). After the initial reaction had subsided the mixture was refluxed for 1 hour, cooled, and the crystalline product filtered off, washed with acetone and dried in air to give 23 g of the hydrochloride which on conversion to the free base yielded 20 g of 2-anilino-4-(N,N-diethylethylenediamine)-6-chloro-1,3,5-triazine (Intermediate 2). Melting point = 152-3°C, yield 84%.

A solution of 1-(chloromethyl)napthalene (22 g), a twofold excess, in acetone (50 cm^3), was then added to a solution of Intermediate 2

(20 g) in acetone (100 cm^3). After prolonged refluxing (30 hours) the colourless product was filtered off from the hot solution, washed well with acetone and dried in vacuo at <40°C to yield 28.5 g of the quaternary reagent I, melting point = 179-181°C, yield = 92%.

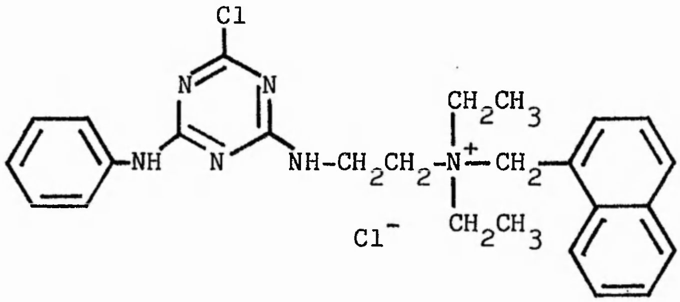


Figure 96. Reagent I - 2-anilino-4-chloro-6-N-[2'-N-ethyl-N-(1-naphthylmethyl)ethylamino]amino-1,3,5-triazine ethochloride.

Reagent III.

A solution of benzyl chloride (15.8 g), a twofold excess, in acetone (50 cm^3), was added to a solution of Intermediate 2 (20 g) in acetone (100 cm^3). After refluxing for 20 hours the colourless precipitate was filtered off from the hot solution, washed well with acetone and dried in vacuo at <40°C to yield 26.5 g of the quaternary reagent III, melting point = 214-216°C, yield = 95%.

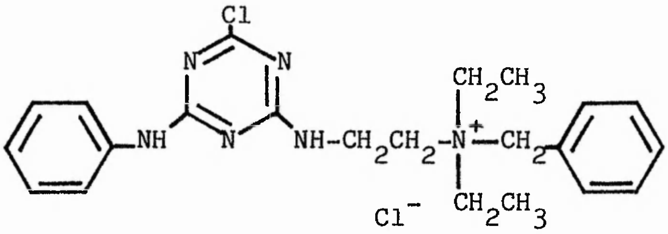
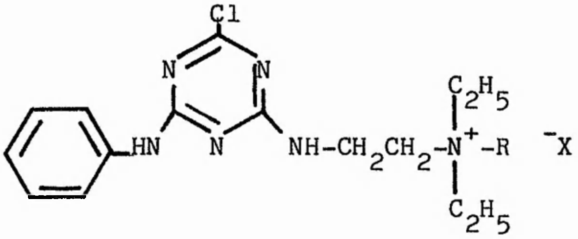
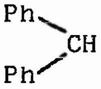


Figure 97. Reagent III - 2-anilino-4-chloro-6-N-[2'-N-ethyl-N-(benzyl)ethylamino]amino-1,3,5-triazine ethochloride.

All further quaternary reagents were prepared in a similar manner to reagents I and III by refluxing Intermediate 2 with the appropriate alkyl halide in acetone solution. The time required for the reaction decreased with decrease in the size of the alkyl substituent; for example the reaction with methyl iodide required only 2-3 hours.

The compounds prepared may be summarised using the general formula below:



R	Reagent	X	% Yield	M.pt.	Appendix
CH_3	V	I	85	175-176	VI-6
C_2H_5		I	70	196-198	VI-7
C_4H_9		I	62	215-216	VI-8
C_6H_{13}		I	96	149-150	VI-9
$C_{10}H_{21}$		I	80	150-152	VI-10
C_6H_{11} (cyclohexyl)		I	50	151-153	VI-11
		Cl	55	194-195	VI-12
$C_{10}H_7CH_2$	I	Cl	92	179-181	VI-1,2
$C_6H_5CH_2$	III	Cl	95	214-216	VI-4

5.4.2 Anionic reagents

Two anionic reagents were prepared according to the following methods:

Reagent II.

A solution of cyanuric chloride (9.2 g) in acetone (25 cm^3) was run into a well stirred mixture of ice and water (30 g). A solution of p-sulphanilic acid in 5% excess (9.1 g) in water (80 cm^3) was then run into the mixture and a 10% solution of sodium hydroxide (50 cm^3) was added simultaneously so as to maintain a pH of 6.5-7.0 throughout the reaction. The mixture was stirred for 45 minutes keeping the temperature at 0-5^{o}C. The white pasty solid was then filtered off and left to dry in vacuo at <40^{o}C to yield 15.4 g of the crude product as its sodium salt. Yield = 90%.

The sulphanilic acid derivative of cyanuric chloride prepared above (15 g) was then dissolved in water (200 cm^3) to which solution were added simulatneously aniline (4 cm^3) dropwise and a 10% solution of sodium carbonate (50 cm^3) so as to maintain a pH of 6.5-7.0 throughout the reaction. The mixture was stirred for 45 minutes at 40-45°C after which time it was cooled in a salted ice-bath and a small amount of a green precipitate filtered off. Sodium chloride (10 g) was then added to the clear filtrate and after 15 minutes a large mass of a colourless pasty solid precipitated out. The product was filtered off and air dried as much as possible before drying in vacuo at <40°C for several days to yield 15.96 g of the anionic reagent II. Yield = 85%, melting point = >300°C.

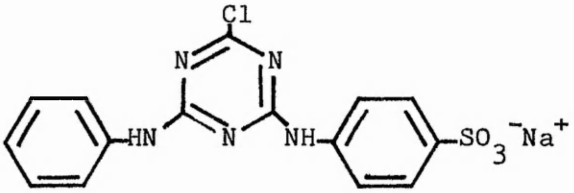


Figure 98. Reagent II - 2-anilino-4-chloro-6-N-(sulphanilic acid)-1,3,5-triazine (Na^+ salt).

Reagent IV.

An aqueous solution of the sodium salt of 1-naphthylamine-4-sulphonic acid was prepared by dissolving the free acid (6.3 g) in 0.4M sodium hydroxide solution (50 cm^3). This solution was added gradually to a solution of Intermediate 1 (4.8 g) in acetone (30 cm^3) with addition of 2M sodium hydroxide as necessary to maintain an alkaline pH throughout. The temperature of the reaction mixture was raised to 40°C and kept at this temperature for 1 hour. It was then raised to 60°C and held at this temperature for a further 2 hours with stirring. The product was filtered off and washed with acetone to yield a white paste which was dried in vacuo at <40°C to give reagent IV, (3.7 g). Melting point = >300°C.

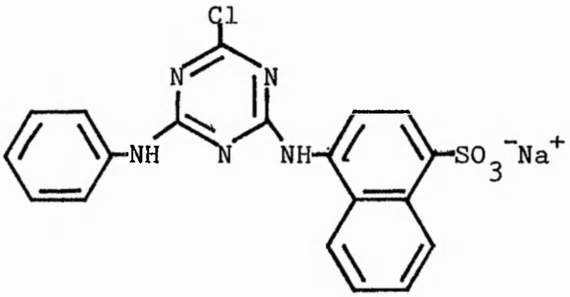


Figure 99. Reagent IV - 2-anilino-4-chloro-6-N-(1-naphthylamine-4-sulphonic acid)-1,3,5-triazine (Na^+ salt).

5.5 Extinction coefficient determinations

Unless otherwise stated the extinction coefficients of the various dyes and reagents employed were found by purification of the particular compound in question and preparation of an accurate series of solutions in an appropriate solvent system (usually water). The molar extinction coefficient of the sample could then be found from the slope of a plot of Absorbance versus Concentration in molsdm^{-3}.

5.6 Treatment of yarn and fabric

Treatment of yarn and fabric on a small scale (1-15 g samples) was carried out on an Ahiba laboratory dyeing machine, TEXOMAT G VI B, with temperature control unit TC 101. The machine ensured very thorough agitation of samples in the dye liquor by employing a twist rake action and a constant stirring speed of 30 rpm. The external bath medium could be uniformly heated throughout via two mechanically driven spirals arranged horizontally in the bath which maintained the liquor in constant turbulence. Heat up time was set to 100%. Samples could be dyed on double anchor stirrers or in perforated baskets.

5.6.1 Treatment of yarn (small-scale)

The reagent (2.5-15% o.w.f.) was dissolved in water and wet out, and bleached cotton yarn was entered into the treatment bath at 60°C (liquor ratio 50:1). Sodium chloride (40 g/l) was added portionwise over 10 minutes and the treatment continued at 60°C for 45 minutes. Sodium carbonate (20 g/l) dissolved in a small volume of the treatment liquor was then added to the bath and the temperature raised to 80°C. The reaction was continued at this temperature for 2 hours, after which time the yarn was removed, rinsed and then soaped at 60°C for 30 minutes using a non-ionic detergent (2% o.w.f.), rinsed and dried.

5.6.2 Treatment of fabric (small-scale)

The reagent (10% o.w.f.) was dissolved in water and wet out bleached cotton fabric pieces were entered into the treatment bath at 60°C (liquor ratio 50:1). Sodium chloride (40 g/l) was added portionwise over 10 minutes and the treatment continued at 60°C for 45 minutes. Sodium carbonate (20 g/l) dissolved in a small volume of the treatment liquor was then added to the bath and the temperature raised to 80°C. The reaction was continued at this temperature for 2 hours, after which time the fabric was removed, rinsed and then soaped at 60°C for 30 minutes using a non-ionic detergent (2% o.w.f.), rinsed and dried.

5.6.3 Treatment of yarn in bulk

5.6.3.1 In package form

The reagent (10% o.w.f.) was dissolved up as far as possible in 2.5 litres of hot water (<80°C). Bleached, unwaxed cotton yarn (500 g) was wound onto a stainless steel spring and loaded into a package dyeing machine, the maximum capacity of which was 10 litres. The reagent solution was added to the dyeing chamber and the dyebath volume made up to 10 litres with softened water (liquor ratio 20:1). Exhaustion was carried out for 1 hour at 60°C in the presence of sodium chloride (40 g/l). Dissolved sodium carbonate (20 g/l) was then added to the treatment bath and the temperature of the bath raised to 80°C by steam injection. Fixation was continued for 2 hours at 80°C ensuring adequate flow of the treatment liquor through the yarn package in both directions. After 2 hours the dyeing chamber was drained and the package was soaped at 60°C for 30 minutes using a non-ionic detergent (2% o.w.f.). The yarn still in package form, was then rinsed well in distilled water, dried and wound off onto a cone for storage, removing 1 g portions at intervals for dyeing with 5% o.w.f. C.I. Direct Blue 1 to ensure the levelness of the treatment.

5.6.3.2 In hank form

The reagent (10% o.w.f.) was dissolved up as far as possible in 2.5 litres of hot water (<80°C) and transferred to a hank dyeing machine making up the volume to a total of 22 litrs (liquor ratio 40:1) with distilled water. Bleached, unwaxed cotton yarn (550 g) in hank form was thoroughly wet out and entered into the treatment bath at 60°C. Exhaustion was carried out for 1 hour at 60°C in the presence of sodium chloride (40 g/l). A further quantity of sodium chloride (40 g/l) was then added as the temperature of the treatment bath was raised to 80°C. Sodium carbonate (20 g/l) dissolved in 3 litres of the treatment liquor was added to the bath and fixation carried out at 80°C for 4 hours after which time the hanks were soaped at 60°C for 30 minutes using a non-ionic detergent (liquor ratio 40:1), rinsed thoroughly in distilled water and dried. The hanks were then wound onto a cone for convenience of handling, taking 1 g samples at intervals for dyeing with 2% o.w.f. C.I. Direct Blue 1 to ensure the levelness of the treatment.

5.7 Determination of the concentration of cationic sites in modified cotton

5.7.1 Ion-exchange method

A 20 g ± 0.01 g sample of cotton yarn (C1) modified in bulk with 5% o.w.f. of the cationic reagent I, was immersed for 16 hours in an ammonia solution (0.3 molsdm^{-3}) to ensure that all available chloride counter-ions were exchanged for hydroxide ions. The yarn was then washed free of excess hydroxide ion using several portions of distilled water and oven dried at <70°C until quite dry and free from traces of residual ammonium hydroxide which were readily removed as ammonia and water vapour.

The yarn was then transferred to a clean, dry container and a known volume of dilute hydrochloric acid (solution A) was added, completely immersing the sample. After allowing 16 hours for the neutralisation reaction to go to completion, three 20 cm^3 aliquots of the acid treatment bath were removed and titrated against a dilute standard solution of sodium hydroxide using Phenol Red as indicator [pH 6.8-8.4 Yellow-Red]. Phenolphthalein was not used because in dilute solution ($\leq$0.01M) the end point is difficult to see.

Three 20 cm^3 aliquots of the original hydrochloric acid solution were then also titrated against the standard solution of sodium hydroxide to determine the initial concentration of the acid treatment bath. The site content of the modified yarn could then be determined from the equation cited in section 3.3.3.2.

5.7.2 Dye uptake method

Six 2 g ± 0.01 g hanks of modified cotton (C1) were dyed to equilibrium under reflux in baths containing dye concentrations in the range 0.2-2.5 x 10^{-3} $molsdm^{-3}$ of C.I. Acid Orange 7 (C.I. 15510). The dyed samples were then removed and the dyebaths cooled, and diluted where necessary, prior to taking absorbance measurements at $\lambda max = 486$ nm to determine the concentration of dye remaining in solution and hence the concentration of dye on the fibre by subtraction. A $[Df]_\infty$ versus $[Ds]_\infty$ equilibrium isotherm was then drawn up and the site content of the yarn determined by extrapolating the graph back to the y axis, or finding where the graph levelled off and saturation of the available dye sites was complete.

5.8 Test for differential dye uptake

5.8.1 Anionic dyes

In order to determine whether the treatment of yarn or fabric with cationic reagents was successful the cotton samples were wet out and, together with an equal weight of untreated cotton, were entered into a bath at 60°C containing 1% o.w.f. of C.I. Direct Blue 10 (liquor ratio 40:1). The temperature of the bath was then raised to 96°C and dyeing continued at this temperature for 1 hour in the absence of salt. The samples were then rinsed and soaped for 30 minutes at 60°C using 2% o.w.f of a non-ionic detergent (liquor ratio 40:1), rinsed and dried.

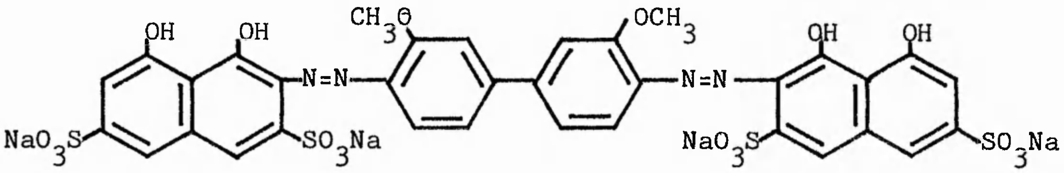


Figure 100. C.I. Direct Blue 10; C.I. 24340.

5.8.2 Cationic dyes

To establish whether anionic dye sites had been incorporated into the cotton yarn or fabric as a result of treatment with the anionic reagents, treated and untreated cotton samples were wet out and entered into a dyebath set at 60°C and containing 1% o.w.f. of C.I.

Basic Red 18 (see Figure 86) at a liquor ratio of 40:1. The temperature of the bath was then raised to 96°C and dyeing continued at this temperature for 1 hour in the absence of the normal dyeing assistants used with basic dyes in their more usual application to acrylic fibres. The samples were then rinsed and soaped for 30 minutes at 60°C using 2% o.w.f. of a non-ionic detergent (liqor ratio 50:1), rinsed and dried.

5.9 Dyeing of treated yarn/untreated yarn in combinations

In each case yarn treated with 10% reagent I (o.w.f.) was used as the treated yarn.

5.9.1 Direct dyes

Hanks of treated and untreated yarn were dyed together in a bath containing 3% o.w.f. C.I. Direct Blue 1 at a liquor ratio of 50:1. The hanks were entered at 60°C, the temperature raised to 95°C over 15 minutes and dyeing continued for 45 minutes at this temperature. No sodium chloride was used in the dyeing. The hanks were then soaped for 30 minutes at 60°C with 2% o.w.f. non-ionic detergent at a liquor ratio of 50:1, rinsed and dried.

5.9.2 Reactive dyes

Hanks of treated and untreated yarn were wet out together in a dyebath set at 50°C with 2% C.I. Reactive Blue 5 (o.w.f.) at a liquor ratio of 50:1. After 20 minutes treatment at this temperature sodium carbonate (100% o.w.f.) was added and the temperature raised to the boil. After dyeing at the boil for 45 minutes the hanks were removed, rinsed, soaped twice at the boil for 30 minutes using 2% non-ionic detergent (o.w.f.) then rinsed and dried.

5.9.3 Vat dyes

Hanks of treated and untreated yarn were wet out and placed together in a dyebath set at 25°C with 5% sodium hydroxide (o.w.f.), 5% sodium dithionite (o.w.f.) and 2% C.I. Vat Yellow 3 (o.w.f.) previously reduced at 50°C with sodium hydroxide and sodium dithionite. The final liquor ratio in the dyebath was 60:1. Dyeing was carried out at 25°C for 40 minutes after which the dyed hanks were removed, oxidised in air, soured in dilute acetic acid, rinsed and then soaped at the boil for 20 minutes using 2% non-ionic detergent and a liquor ratio of 50:1.

5.9.4 Sulphur dyes

Hanks of treated and untreated yarn were wet out and placed together in a dyebath set at 25°C with 15% sodium dithionite, 7.5% sodium carbonate and 15% C.I. Solubilised Sulphur Black 1 (all o.w.f.) at a liquor ratio of 25:1. The dyebath was raised to the boil and held at this temperature for 40 minutes then cooled to 50°C over 20 minutes. The hanks were then squeezed to remove surplus dye liquor, allowed to oxidise in the air at room temperature and soaped at 50°C with 2% non-ionic detergent (o.w.f.).

5.9.5 Azoic dyes

Hanks of treated and untreated yarn were wet out then worked together for 30 minutes at 25°C in a bath containing 2.25% C.I. Azoic Coupling Component 34 (o.w.f.) dissolved in 1% (w/v) sodium hydroxide solution. The liquor ratio was 25:1. The hanks were removed, squeezed to remove surplus liquor, and coupled at 25°C with C.I. Azoic Diazo Component 8 [1.25% (w/v) solution, liquor ratio 25:1]. The samples were then rinsed in cold water, acid rinsed for 20 minutes in dilute HCl, rinsed in cold water and boiled for 20 minutes in a solution containing 2% non-ionic detergent and 5% sodium carbonate (o.w.f.). The samples were then rinsed and dried.

5.9.6 Acid dyes

Hanks of treated and untreated yarn were wet out and placed in a dyebath at 50°C containing 1% C.I. Acid Red 88 (o.w.f.). The temperature was raised to the boil over 15 minutes and dyeing continued for 30 minutes. The hanks were then rinsed, soaped for 30 minutes at 60°C using 2% non-ionic detergent (o.w.f.) and a liquor ratio of 50:1, rinsed and dried.

5.10 Dyeing of modified cotton with mixtures of anionic dyes

The dyeing of yarns pretreated with 10% o.w.f. of the cationic reagent I with mixtures of anionic dyes was carried out using both acid and direct dyes.

5.10.1 Dyeing with mixtures of acid dyes

Using commercial dye samples, two acid dye mixtures were made up containing 2% o.w.f. each of C.I. Acid Blue 47 and C.I. Acid Yellow 17 in the first dyebath and 2% o.w.f. each of C.I. Acid Blue 45 and C.I. Acid Yellow 17 in the second dyebath (liquor ratio 50:1). In each case a hank of cotton yarn pretreated with cationic reagent I was wet out and entered into the dyebath at 50°C. The temperature of the bath was raised to 96°C and dyeing continued at this temperature for 45 minutes. The hank was then removed and a second hank of the treated yarn, of a similar weight to the first, was added to the slightly cooled dyebath, the temperature of which was then raised to the boil and dyeing continued for a further 45 minutes. This procedure was then repeated with a further sample of treated cotton and all three dyeings were then rinsed well and soaped individually at 60°C for 30 minutes using a non-ionic detergent (2% o.w.f.).

5.10.2 Dyeing with mixtures of direct dyes

Seven 2 g ± 0.01 g hanks of cotton pretreated with cationic reagent I were wet out and entered into a series of dyebaths at 60°C and containing 1:1 equimolar mixtures of the direct dyes C.I. Direct Blue 22 and C.I. Direct Yellow 12 to give total application levels of pure dye in the range of 6.25×10^{-3} - 0.1 molsKg^{-1}. The temperature of the baths were raised to 96°C and dyeing carried out for 1 hour in the absence of added electrolyte. The hanks were then removed, rinsed well and soaped at 60°C for 30 minutes in a non-ionic detergent (2% o.w.f.), rinsed and dried.

A similar procedure was adopted for the direct dye mixture employing C.I. Direct Blue 1 and C.I. Direct Yellow 12, except that the total application levels of pure dye were in the range 2.5×10^{-3} - 0.1 molsKg^{-1}.

5.11 Cross-dyeing of modified yarns

The cross-dyeing of yarns pretreated with 10% o.w.f. of cationic reagent I was carried out successfully using yarns pretreated with the anionic reagents II and IV and with the anionic proprietary reagent Sandospace R , of undisclosed chemical constitution (now no longer commercially available). An example of a typical cross-dyeing is given below. (See also Appendix V for photographs of test samples).

Two hanks of cotton yarn, one pretreated with 10% o.w.f. of cationic reagent I and the other with 10% o.w.f. of anionic reagent II, were wet out and entered into a dyebath at 60°C and containing 1% C.I. Acid Red 88, 1% C.I. Basic Yellow 15 and 5% non-ionic detergent (all o.w.f.). The liquor ratio was 50:1. The temperature was raised to 96°C and the dyeing carried out for 30 minutes after which time the dyed hanks were removed, rinsed and soaped for 30 minutes at 60°C using a non-ionic detergent (2% o.w.f.).

5.12 Application of reagents I and II in printing

Print pastes were made up containing:

1	part reagent I or reagent II
100	parts water
20	parts urea
3	parts sodium bicarbonate
10	parts Solvitose C5

Samples of cotton fabric were screen printed using this paste, steamed to bring about fixation of the reagent and washed to remove the residue of thepaste. Individual samples were then dyed as described above for combinations of treated and untreated yarns or, in the case of samples printed with paste containing anionic reagent II, as follows:

The fabric was wet out and placed in a dyebath set at 50°C, liquor ratio 50:1, and containing 1% C.I. Basic Yellow 15 (o.w.f.). The temperature was raised to 90°C and dyeing continued for 30 minutes at this temperature. The fabric was then soaped at 60°C for 30 minutes with 2% non-ionic detergent (o.w.f.), then rinsed and dried.

5.13 Ancillary treatments of differential-dyeing cotton

5.13.1 Bleaching of differential-dyeing cotton

5.13.1.1 Bleaching with sodium hypochlorite

Unwaxed cotton yarn modified with reagent I (10% o.w.f.) was steeped for 30 minutes at room temperature in a solution of sodium hypochlorite containing 0.15% w/v available chlorine at a liquor ratio of 50:1. The cotton yarn was then washed well in distilled water and soured in hydrochloric acid (0.5% w/v) for 15 minutes at room temperature. After thorough rinsing in distilled water the yarn was steeped in sodium bisulphite (1% w/v) to 'anti-chlor', washed and dried.

5.13.1.2 Bleaching with hydrogen peroxide

Unwaxed cotton yarn modified with reagent I (10% o.w.f.) was treated for 1 hour at 90°C in a 2 volume solution of hydrogen peroxide, made up using hard (undistilled) water and containing sodium metasilicate (0.25% w/v) as stabiliser, and ensuring that the bath was alkaline to phenolphthalein paper (liquor ratio 50:1). The yarn was then washed well in distilled water and dried.

5.13.1.3 Bleaching with sodium chlorite

Unwaxed cotton yarn modified with reagent I (10% o.w.f.) was treated for 45 minutes at 90°C in a sodium chlorite solution (0.15% w/v) containing a non-ionic wetting agent (0.1% w/v) and acetic acid (0.25% w/v) at a liquor ratio of 50:1. The yarn was then washed well in distilled water and dried.

5.13.2 Mercerisation of differential-dyeing cotton

Unwaxed cotton yarn modified with reagent I (10% o.w.f.) was treated at room temperature with 24% w/v sodium hydroxide under tension for 10 minutes (liquor ratio 100:1). The yarn was then washed well in running water and treated with dilute acetic acid (10% w/v) to neutralise residual alkali. It was then washed again in running water, rinsed in distilled water and dried.

5.14 Preparation of samples for fastness tests

Cotton fabric was treated with 10% o.w.f. of the cationic reagent according to the method outlined in section 5.6.2.

Treated and untreated cotton fabric was then dyed to two standard depths ($^1/3$ and $^1/1$ of normal) for each of the two dyes under investigation according to the following methods.

5.14.1 C.I. Direct Blue 1

5.14.1.1 Treated cotton - $^1/3$ depth

Treated cotton fabric was wet out and entered into a bath at 60°C containing 1% o.w.f. C.I. Direct Blue 1 (liquor ratio 50:1). No sodium chloride was added. The temperature was raised to 96°C and dyeing was continued at this temperature for 1 hour, after which time the fabric was removed, rinsed well in distilled water and dried.

5.14.1.2 Treated cotton - $^{1}/1$ depth

As above for $^{1}/3$ depth except using 4% o.w.f. C.I. Direct Blue 1.

5.14.1.3 Untreated cotton - $^{1}/3$ depth

Untreated cotton fabric was wet out and entered into a bath at 60°C containing 3% o.w.f. C.I. Direct Blue 1 (liquor ratio 50:1). Sodium chloride (20% o.w.f.) was then added portionwise over 10 minutes and the temperature of the bath then raised to 96°C. Dyeing was continued at this temperature for 1 hour, after which time the fabric was removed, rinsed and then soaped at 60°C for 30 minutes using a non-ionic detergent (2% o.w.f.), rinsed and dried.

5.14.1.4 Untreated cotton - $^{1}/1$ depth

As above for $^{1}/3$ depth except using 12% o.w.f. C.I. Direct Blue 1.

5.14.2 C.I. Reactive Blue 5

5.14.2.1 Treated cotton - $^{1}/3$ depth

Treated cotton fabric was wet out and entered into a bath at 60°C containing 4.5% o.w.f. C.I. Reactive Blue 5 (liquor ratio 50:1). Exhaustion was continued for 20 minutes at 60°C in the absence of sodium chloride. Dissolved sodium carbonate (100% o.w.f.) was then added and the temperature of the bath raised to 96°C. Dyeing was continued for 1 hour at this temperature after which time the fabric was removed, rinsed and then soaped at the boil for 30 minutes in a non-ionic detergent (5% o.w.f.), rinsed and dried.

5.14.2.2. Treated cotton - $^{1}/1$ depth

As above for $^{1}/3$ depth except using 11% o.w.f. C.I. Reactive Blue 5.

5.14.2.3 Untreated cotton - $^1/3$ depth

Untreated cotton fabric was wet out and entered into a bath at 60°C containing 4% o.w.f. C.I. Reactive Blue 5 (liquor ratio 30:1). Sodium chloride (400% o.w.f.) was added to the bath portionwise over 10 minutes and exhaustion continued at this temperature for 20 minutes. Dissolved sodium carbonate (100% o.w.f.) was then added and the temperature of the bath raised to 96°C. Dyeing was continued for 1 hour at this temperature after which time the fabric was removed, rinsed and then soaped at the boil for 30 minutes in a non-ionic detergent (5% o.w.f.), rinsed and dried.

5.14.2.4 Untreated cotton - $^1/1$ depth

As above for $^1/3$ depth except using 12% o.w.f. C.I. Reactive Blue 5.

5.15 Preparation of differential-dyeing viscose rayons

Cellulose pretreated with reagents I and II was converted to differential-dyeing viscose rayons with high affinity for acid and basic dyes respectively, using the following method outlined below for the cationic reagent I.

A sample of cellulose was treated with 10% reagent I (o.w.f.) as described above for treatment of yarn. One part of dry pretreated cellulose was then steeped in 10 parts 20% (w/v) sodium hydroxide solution, care being taken to ensure uniform treatment. The treated cellulose was removed after 15 minutes, as much of the alkali as possible squeezed out, then placed in a sealed container together with 10 parts of carbon disulphide and let stand for 18 hours at room temperature.

The orange coloured cellulose xanthate was separated from the reaction mixture and, after the excess carbon disulphide had been removed, placed in 20 parts of 10% (w/v) sodium hydroxide. The mixture was shaken until a uniform suspension of the xanthate was obtained and this was allowed to stand for 3 days during which time a golden yellow solution of sodium cellulose xanthate formed.

Cellulose was regenerated from this in the form of viscose rayon by extruding the solution from a syringe into a coagulating bath containing sodium sulphate, zinc sulphate and sulphuric acid. After a 30 minute desulphurising treatment in 1.5% (w/v) sodium sulphide at 60-70°C, the dried regenerated cellulose was dyed from a bath containing C.I. Acid Red 88 as described above in section 5.9.6 when it showed excellent affinity for the dye compared to regenerated cellulose prepared from normal cellulose.

A sample of cellulose pretreated with 10% anionic reagent II (o.w.f.) behaved similarly on treatment with sodium hydroxide/carbon disulphide, yielding a product on regeneration which possessed excellent affinity for basic dyes.

5.16 Preparation of differential-dyeing cellulose triacetates

Celluloses pretreated with reagents I and II were converted into differential-dyeing cellulose triacetates, with high affinity for acid and basic dyes respectively, using the following method.

A sample of cellulose was treated with 10% reagent I (o.w.f.) as described above for treatment of yarn. The dry material was steeped in water for 15 minutes then filtered to remove as much water as possible and transferred to glacial acetic acid. After steeping for 30 minutes it was again filtered off then steeped a second time in glacial acetic acid and filtered off. The activated cellulose produced in this way was added to an acetylating mixture consisting of 35 parts glacial acetic acid and 15 parts acetic anhydride to 1 part cellulose (dry weight). The mixture was stirred and a few drops of perchloric acid added.

After standing with occasional stirring for 45 minutes, during which time the polymer went into solution, the cellulose triacetate was precipitated out by addition to a large excess of methanol. The precipitate was filtered off, washed well with water, suspended in water, neutralised with sodium carbonate to phenolphthalein, washed, filtered and dried. The product was soluble in dichloromethane: methanol (9:1) and inspection of the infrared spectrum showed that almost complete acetylation of the hydroxyl groups had taken place (see Figure 95). The material showed high affinity for acid dyes when dyed at the boil.

A sample of cellulose pretreated with 10% anionic reagent II (o.w.f.) behaved similarly on acetylation to give a product that was readily dyed at the boil with basic dyes.

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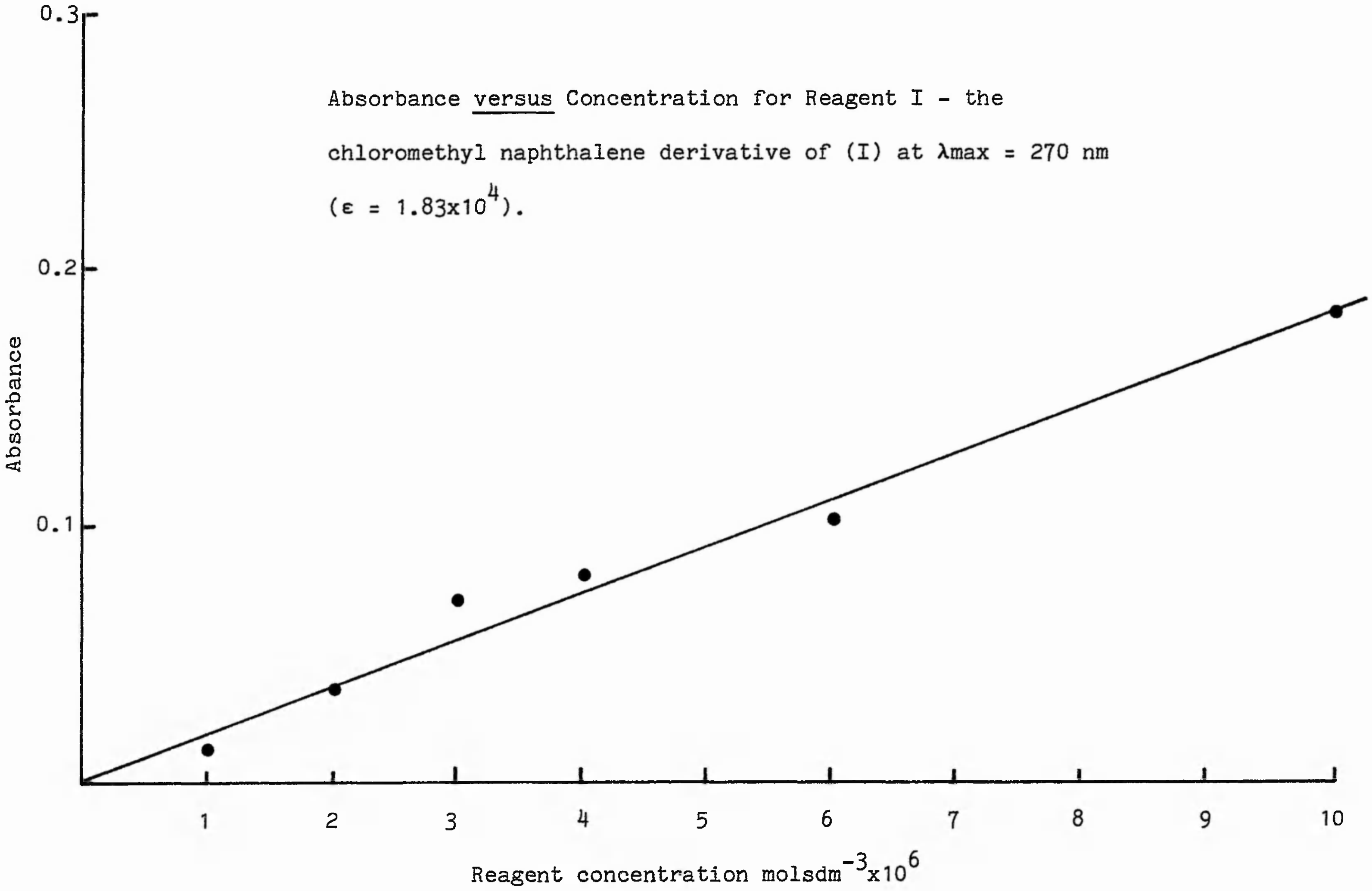
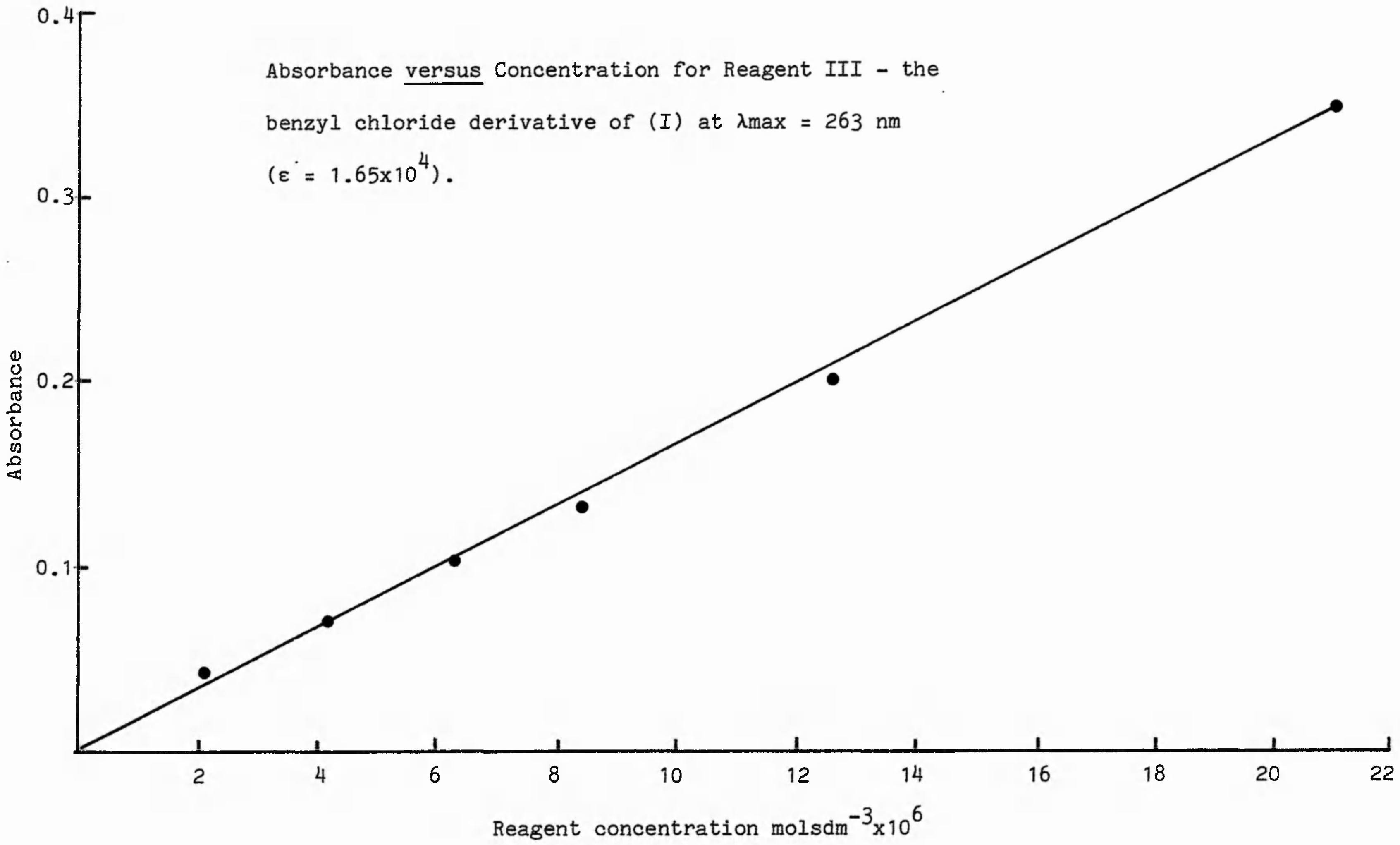
APPENDIX I

Absorbance *versus* Concentration data for the cationic reagents I, III and V.

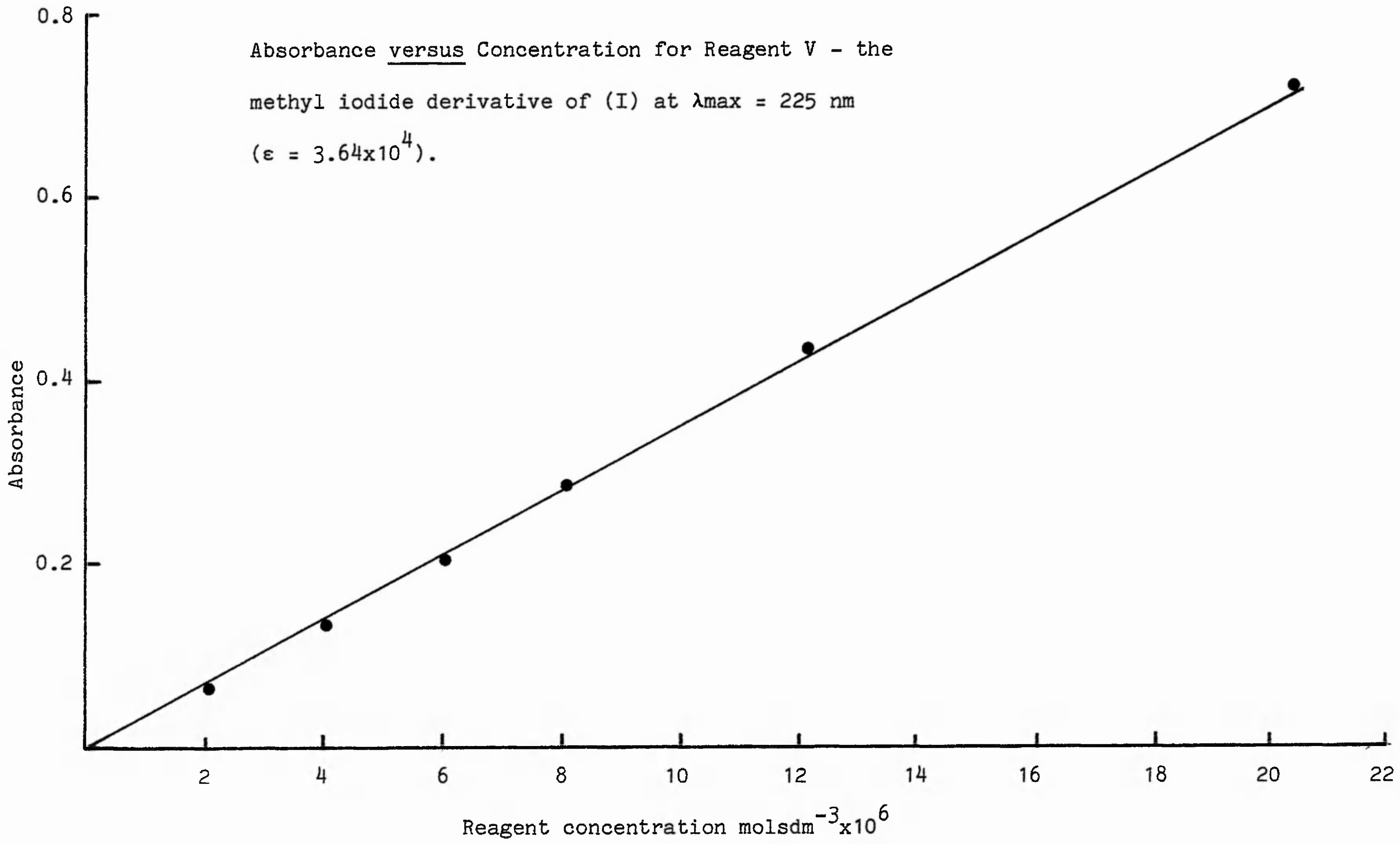
Reagent	Reagent concentration molsdm^{-3}x10^{6}	λmax	Absorbance λmax	εmax
I	1.01	270	0.014	
"	2.02	"	0.035	
"	3.03	"	0.071	1.83x10^{4}
"	4.04	"	0.085	
"	6.06	"	0.107	
"	10.01	"	0.185	
III	2.10	263	0.047	
"	4.20	"	0.078	
"	6.30	"	0.104	1.65x10^{4}
"	8.40	"	0.136	
"	12.60	"	0.200	
"	21.00	"	0.349	
V	2.03	225	0.063	
"	4.06	"	0.135	
"	6.09	"	0.206	3.64x10^{4}
"	8.12	"	0.288	
"	12.18	"	0.435	
"	20.30	"	0.721	



Absorbance versus Concentration for Reagent I - the chloromethyl naphthalene derivative of (I) at λmax = 270 nm (ε = 1.83x10^{4}).



Absorbance versus Concentration for Reagent III - the benzyl chloride derivative of (I) at λmax = 263 nm ($\varepsilon' = 1.65 \times 10^4$).



Absorbance *versus* Concentration for Reagent V - the methyl iodide derivative of (I) at λmax = 225 nm ($\varepsilon = 3.64 \times 10^4$).

APPENDIX II

Data required to examine the application of the Kubelka-Munk reflectance function to the adsorption of C.I. Direct Blue 1 on cotton treated with Reagent I.

Dye conc. % o.w.f.	Dye conc. g/Kg	Log_{10} conc.	% Average reflectance	F(R)	LogF(R)
0.1	1.0	-1.0	33.82	0.648	-0.189
0.25	2.5	-0.602	21.70	1.413	0.150
0.50	5.0	-0.301	15.94	2.216	0.346
0.75	7.5	-0.125	11.35	3.462	0.539
1.00	10.0	0.0	9.57	4.273	0.631
1.50	15.0	0.176	7.07	6.107	0.786
2.00	20.0	0.301	5.45	8.202	0.914
2.50	25.0	0.398	4.65	9.776	0.990
3.00	30.0	0.477	4.01	11.489	1.060

where $F(R) = \frac{(1-R)^2}{2R}$ (R on a scale of 0-1).

Regression analysis of the above results for plots of:

1) Dye concentration (% o.w.f.) versus F(R)

2) Log_{10} dye concentration versus LogF(R)

Plot	Intercept	Slope	Correlation coefficient (R^2)
1)	0.468	0.374	0.999
2)	0.644	0.848	0.999

APPENDIX III

Colour Strength *versus* $[Df]_{\infty}$ calibration data for C.I. Direct Yellow 12 and C.I. Direct Blue 22.

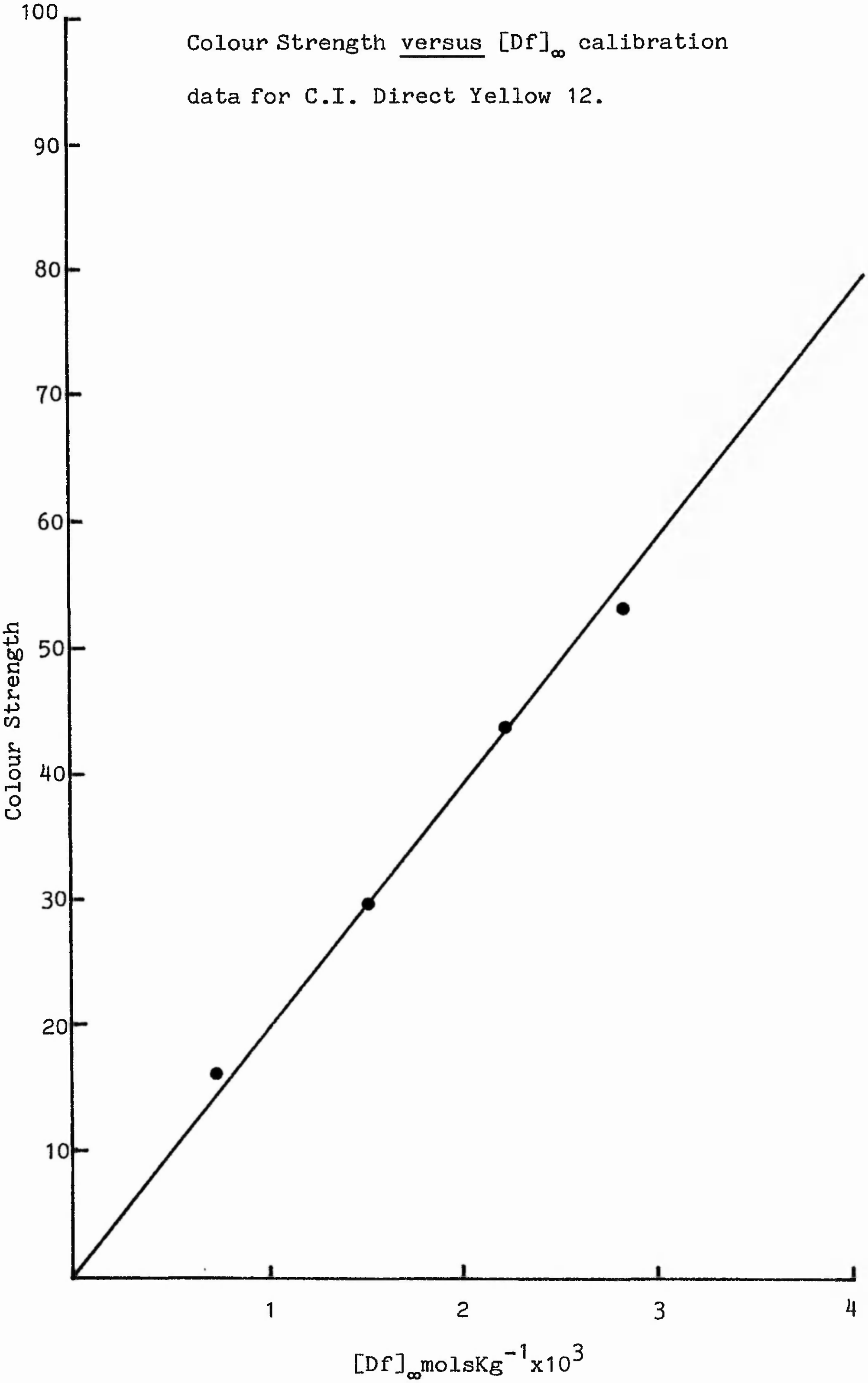
C.I. Direct Yellow 12.

$[Ds]_o$ molsdm^{-3}x10^5	Aλmax 393 nm	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^6	$[Df]_\infty$ molskg^{-1}x10^3	Colour Strength
1.58	0.017	-	0.34	0.773	16.00
3.16	0.051	-	1.02	1.53	29.93
4.74	0.137	-	2.74	2.23	50.28

Regression analysis

Intercept	3.64
Slope (K)	17.01
Correlation coefficient	0.994

$$[Df]_\infty \text{mmolsKg}^{-1} = \frac{\text{Colour Strength} - 3.64}{17.01}$$



Colour Strength versus $[Df]_\infty$ calibration data for C.I. Direct Yellow 12.

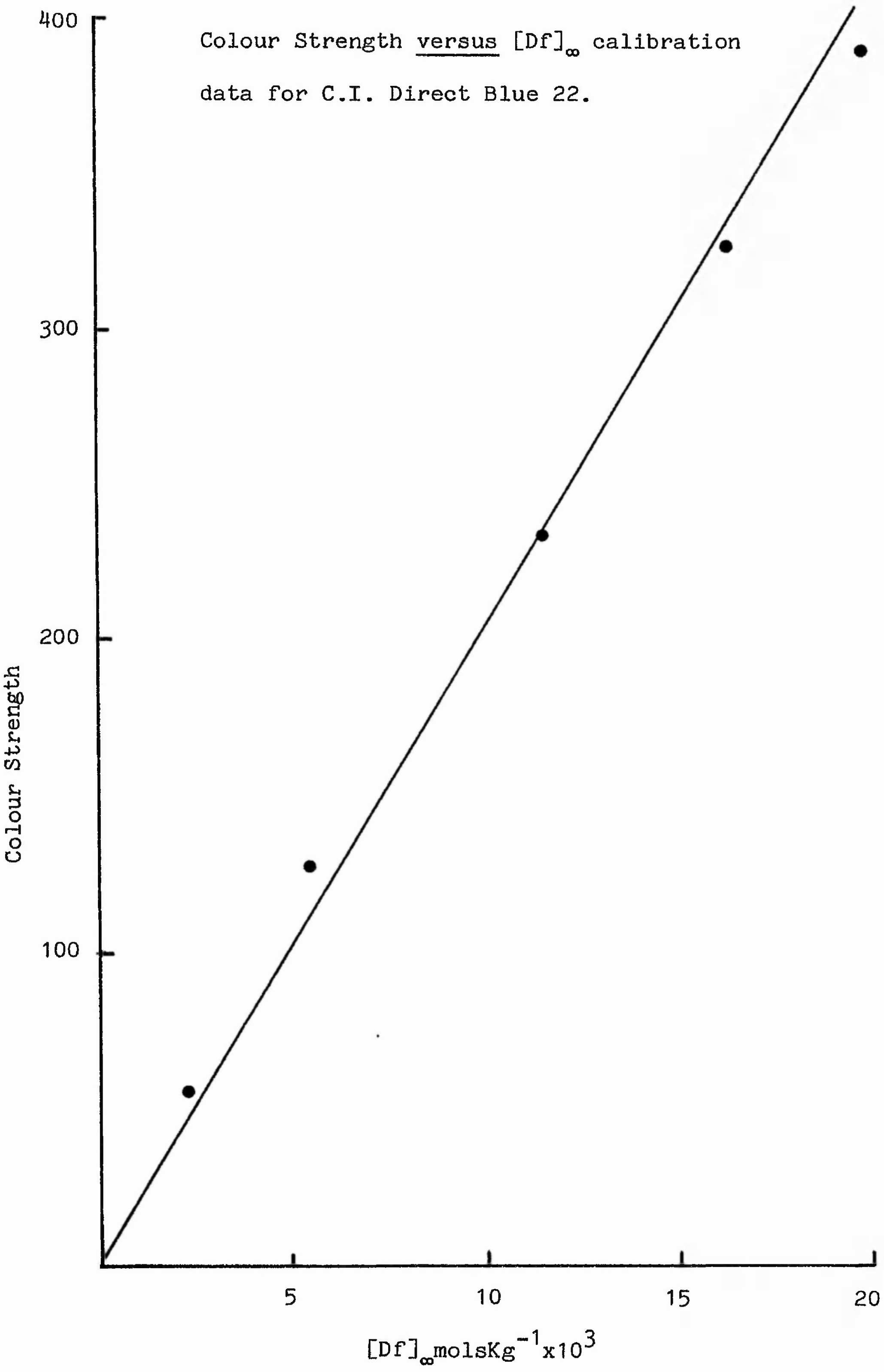
C.I. Direct Blue 22

$[Ds]_o$ molsdm^{-3}x10^4	$A\lambda max$ 575 nm	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^5	$[Df]_\infty$ molsKg^{-1}x10^3	Colour Strength
0.484	0.072	2	0.238	2.30	55.30
1.211	0.193	-	0.320	5.90	127.09
2.422	0.557	-	0.922	11.65	233.88
3.633	0.430	5	3.560	16.39	326.94
4.843	0.525	10	8.692	19.87	389.85

Regression analysis

Intercept	12.92
Slope (K)	19.04
Correlation coefficient	0.999

$$[Df]_\infty \text{mmolsKg}^{-1} = \frac{\text{Colour Strength} - 12.92}{19.04}$$



Colour Strength versus $[Df]_\infty$ calibration data for C.I. Direct Blue 22.

APPENDIX IV

Equilibrium adsorption measurements for C.I. Direct Yellow 12, C.I. Direct Blue 1 and C.I. Direct Blue 22 on cotton treated with Reagent I to depths C1 and C2 and for C.I. Direct Blue 22 on untreated cotton.

C.I. Direct Yellow 12 (C1)

$[Ds]_o$ $molsdm^{-3}x10^4$	Aλmax 393 nm	Dilution factor	$[Ds]_\infty$ $molsdm^{-3}x10^4$	$[Df]_\infty$ $molsKg^{-1}x10^3$	Colour Strength
0.394	0.084	-	0.017	1.89	43.49
0.788	0.797	-	0.159	3.14	53.85
1.576	0.380	10	0.760	4.08	66.83
2.364	0.288	25	1.440	4.62	78.33
3.152	0.215	50	2.150	5.01	83.66
3.940	0.307	50	3.07	4.35	84.53

Using the calibration data for C.I. Direct Yellow 12 (Appendix III) the $[Df]_\infty$ in $molsKg^{-1}$ was obtained after soaping:

Colour Strength	$[Df]_\infty molsKg^{-1}x10^3$
43.49	2.34
53.85	2.95
66.83	3.71
78.33	4.39
83.66	4.70
84.53	4.75

C.I. Direct Blue 1 (C1)

$[Ds]_o$ molsdm^{-3}x10^4	Aλmax 620 nm	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^4	$[Df]_\infty$ molsKg^{-1}x10^3	Colour Strength
2.012	0.245	25	0.931	5.41	137.38
5.030	0.419	50	3.184	9.23	192.83
10.06	0.961	50	7.302	13.79	223.96
15.09	0.747	100	11.35	18.69	258.85
20.12	0.424	250	16.11	20.05	280.64
25.15	0.530	250	20.14	25.07	306.38

Using the calibration data for C.I. Direct Blue 1 (section 3.3.4) and multiplying by a factor of 20.87/99,200 the $[Df]_\infty$ in molsKg^{-1} was obtained after soaping:

Colour Strength	$[Df]_\infty$molsKg^{-1}x10^3
137.38	4.88
192.83	6.88
223.96	8.01
258.85	9.27
280.64	10.06
306.38	11.00

C.I. Direct Blue 22 (C1)

$[Ds]_o$ molsdm^{-3}x10^4	Aλmax 575 nm	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^4	$[Df]_\infty$ molsKg^{-1}x10^3	Colour Strength
1.937	0.117	10	0.194	8.72	210.10
4.843	0.359	25	1.486	16.78	341.93
9.685	0.233	125	4.822	24.32	416.63
14.528	0.200	200	8.278	31.25	461.68
19.371	0.320	250	13.245	30.63	451.38
24.214	0.427	250	17.674	32.70	513.25

Using the calibration data for C.I. Direct Blue 22 (appendix III) the $[Df]_\infty$ in molsKg^{-1} was obtained after soaping:

Colour Strength	$[Df]_\infty$molsKg^{-1}
210.10	10.36
341.93	17.28
416.63	21.20
461.68	23.57
451.38	23.03
513.25	26.28

C.I. Direct Yellow 12 (C2)

$[Ds]_o$ molsdm^{-3}x10^3	Aλmax 393 nm	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^4	$[Df]_\infty$ molsKg^{-1}x10^3	Colour Strength
0.24	*0.143	-	0.029	11.86	155.46
0.48	0.377	10	0.754	20.23	178.80
0.72	0.546	25	2.73	22.35	184.34
0.96	0.489	50	4.89	23.55	188.32
1.20	0.354	100	7.080	24.60	185.47

(*λmax observed to shift bathochromically from 393 nm - 410 nm)

See Appendix III for calibration data for C.I. Direct Yellow 12.

Colour Strength	$[Df]_\infty$molsKg^{-1}x10^3
155.46	8.93
178.80	10.30
184.34	10.62
188.32	10.86
185.47	10.69

C.I. Direct Blue 1 (C2)

$[Ds]_o$ molsdm^{-3}x10^3	Aλmax 620 nm	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^4	$[Df]_\infty$ molsKg^{-1}x10^3	Colour Strength
0.246	*0.112	-	0.017	12.22	255.95
0.492	0.496	10	0.754	21.09	341.62
0.985	0.245	125	4.654	25.97	386.35
1.477	0.244	250	9.271	27.51	408.46
1.970	0.685	125	13.013	33.42	421.25
2.462	0.467	250	17.743	34.38	439.99

(*λmax observed to shift hypsochromically from 620 nm - 600 nm)

See section 3.3.4 for calibration data for C.I. Direct Blue 1.

Colour Strength	$[Df]_\infty$molsKg^{-1}x10^3
255.95	9.17
341.62	12.27
386.35	13.89
408.46	14.69
421.25	15.16
439.99	15.83

C.I. Direct Blue 22 (C2)

$[Ds]_o$ molsdm^{-3}x10^3	Aλmax 575 nm	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^4	$[Df]_\infty$ molsKg^{-1}x10^3	Colour Strength
0.226	*0.116	-	0.019	11.18	328.96
0.451	0.128	5	0.106	22.03	388.10
0.902	0.611	10	1.012	40.06	528.61
1.354	0.877	25	3.630	49.53	570.92
1.805	0.480	100	7.947	50.49	626.25
2.256	0.726	100	12.020	52.69	617.51

(*λmax shifted bathochromically from 575 nm - 598 nm)

See Appendix III for calibration data for C.I. Direct Blue 22.

Colour Strength	$[Df]_\infty$molsKg^{-1}x10^3
328.96	16.60
388.10	19.70
528.61	27.08
570.92	29.31
626.25	32.21
617.51	31.75

C.I. Direct Blue 22 (untreated)

$[Ds]_o$ molsdm^{-3}x10^3	Aλmax 575 nm	Dilution factor	$[Ds]_\infty$ molsdm^{-3}x10^4	$[Df]_\infty$ molsKg^{-1}x10^3
0.117	0.466	10	0.772	1.97
0.233	0.391	25	1.618	3.56
0.583	0.519	50	4.296	7.65
1.165	0.564	100	9.338	11.57
1.748	0.700	125	14.487	14.95
2.330	0.489	250	20.240	15.31

APPENDIX V

Photographs of samples of treated and untreated cotton dyed together in the same bath, showing the preferential uptake of dyes from various classes by the treated material.

Key to V-2 Application of various dye classes to cotton treated with 10% o.w.f. of the cationic reagent I, in the presence of an equal weight of untreated cotton and in the absence of additional electrolyte. Dyebaths consisted of:

a) 3% o.w.f. C.I. Direct Blue 1, L.R. 20:1.

b) 3% o.w.f. C.I. Direct Yellow 12, L.R. 50:1.

c) 3% o.w.f. C.I. Direct Blue 22, L.R. 50:1.

d) 2% o.w.f. C.I. Reactive Blue 7, 100% o.w.f. sodium carbonate, L.R. 50:1.

e) 2% o.w.f. C.I. Reactive Red 8, 40% o.w.f. sodium carbonate, L.R. 50:1.

f) Pad liquor consisted of a 1% w/v solution of C.I. Reactive Blue 19, L.R. 25:1.

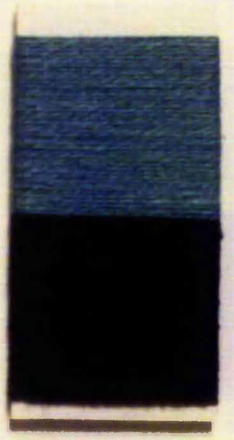
g) 4.5% o.w.f. C.I. Azoic Coupling Component 5 and a 1.25% w/v solution of C.I. Azoic Diazo Component 5, L.R. 25:1.

h) 2.25% o.w.f. C.I. Azoic Coupling Component 34 and a 1.25% w/v solution of C.I. Azoic Diazo Component 8, L.R. 25:1.

i) 5.5% o.w.f. C.I. Azoic Coupling Component 15 and a 0.58% w/v solution of C.I. Azoic Diazo Component 8, L.R. 25:1.

a

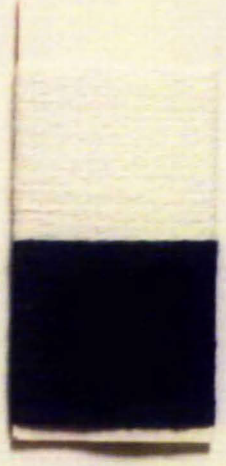
b



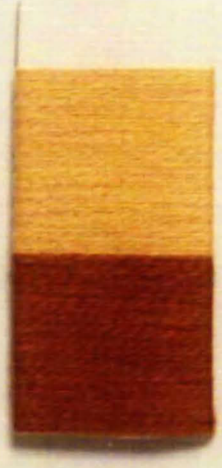
c

d

e



f



g

V-2

h

i

Key to V-4

Effect of bleaching and mercerisation treatments on the preferential dye uptake exhibited by cotton yarn treated with 10% o.w.f. reagent I and subsequently dyed with 3% o.w.f. C.I. Direct Blue 1.

a i) Standard sample (no ancillary treatments applied).

a ii) Mercerised under tension.

a iii) Sodium hypochlorite bleached.

a iv) Hydrogen peroxide bleached.

a v) Sodium chlorite bleached.

Application of various dye classes (continued from V-1).
Dyeings b) to f) consisted of:

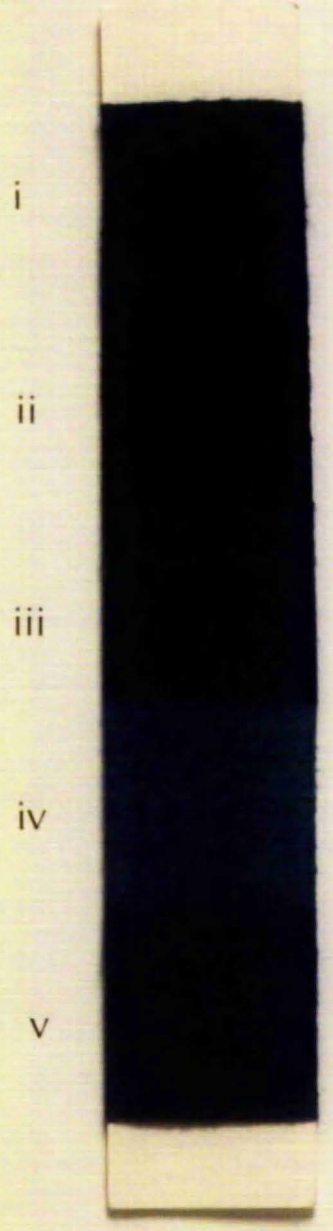
b) 2% o.w.f. C.I. Vat Green 1, 2% Matexil DA-AC, L.R. 60:1, air oxidised.

c) 2% o.w.f. C.I. Vat Blue 1, L.R. 60:1, air oxidised.

d) 2% o.w.f. C.I. Vat Yellow 3, L.R. 60:1, air oxidised.

e) 2.5% o.w.f. C.I. Solubilised Sulphur Violet 1, L.R. 25:1.

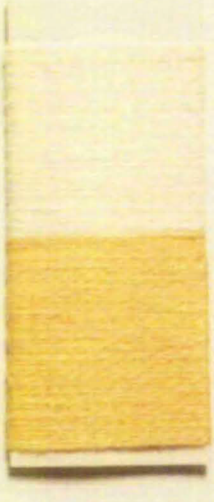
f) 15% o.w.f. C.I. Solubilised Sulphur Black 1, L.R. 25:1.



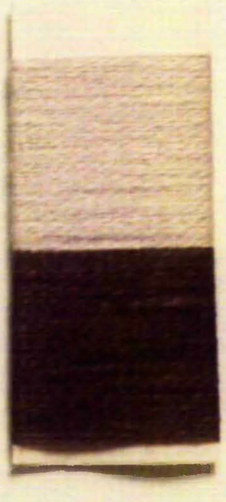
a

b

c



d



e

f

V-4

Key to V-6

Application of basic dyes to modified cotton. Dyeing a) was carried out on cotton treated with 10% o.w.f. of the anionic reagent Sandospace R, and b) and c) on cotton modified with 10% o.w.f. of the anionic reagent II. All the dyeings were carried out in the presence of an equal weight of untreated cotton, and in the absence of additional electrolyte.

a) 1.0% o.w.f. C.I. Basic Red 18, L.R. 50:1.

b) 1.0% o.w.f. C.I. Basic Yellow 15, L.R. 50:1.

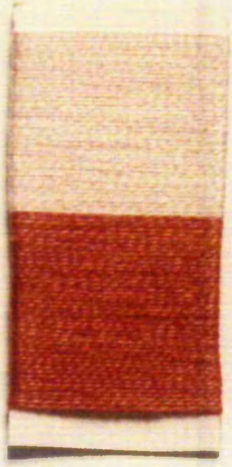
c) 1.0% o.w.f. C.I. Basic Green 4, L.R. 50:1.

d) Tone-on-tone dyeings: From left to right; untreated cotton, cotton modified with 2.5% o.w.f. and 10% o.w.f. of the cationic reagent I, dyed simultaneously with 2% o.w.f. C.I. Acid Orange 7 in the absence of additional electrolyte.

e) and f) Cross-dyed samples: From left to right; cotton treated with 10% o.w.f. of anionic reagent II, untreated cotton and cotton treated with 10% o.w.f. of cationic reagent I, cross-dyed simultaneously in the absence of additional electrolyte in baths containing:

e) 1% o.w.f. each of C.I. Basic Yellow 15 and C.I. Acid Red 13 - showing minimal cross-staining.

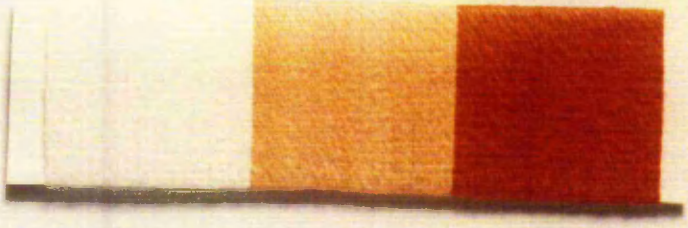
f) 1% o.w.f. each of C.I. Basic Yellow 15 and C.I. Acid Red 88 - showing a greater degree of cross-staining than in e) above.



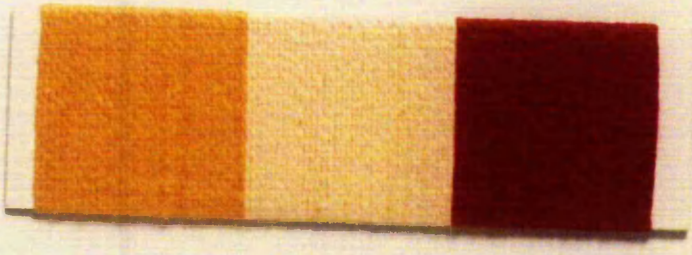
a

b

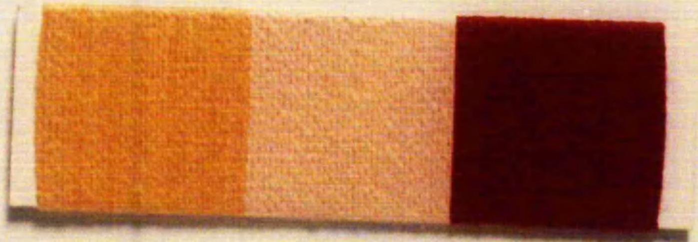
c



d



e



f

Key to V-8

Application of reagents in printing. Reagent printed cotton fabric showing preferential dye uptake by the modified portions of the samples.

a) Cotton fabric screen printed with a paste containing 1% w/v of the cationic reagent V and dyed with 1% o.w.f. C.I. Acid Red 138, L.R. 50:1.

b) Cotton fabric screen printed with a paste containing 1% w/v of the cationic reagent I and dyed with 1% o.w.f. C.I. Direct Blue 10, L.R. 50:1.

c) Cotton fabric screen printed with a paste containing 1% w/v of the anionic reagent II and dyed with 1% o.w.f. C.I. Basic Yellow 15, L.R. 50:1.

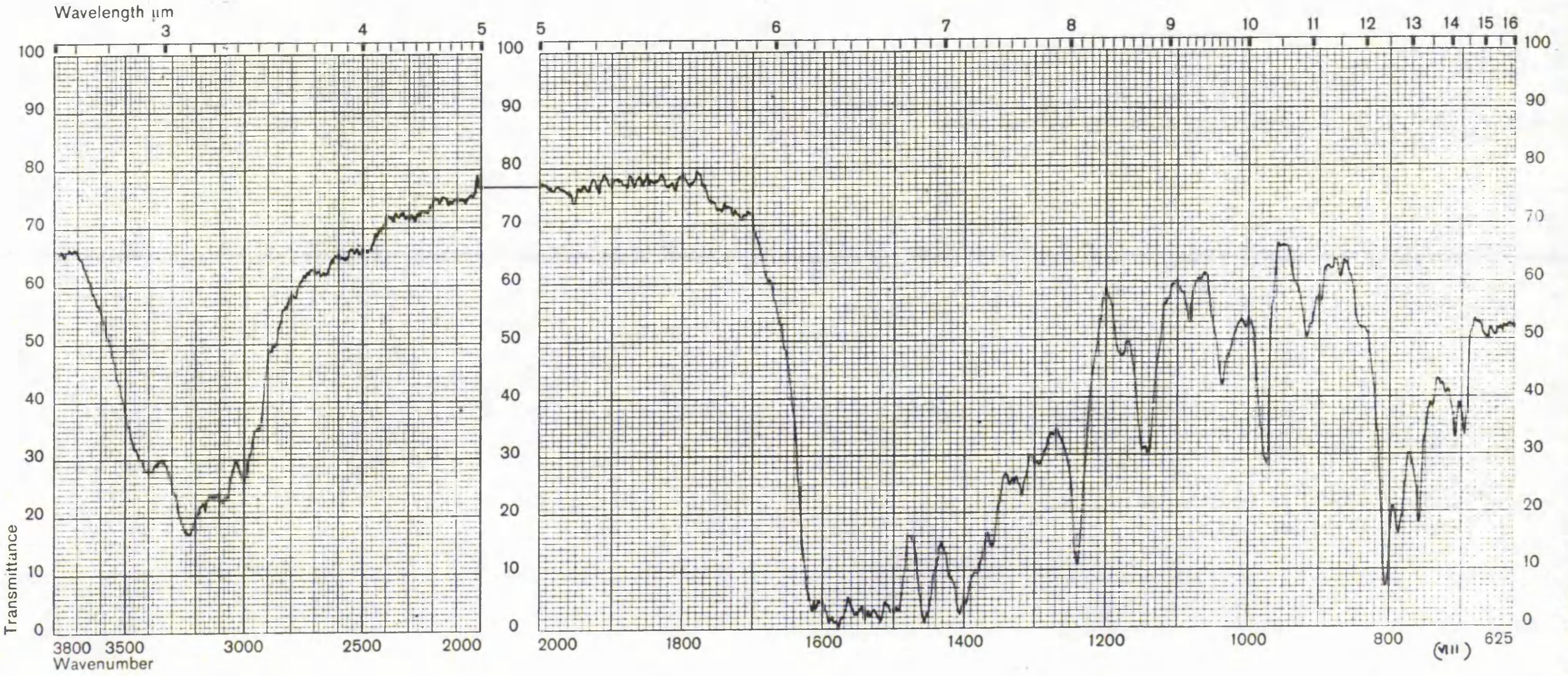
a

b

c

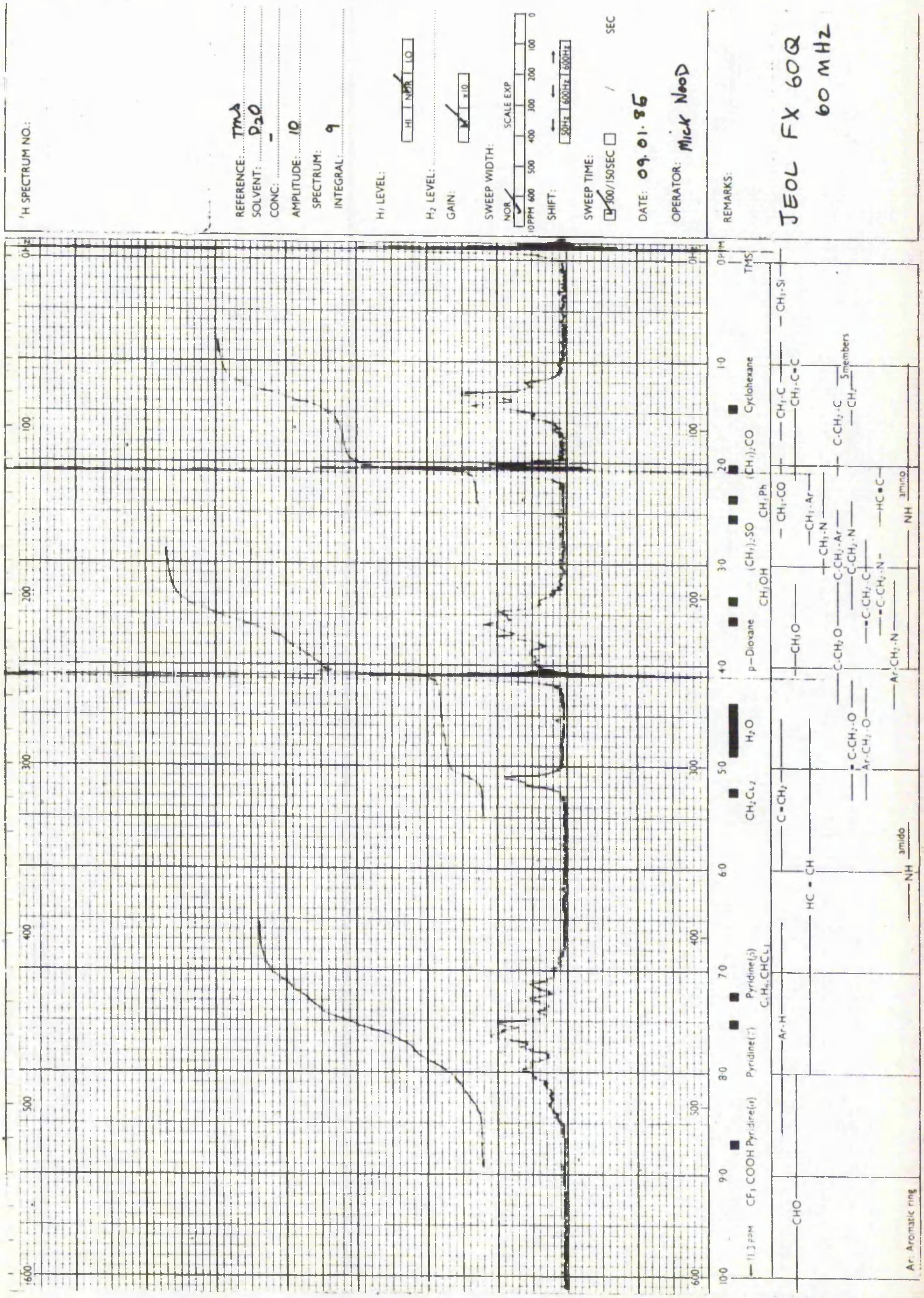
APPENDIX VI

I.r. and n.m.r. spectra of selected samples.



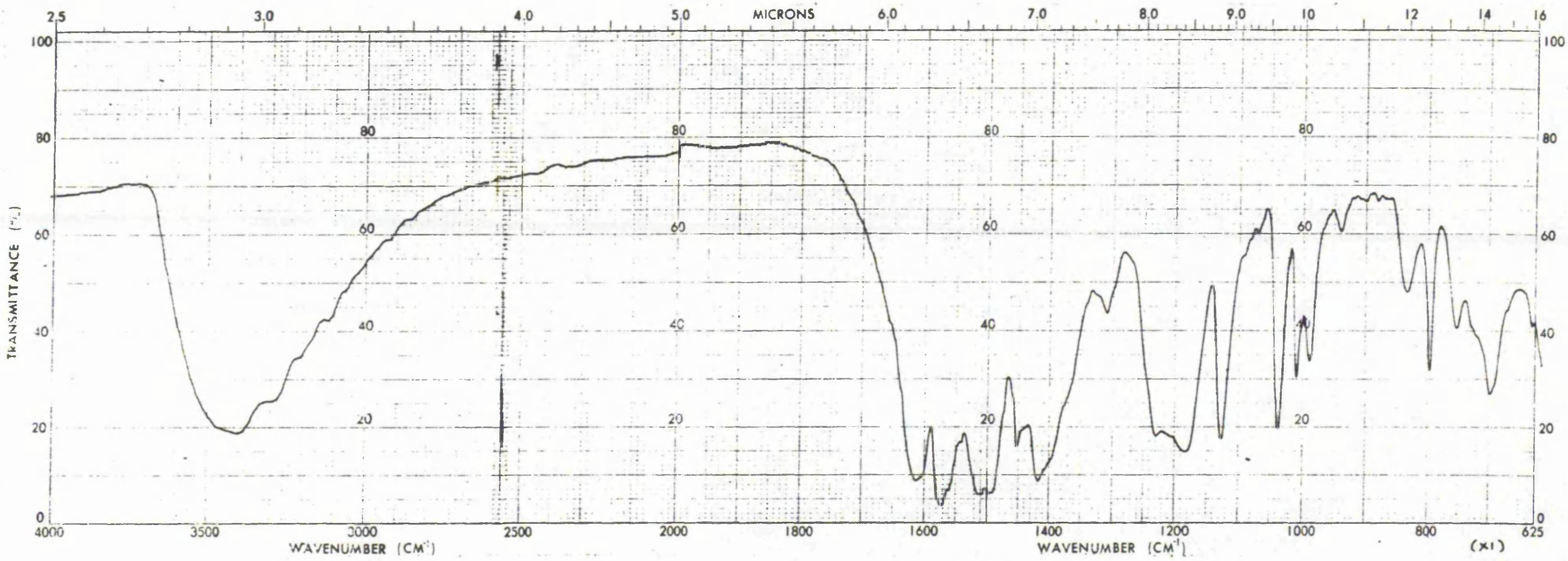
The i.r. spectrum of cationic reagent I - the 1-(chloromethyl)naphthalene derivative of general structure (I) - see section 3.1.

The n.m.r. spectrum of cationic reagent I - the 1-(chloromethyl)-naphthalene derivative of (I).

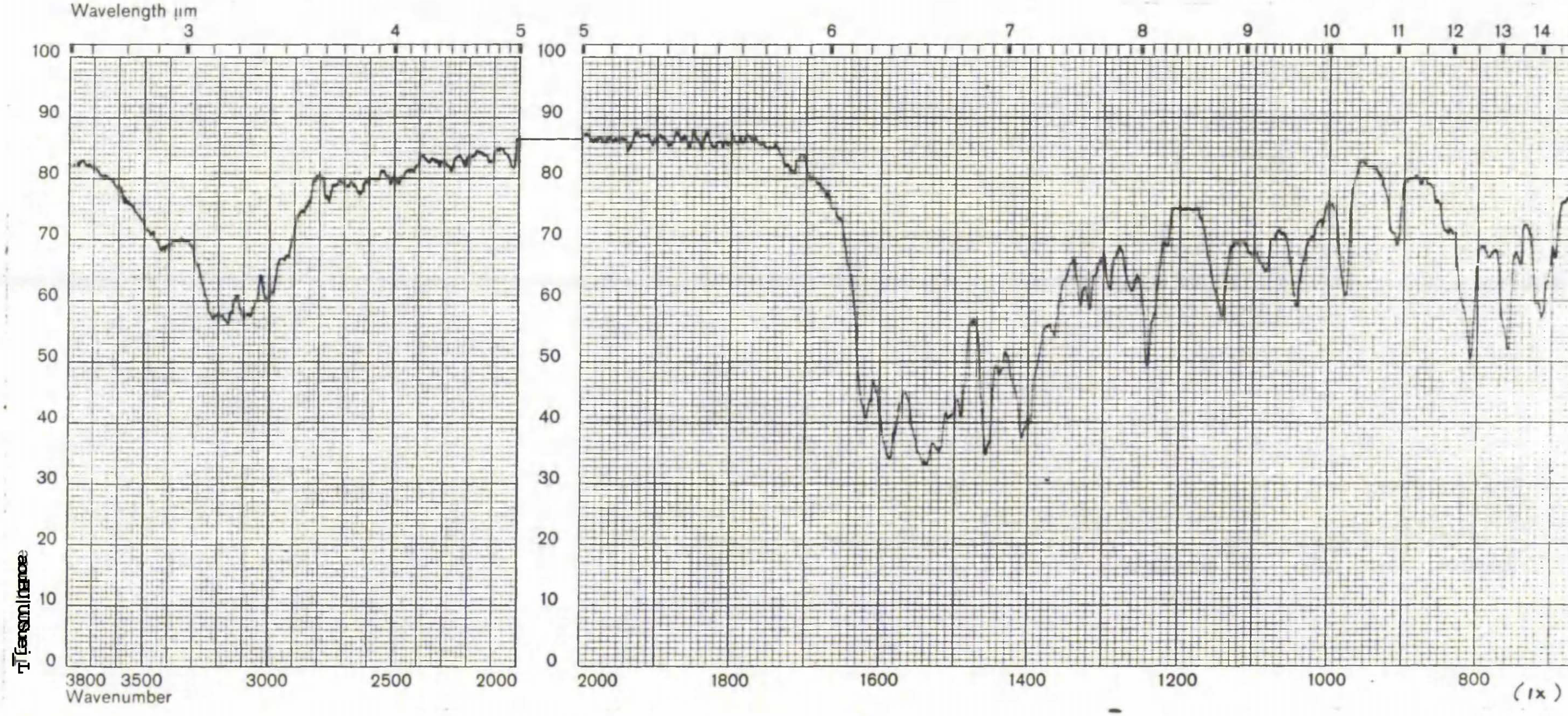


^{1}H SPECTRUM NO.:

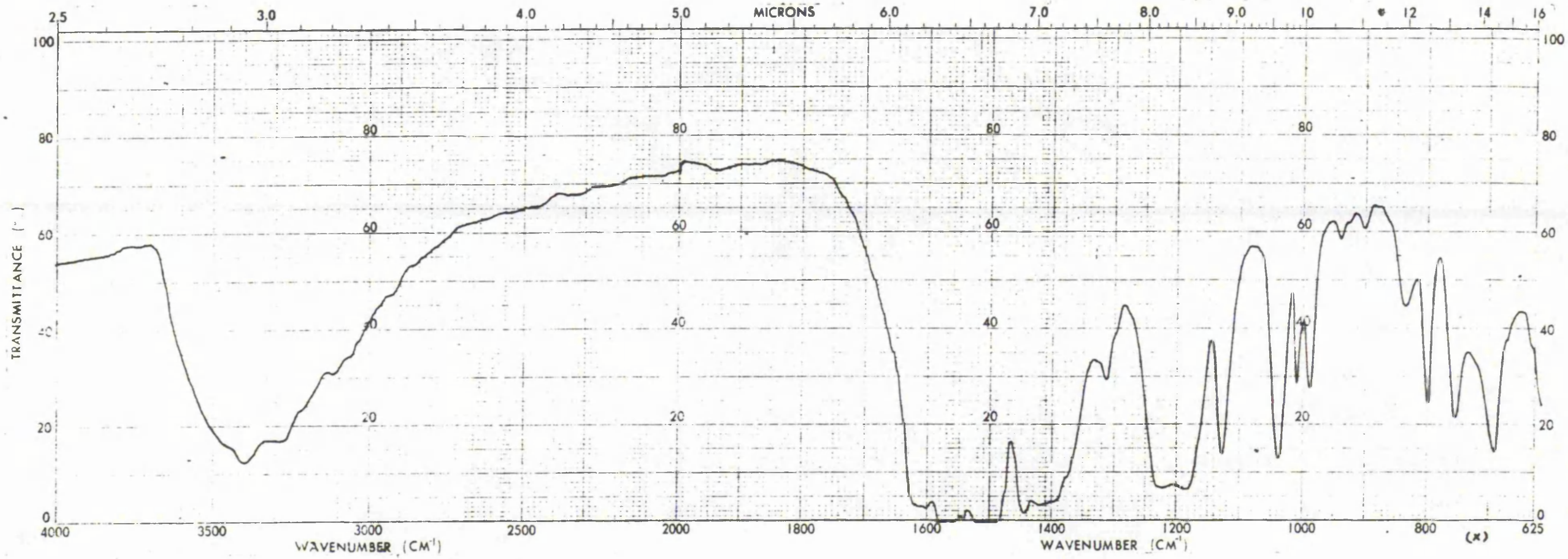
REFERENCE: TMS
SOLVENT: D_2O
CONC.: -
AMPLITUDE: 10
SPECTRUM:
INTEGRAL: 9
H_1 LEVEL: HI [✓ NOR] LO
H_2 LEVEL:
GAIN: [✓ ×1] ×10
SWEEP WIDTH: [✓ NOR] SCALE EXP
SHIFT:
SWEEP TIME: ☑ 300/150SEC ☐ / SEC
DATE: 09.01.85
OPERATOR: Mick Wood
REMARKS: JEOL FX 60Q 60 MHz



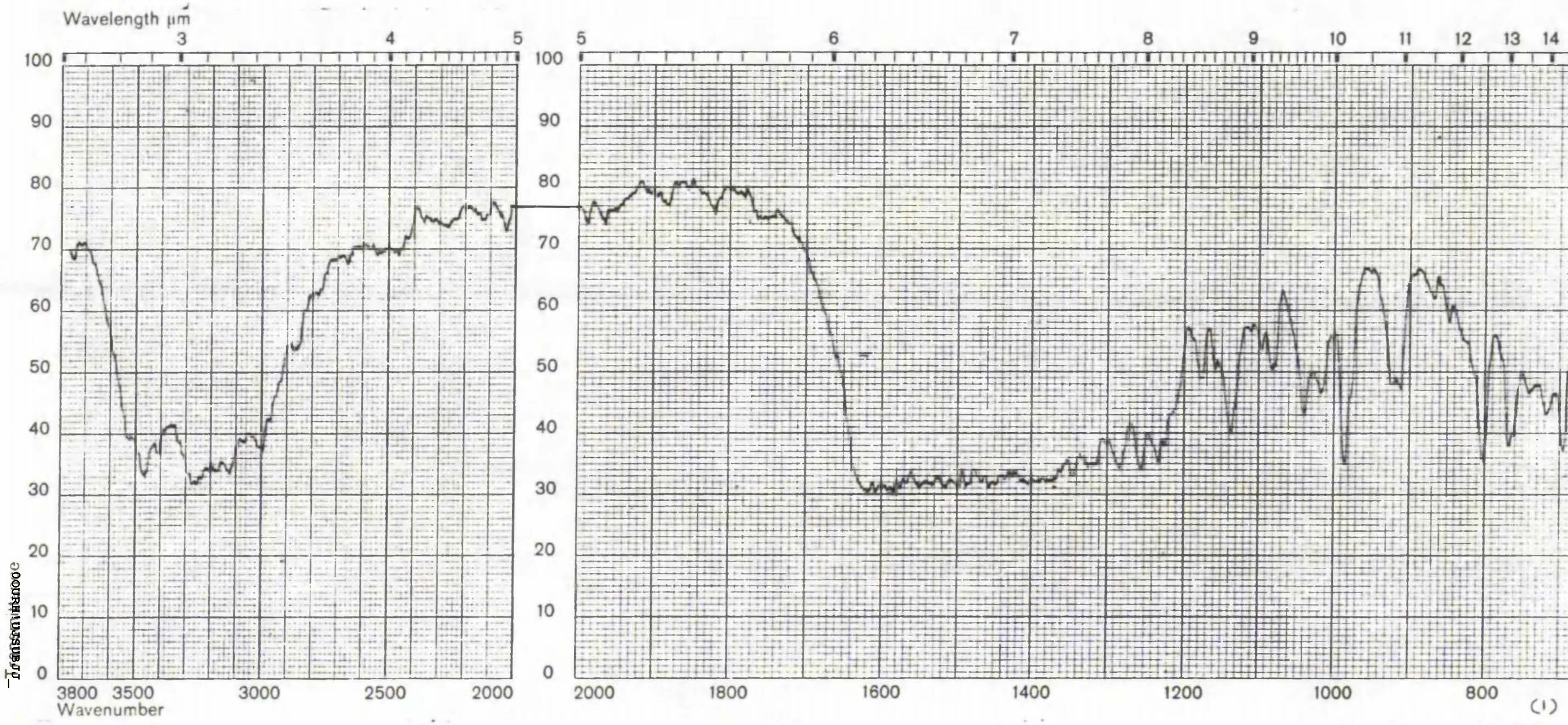
The i.r. spectrum of anionic reagent II, derived from p-sulphanilic acid.



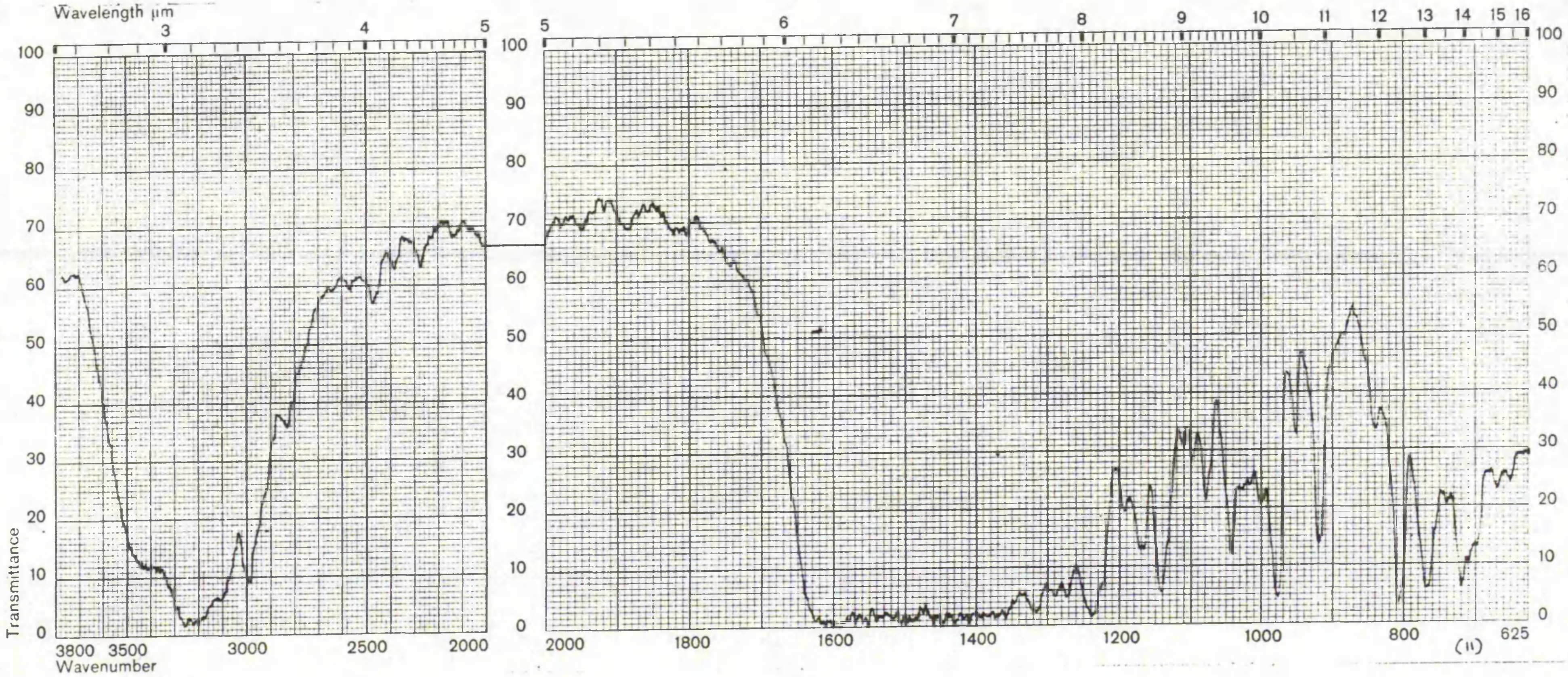
The i.r. spectrum of cationic reagent III - the benzyl chloride derivative of (I).



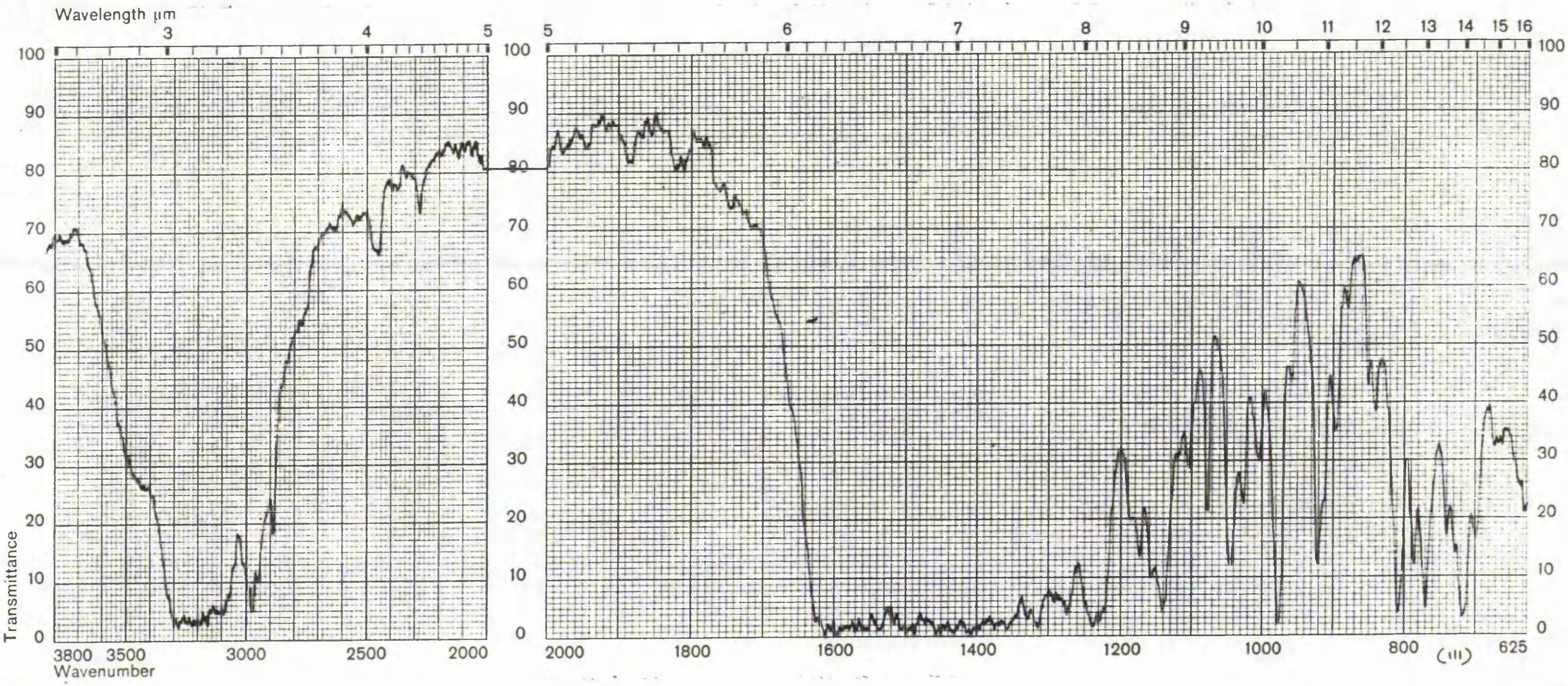
The i.r. spectrum of anionic reagent IV, derived from 1-naphthylamine-4-sulphonic acid.



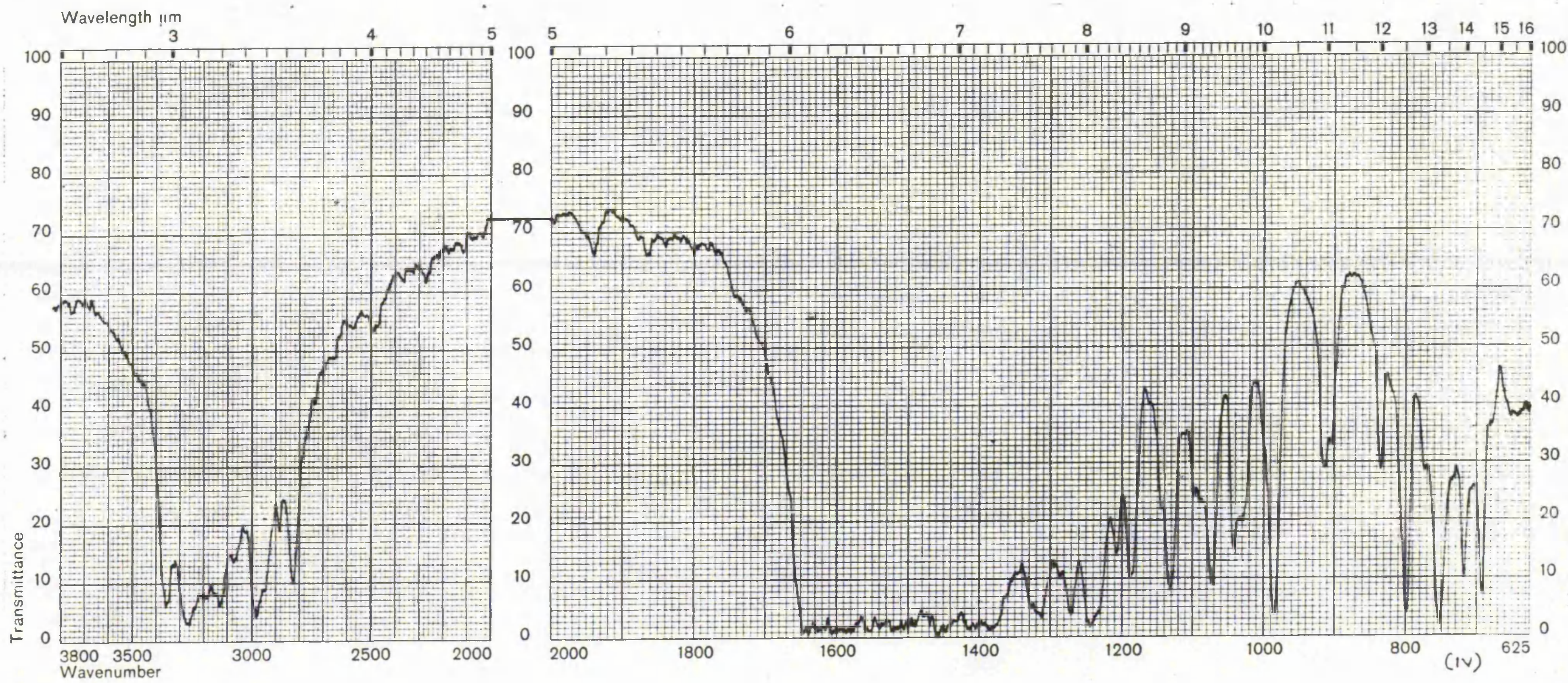
The i.r. spectrum of cationic reagent V - the methyl iodide derivative of (I).



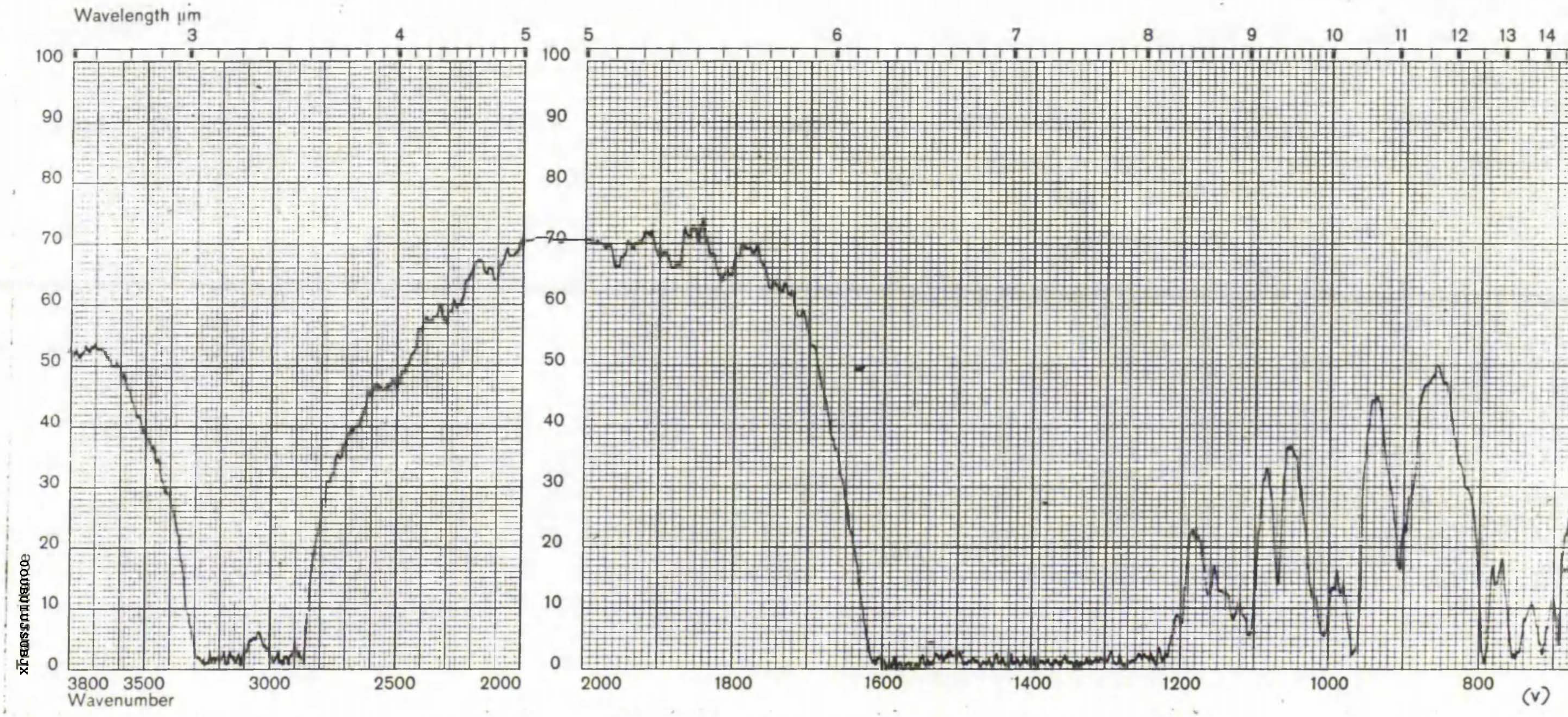
The i.r. spectrum of the ethyl iodide derivative of (I).



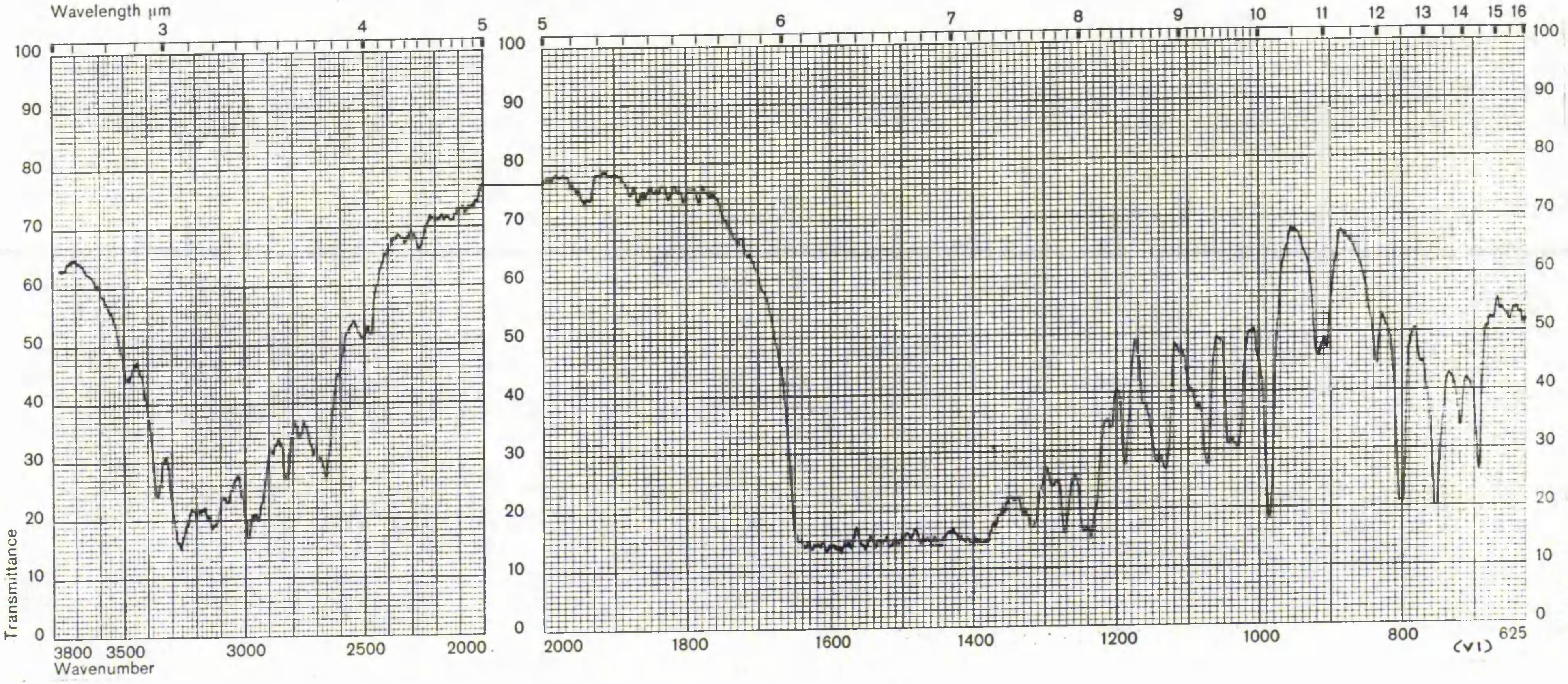
The i.r. spectrum of the butyl iodide derivative of (I).



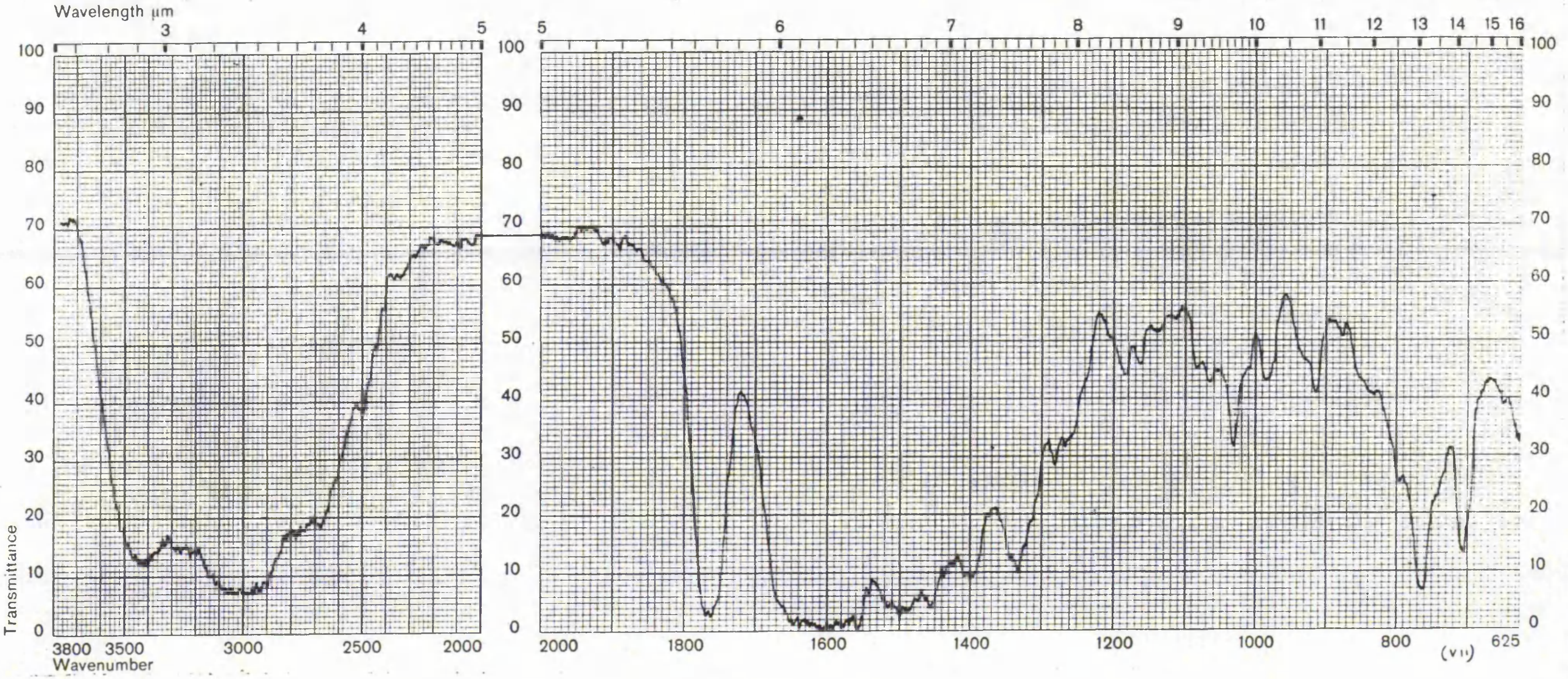
The i.r. spectrum of the hexyl iodide derivative of (I).



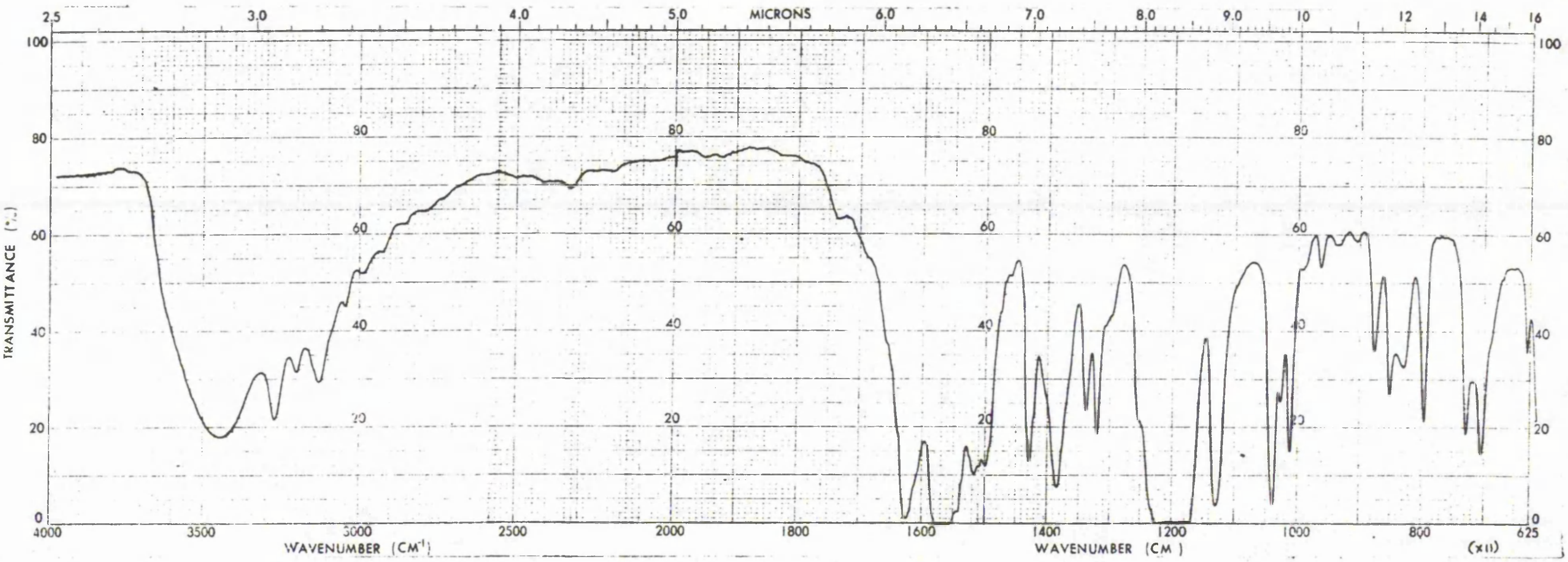
The i.r. spectrum of the iododecane derivative of (I).



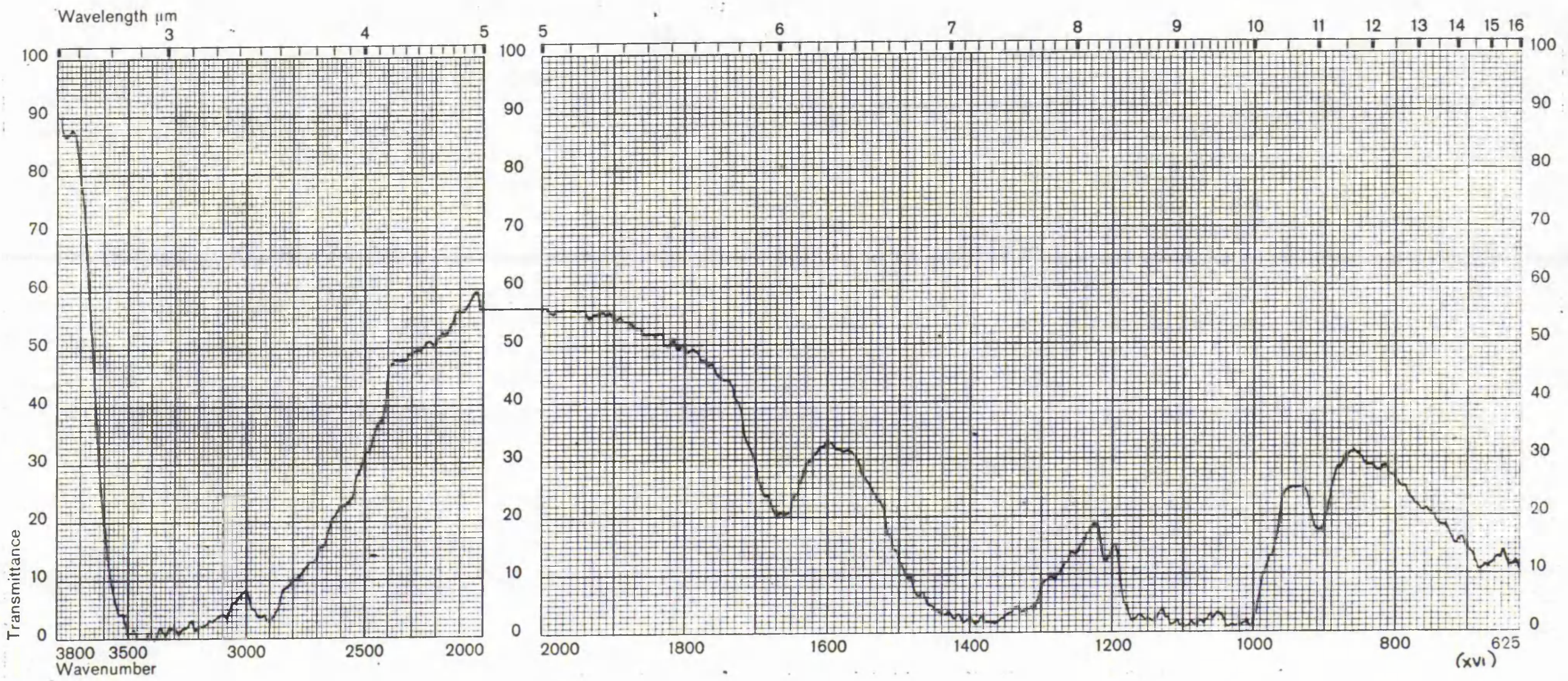
The i.r. spectrum of the cyclohexyl iodide derivative of (I).



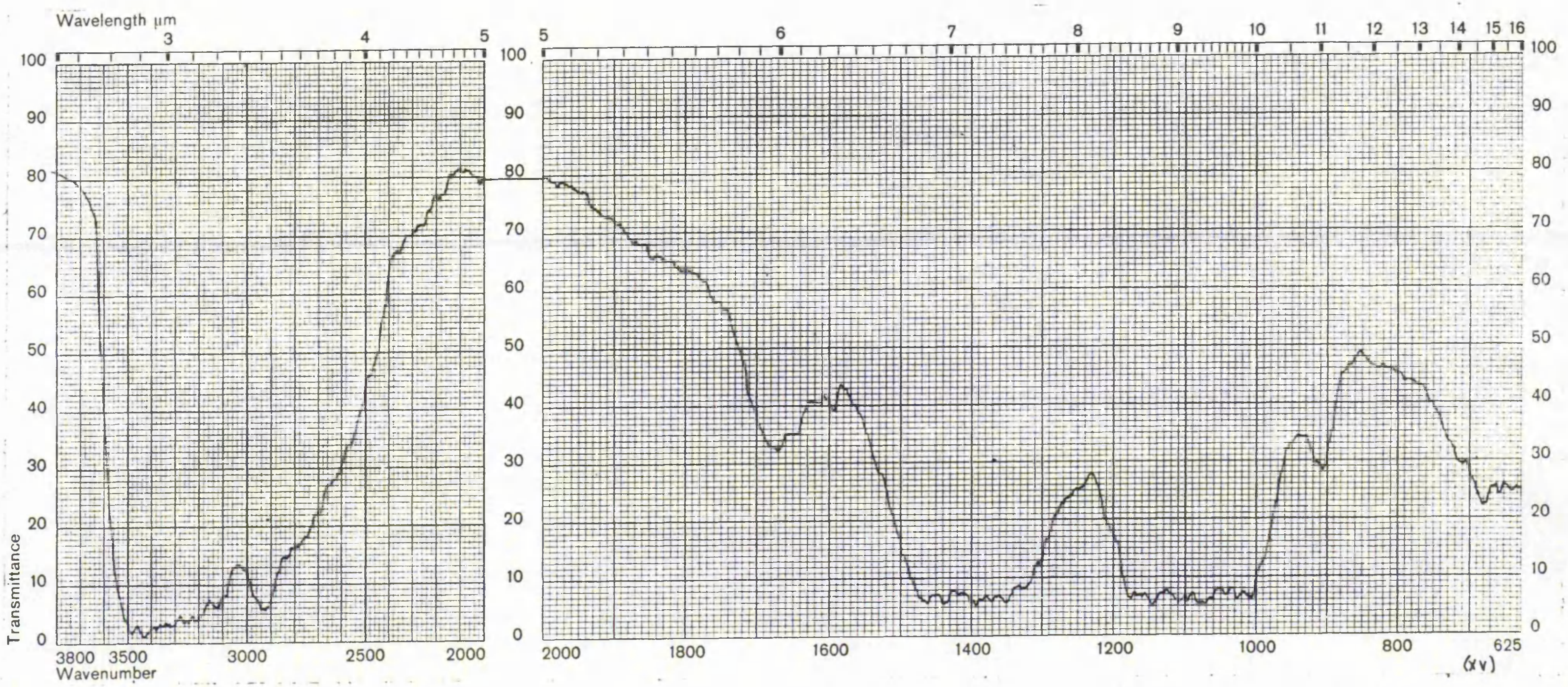
The i.r. spectrum of the chlorodiphenyl methane derivative of (I).



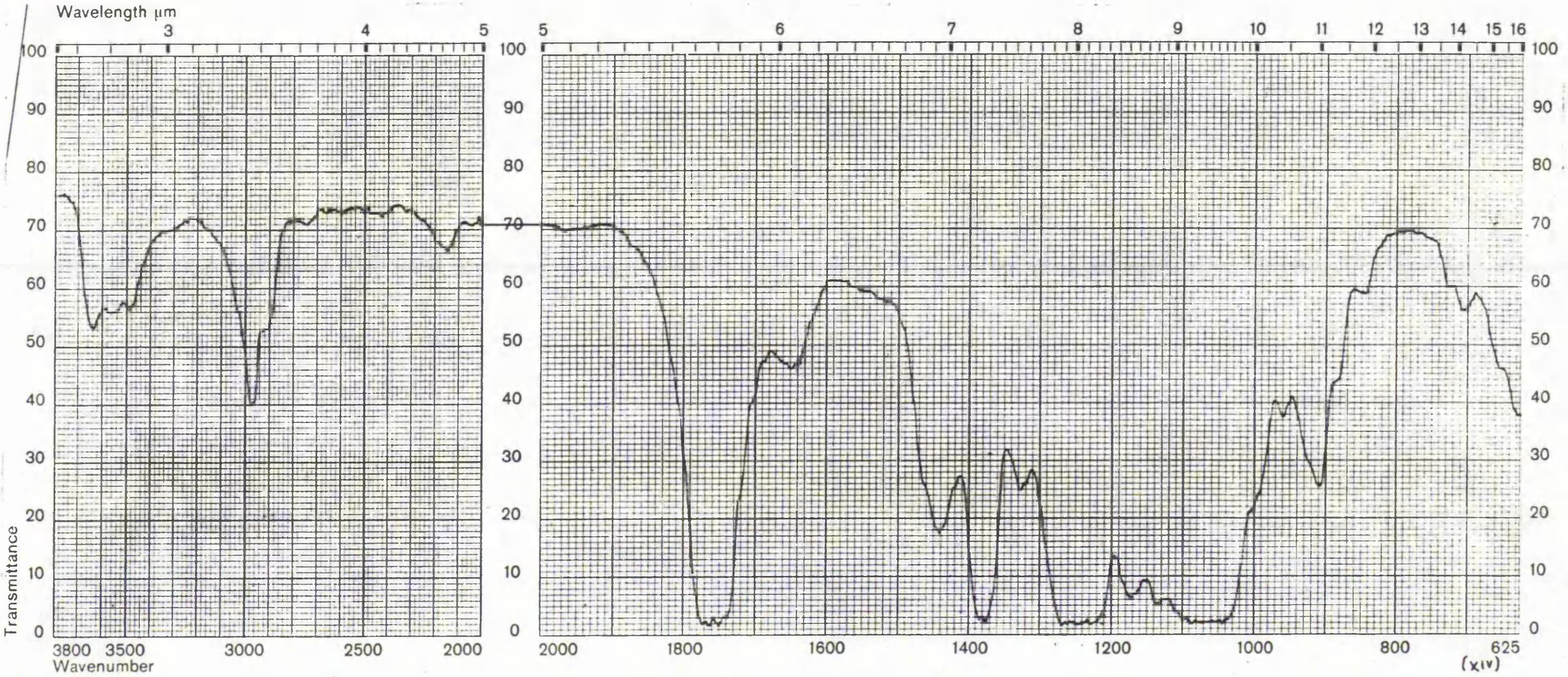
The i.r. spectrum of the commercial anionic reagent Sandospace R.



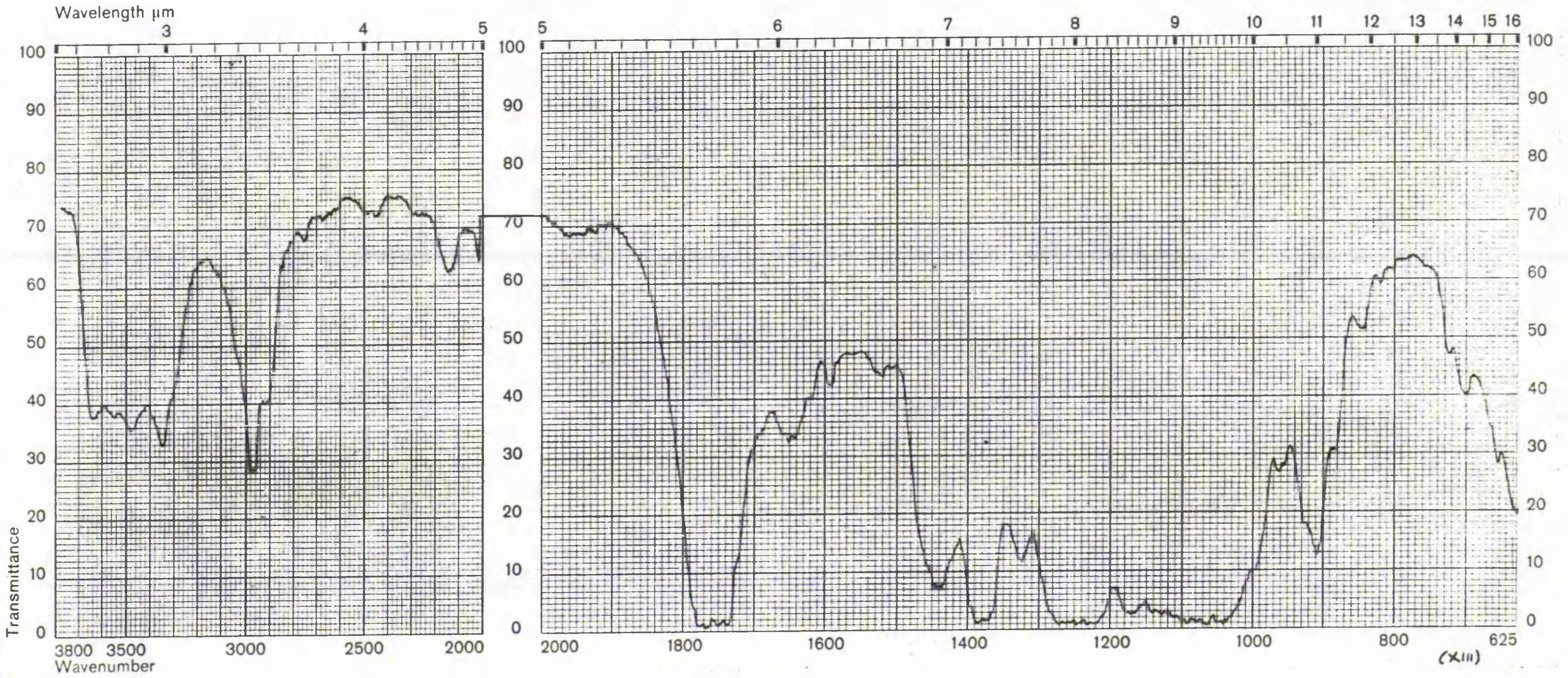
The i.r. spectrum of purified native cellulose in film form.



The i.r. spectrum of differential-dyeing cellulose, in film form treated with reagent I (evidence of the chemical modification is visible at 1590 cm^{-1}).



The i.r. spectrum of cellulose triacetate in film form.



The i.r. spectrum of differential-dyeing cellulose triacetate in film form treated with reagent I.

APPENDIX VII

Reprint of publication in the International Dyer and Textile Printer, June, 1987.

Differential dyeing of cotton: an 80-year quest concluded

A special report by George A.F. Roberts and Jacqueline A. Clipson, Physical Sciences Department, Trent Polytechnic, Nottingham.

IN 1906 the Society of Dyers and Colourists offered a prize for the development of a practical process for the production of differential dyeing cotton [1].

> The object desired is the production of a pattern or mixed effect in the piece dyeing of all cotton goods.

Despite numerous attempts over the subsequent 80 years it is only now that the problem has been solved by the authors, although differential dyeing varieties of the main synthetic fibres have been produced.

Most approaches, including the original attempts submitted in the SDC's competition, have been based on the concept of producing dye-resistant cotton yarns which, when knitted or woven into a fabric together with untreated cotton yarns, would give a reserve effect. The most successful of these approaches was that of partial acetylation which was used commercially for the production of "Cotopa" yarns [2]. However, disadvantages of this process were that tone-on-tone effects could not be produced and that the physical properties of the cotton fibres were altered, e.g. the moisture regain was reduced to 2.8–3.3% depending on the precise extent of acetylation [3].

During the period 1983–86 the authors, funded by the British Technology Group, approached the problem in a different way, namely increasing the affinity of cotton fibres for anionic dyes by the introduction of positively charged sites through treatment of cotton fibre or yarn with colourless cationic reagents having a functional group capable of reacting with cellulose under conditions similar to those used in the application of reactive dyes. Similar compounds had previously been claimed as dyeing auxiliaries to increase the degree of exhaustion of anionic reactive dyes on cotton, and other cellulosic fibres, when applied at the same time as, or prior to, the dyestuff [4,5]. However, no mention was made of the possibility of prior treatment of loose fibre or yarn so as to impart differential dyeing behaviour when combined with untreated yarn.

Yarns pre-treated with such cationic reagents, or spun from treated fibre, show preferential dye uptake when dyed together with untreated cotton yarn. Furthermore, since the extent of dye uptake can be controlled through control of the level of pre-treatment, a range of yarns of differing dye capacities can be easily produced, enabling tone-on-tone effects of any desired number of tones to be achieved.

The treated yarns show differential dyeing behaviour with all the normal cellulosic dye classes — azoic, direct, reactive, sulphur and vat — and also with acid dyes. As the dyesites are quaternary nitrogen groups they will be positively charged over the whole pH range so that it is not necessary to dye at acid pH values in order to obtain the differential dyeing effect. This is a considerable advantage over the previously produced differential dyeing viscose rayon fibre, "DD", where cationic dyesites were produced during the dyeing process by protonation of amine groups attached to the cellulose chains. This excluded the use of azoic, sulphur or vat dyes if differential uptake was to be obtained.

The extent of reservation of the untreated yarn depends on the level of treatment of the modified cotton, the depth of shade of the dyeing and the particular dye or dyes being applied. As might be anticipated, the reservation is better the lower the dye's affinity for normal cotton, but good contrast can be obtained even with vat dyes of high affinity such as C.I. Vat Green 1. In general the contrast between treated and untreated yarns increases with decreasing concentration of added electrolyte, increasing temperature and increasing liquor ratio.

Once incorporated together with untreated yarn in fabrics the treated yarn may have to be subjected to conventional preparatory processes prior to dyeing. It has been found that such fabrics may be mercerised or bleached with sodium hypochlorite, without noticeable loss in the contrast obtained. Again this is an advantage compared with the DD viscose rayon referred to above whose enhanced dye capacity was destroyed on bleaching.

In an extension of this work samples of cotton fibre and yarn have been treated with analogous reactive anionic reagents in order to produce basic-dyeable cotton yarns. Fabrics prepared from combinations of cationic/anionic or cationic/anionic/untreated yarns can be cross-dyed in a single bath treatment using a mixture of anionic and cationic dyes. The extent of cross-staining depends on the particular dyes used; C.I. Basic Blue 47, an anthraquinone-based dye, gives noticeably more staining on both cationic and untreated yarns than does the azo basic dye C.I. Basic Yellow 15 while C.I. Acid Red 13, which contains two sulphonic acid groups, gives much less staining of anionic and untreated yarn than does C.I. Acid Red 88 which is structurally similar except that it only contains one sulphonic acid group.

Thus the technical problem set by the SDC 80 years ago has at last been solved. However, successful application of the process will require careful screening of the dyes currently available in order to select the most suitable dyes from each class to ensure good contrast effects together with fastness ratings appropriate to the end use.

A further account of the process, for which a patent application has been filed, will be published. The authors wish to thank the British Technology Group for funding the research work.

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INTERNATIONAL DYER & TEXTILE PRINTER - JUNE, 1987