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LA FIXATION DES COLORANTS RÉACTIFS AU COTON AUX MOYENS DU RAYONNEMENT INFRAROUGE

FIXATION OF REACTIVE DYES ON COTTON USING INFRARED RADIATION

Thèse de doctorat ès sciences appliquées
Spécialité: génie chimique

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RÉSUMÉ

Le but de ce projet est l'établissement des conditions optimales pour la teinture de coton avec les colorants réactifs aux moyens d'un procédé dans lequel la fixation du colorant s'effectue par rayonnement infrarouge. L'efficacité de ce procédé est comparée aux autres modes de fixation.

On a examiné des colorants de réactivité faible, moyenne et élevée dans un procédé de teinture comprenant le foulardage suivi de la fixation en continu à chaud au moyen des émetteurs infrarouges. Le rendement de fixation déterminé par spectrophotométrie des solutions appropriées du colorant est corrigé par une nouvelle méthode tenant compte de la quantité du colorant qui a réagi avec le coton avant qu'il pourrait être extrait par l'eau. Le rendement de couleur d'une teinture est évalué par mesure de son spectre de réflexion et par calcul de la valeur de K/S de Kubelka-Munk. Une nouvelle méthode pour la correction du rendement de fixation rend compte du colorant qui a réagi avec le coton pendant la courte période avant son extraction.

Les études préliminaires ont montré que le rendement de fixation est plus élevé, plus est élevée la réactivité du colorant, plus est élevée la puissance électrique fournie aux sources infrarouges et plus le temps de séjour est long dans le four infrarouge, respectant toujours la limite de température du tissu qui évite sa dégradation thermique. Le rendement de fixation est assez sensible aux variations de ces deux derniers paramètres. Le rendement de fixation de certains colorants est assez sensible à la nature et à la concentration de l'alcali utilisé pour amorcer la réaction de fixation. Pour les colorants de faible réactivité, la fixation optimale au coton nécessite une concentration appréciable de NaOH dans la solution du colorant tandis que le plus faible alcali Na_2CO_3 fixe bien les colorants de haute réactivité. Il s'avère possible d'obtenir des rendements de fixation supérieurs à 85% pour la plupart des colorants étudiés, les valeurs dépassant 90% pour quelques-uns, même si on n'a pas optimisé le pH du bain du colorant. L'addition du sel à la solution du colorant n'augmente que peu les rendements de fixation en accord avec la généralisation que son influence est mineure aux faibles rapports du bain. L'influence de l'addition de l'urée est variable. Elle est capable d'augmenter des rendements de fixation des colorants de faible réactivité. L'extraction sous-vide du tissu imprégné d'une solution alcaline du colorant avant son chauffage dans le four infrarouge améliore la performance du procédé puisque le tissu sèche plus rapidement. Le rendement de fixation du colorant est mieux après l'extraction sous vide mais l'effet n'est pas significatif lorsque les tissus comparés ont la même température finale.

Une étude quantitative de l'influence des variables opérationnelles de la thermofixation à infrarouge est effectué au moyen de plans factoriels et d'analyses statistiques des réponses pour le colorant rouge Drimarene X-6BN. On a dérivé des relations linéaires entre les variables contrôlées et les réponses du procède de teinture au moyen de deux plans factoriels. Les résultats montrent que les variables les plus importantes déterminant le rendement de fixation sont la vitesse du tissu dans le four infrarouge, la puissance fournie aux émetteurs et la concentration de NaOH dans le bain du colorant. Ceci confirme les résultats préliminaires. La vitesse du tissu et la puissance électrique aux émetteurs influencent significativement la température finale du tissu chauffé et sa teneur en eau à la fin du procédé. L'extraction sous-vide s'avère une technique permettant d'obtenir plus facilement une plus haute température du tissu chauffé. Elle permet des améliorations considérables du rendement de fixation du colorant, mais pas dans une situation où le rendement est déjà assez élevé.

Puisque le rayonnement infrarouge pénètre dans l'intérieur d'une nappe textile, le séchage par infrarouges permet une évaporation rapide de l'eau partout dans la nappe et supprime significativement la migration du colorant non fixé pendant la période initiale du séchage. Pendant le séchage à l'air chaud, l'évaporation de l'eau a lieu principalement aux surfaces des filés. Tout colorant non fixé est libre de migrer à la surface d'évaporation pendant la période de séchage à taux constant. Le chauffage des nappes imprégnées d'une solution alcaline du colorant réactif aux moyens des émetteurs tubulaires de type T-3 donne un rendement de fixation au coton un peu plus élevé que le chauffage avec les sources tubulaires de quartz. Cependant, les tubes T-3 ont produit des teintures ayant un rendement de couleur inférieur probablement en conséquence de leur effet sur la suppression de la migration. Les rendements de fixation des teintures faites par fixation à l'air chaud sont considérablement plus faibles que de ceux obtenus au moyen du chauffage par infrarouges et la teinte a indiqué que l'air chaud a conduit à une migration importante du colorant à la surface des filés. Le pré-séchage de la nappe imprégnée avant la fixation du colorant à l'air chaud a diminué un peu le degré de migration et produit des rendements de fixation un peu plus élevés.

L'examen des coupes transversales de fibres teintes par microscopie optique montre une distribution uniforme du colorant pour les tissus teints par thermofixation à l'infrarouge. Les fibres des tissus pour lesquels le colorant est fixé par air chaud montrent une coloration superficielle.

Le procédé de teinture en continu utilisant la thermofixation aux infrarouges pour un colorant de faible réactivité donne un rendement élevé de fixation sans variation de la couleur perçue tout au long de la nappe teinte. Pour un solution du colorant contenant de l'urée mais sans sel, le rendement de fixation pour le procédé en continu a atteint 90%.

La possibilité d'obtenir les hauts rendements de fixation des colorants réactifs au coton (> 90%) par application du chauffage infrarouge rend ce procède d'intérêt commercial. Les hauts rendements sont possibles avec les colorants de réactivité faible, moyenne et élevée dans un temps court de traitement, sans migration du colorant aux surfaces des filés pendant le séchage initial. La quantité résiduelle du colorant non fixé dans le tissu de coton conduirait à une réduction de l'intensité de la couleur dans l'effluent du procédé de lavage après la teinture. Le degré de coloration des eaux usées est un problème environnemental actuel pour bon nombre de teintureries utilisant les colorants réactifs. De plus, les hauts rendements de fixation possibles sans les addition du sel et de l'urée au bain du colorant permettraient une diminution de la charge polluante de la teinturerie.

SUMMARY

The objective of this project was to establish optimum conditions for the continuous dyeing of cotton with reactive dyes in a pad-dry-heat process using infrared heating, and to compare the efficiency of infrared dye fixation with that obtained in other dyeing processes.

Dyes with low, medium and high reactivity towards cotton were used in a pad dyeing and infrared fixation process. The determination of dye fixation yields was accomplished by spectrophotometry of the appropriate dye solutions. The color yields were determined by reflectance spectrophotometry and calculation of the Kubelka-Munk K/S values. A new method for correction of the fixation yield was used to account for dye which had reacted with the cotton during the short time before it could be extracted for analysis.

The preliminary work showed that the higher the reactivity of the dye, the higher the fixation yield. The latter increased significantly with decrease in fabric speed through the infrared oven and with increase in the emitter power, within the limits of fabric temperature imposed to avoid thermal damage to the cotton. The fixation yield was quite sensitive to changes in these two variables. The fixation yields of some dyes were quite sensitive to the type and concentration of the alkali used for the dye fixation reaction. The weaker alkali Na_2CO_3 was suitable for fixation of high reactivity dyes, but for dyes of low reactivity, the stronger NaOH was necessary to achieve high fixation. Despite the fact that the alkali type and concentration were not optimized, it was possible to obtain fixation yields over 85% for most dyes, and in some cases over 90%. The effect of increasing the salt concentration in the dye solution did not correspond to the generalization that salt is much less effective at low liquor to goods ratios. Addition of urea to the dye solution had variable effects on the fixation yields obtained using infrared heating. It was effective in increasing the fixation yields of some dyes of lower reactivity.

The fixation yield of the reactive dye on cotton was improved to a certain extent by vacuum extraction, but the effect was not significant when the final fabric temperatures were the same. Vacuum extraction significantly improves the performance of the operation because the fabric can be dried much more quickly.

In infrared fixation, the most important parameters influencing the fixation yield were the reactivity of the dye, the fabric speed through the oven, the emitter power and the concentration and nature of the alkali. A quantitative examination of the effects of the process variables in infrared fixation using a factorial plan was carried out using the dye Drimarene Red X-6BN. Relatively simple linear relationships between controlled process variables and output responses were obtained for the fixation of a reactive dye on cotton using two factorial experimental designs. These indicated that the fabric speed, emitter power and NaOH concentration were the most important variables influencing the dye fixation yield. The fabric speed and emitter power also significantly affected the final fabric temperature and water content. Vacuum extraction prior to drying was one means of obtaining a higher final fabric temperature. It significantly increased the dye fixation yield, but not in those cases where reaction conditions already favored a high degree of fixation.

Since infrared radiation can penetrate into textile materials, infrared drying will result in rapid water evaporation throughout the material and considerably reduce dye migration during the early stages of drying. For convective drying with hot air, water evaporation occurs mainly at the yarn surfaces. Any reactive dye which has not reacted with the cotton fiber will be free to migrate to the surface of evaporation during the constant rate period of drying. Infrared heating using T-3 tubes gave slightly higher dye fixations than when using quartz tube sources but the former gave dyeings of lower color yield presumably because of their greater effect in suppressing migration of the dye solution in the early stages of drying. The fixation yields obtained using hot air heating were considerably lower than those obtained using the infrared process and the dyeings showed that considerable migration had occurred. Pre-drying of the padded fabric before hot air fixation did lower the dye migration slightly and gave somewhat higher fixation yields.

Examination of cross sections of dyed fibers by optical microscopy showed uniform dye distribution within the fabrics dyed by the infrared process but fibers from fabric dyed using hot air were ring dyed.

The continuous dyeing and fixation process using infrared heating for a low reactivity reactive dye on cotton gave high fixation yields and no visible color variations along the length of dyed fabric. A fixation yield of about 90% was achieved with urea added to the dye solution but without added salt.

The possibility of obtaining high fixation yields (> 90%) using a pad-thermofixation process with infrared heating makes this a technologically attractive process for several reasons. Such high yields are possible with dyes of high, medium, and low reactivity, in short processing times, with little migration of the dye to the yarn surfaces during initial drying. Most importantly, very little unfixed dye remains in the cotton fabric so the washing effluent is only slightly colored. This is a current environmental problem for dyehouses using reactive dyes. In addition, high fixation yields are possible without added salt and urea offering further reductions of the pollution load in the dyehouse effluent.

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1. INTRODUCTION

1.1 Development of reactive dyes

Reactive dyes are the only textile colorants designed to bond covalently with the fibrous substrate and are mainly used for the dyeing and printing of cotton. They are valued for their varied and brilliant hues, for their versatile application methods and the high wet fastness of the dyeing produced. Reactive dyes were first used commercially more than forty years ago. During the intervening period, the growth in consumption has been steady rather than spectacular being currently 3.9% per year worldwide. This figure is four times the growth rate of other dyes for cellulose fibers (RENFREW and TAYLOR, 1990).

Reactive dyes are attached to a textile fiber by chemical reaction involving the formation of a covalent dye-fiber bond which results in excellent fastness to washing and wet processes. They are colored compounds which have suitable groups capable of reacting with hydroxyl, amino or mercapto groups in the fiber (BIRD and BOSTON, 1975, TROTMAN, 1984). Therefore, they differ fundamentally from other dyes whose dyeing depends on physical adsorption involving van der Waals forces and hydrogen bonding with the fiber.

The first reactive dyes for cellulose were introduced by ICI in 1956. The original patents awarded to ICI, Rattee and Stephen claimed that application of water-soluble dyes containing a dichlorotriazine group to cellulosic fibers from a neutral dyebath, followed by an increase of the pH value, resulted in covalent bond formation between a triazine carbon atom and an oxygen atom of a cellulose hydroxyl group. All major dyestuff manufacturers immediately started research on new fiber-reactive dyes and on application methods for cellulose fibers. Ciba and ICI both introduced reactive dyes with monochlorotriazine groups in 1957, and, in 1958, Hoechst introduced reactive dyes containing potential vinyl sulphone groups. Since then a variety of other types have been developed and used commercially.

In the period 1972-87, more than 700 new reactive dye entries were made in the Colour Index (SDC-AATCC, 1971-1988). More recent developments include the introduction of monofluorotriazine reactive groups, mixed bifunctional reactive dyes and reactive dyes capable of fixation under neutral conditions. The term mixed bifunctional reactive dye is used to describe dyes which have two dissimilar reactive groups, e.g., a monochlorotriazine and a potential vinyl sulphone group. Such dyes are claimed to be less sensitive to temperature and pH variations during dyeing so that shade reproducibility is improved.

Today, fiber-reactive dyes are widely used in textile dyeing processes and have the highest growth rate of all dyes. They offer a wide color range, bright shades and excellent fastness to laundering and dry cleaning. There is an extensive literature on these dyes, particularly for dyeing cellulosic fibers (PRESTON, 1986), but also for wool (LEWIS, 1992).

1.2 Application of reactive dyes to cotton

1.2.1 Structure of reactive dyes

The characteristic structural features of a reactive dye are illustrated in Figure 1.1. The colored part of a reactive dye, i.e. the chromogen (C), may belong to any of the chemical classes of commercial dyes, provided it has the necessary substantivity for the fiber. The fastness to light and chemical treatments of the reactive dyes are mainly determined by the chromogen. Reactive dyes for cellulose fibers require sulphonic acid groups (W) to promote water-solubility. These are attached to the chromogen or occasionally to the reactive system. In some cases, the reactive group (RG) is attached directly to the chromophoric system without a bridge link (B).

The reactive dyes are usually classified in terms of their reactive groups:

1) Reactive groups undergoing nucleophilic substitution of an activated halogen atom
    a) Dichloro- or monochlorotriazinyl derivatives (DCT and MCT) (Figure 1.1)
    b) Monofluorotriazines (MFT)
    c) Dichloro- or difluorochloropyrimidine derivatives (DCP and DFCP)
    d) Dichloroquinoxaline derivatives (DCQ) (Figure 1.4)
2) Reactive groups undergoing nucleophilic addition
    a) Vinyl sulphones (VS) usually derived in situ by elimination of a sulphate ion from a sulphuric acid ester of a β-hydroxyethylsulphone (Figure 1.5)

1.2.2 Structure and activation of the cotton

The bleached cotton fiber consists largely of cellulose , which is a condensation polymer of β-D-glucopyranose, shown in Figure 1.2.

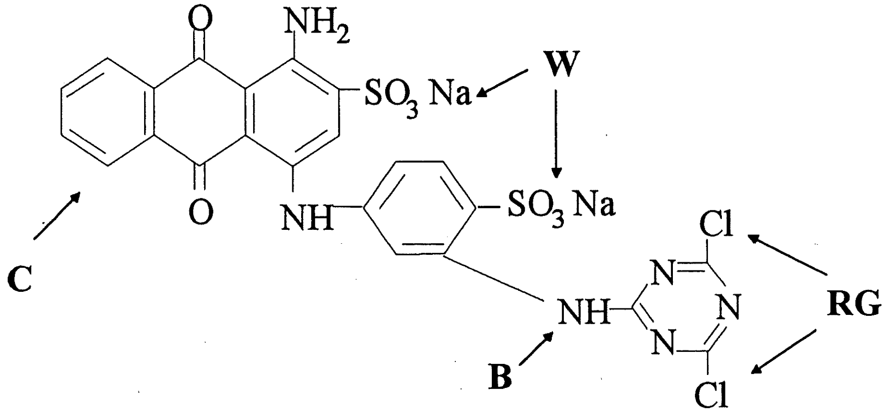


Figure 1.1 The characteristic structural features of a reactive dye (dichlorotriazine)

RG = reactive group,

B = bridge link

C = chromogen

W = water-solubilising group, usually -SO_3Na

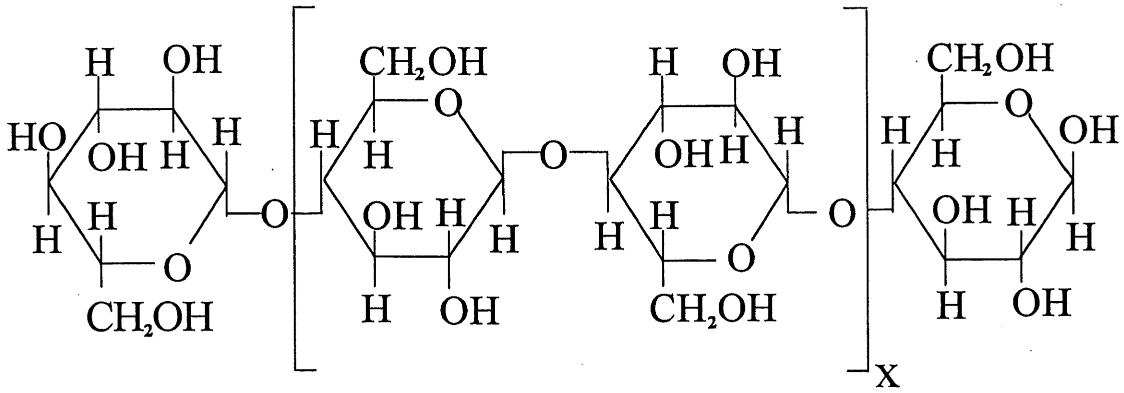


Figure 1.2 Structure of cellulose

$$\text{CELLULOSE}-\text{OH}+\text{OH}^{-} \rightleftharpoons \text{CELLULOSE}-\text{O}^{-}+\text{H}_2\text{O}$$

Figure 1.3. Acidic dissociation of cellulose

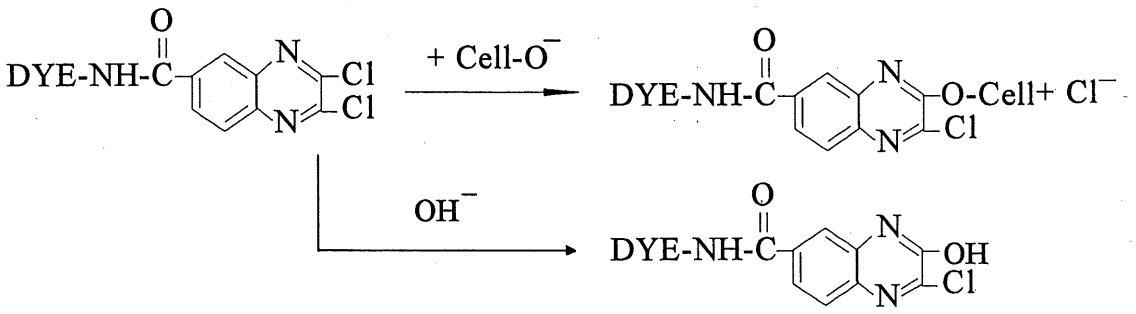
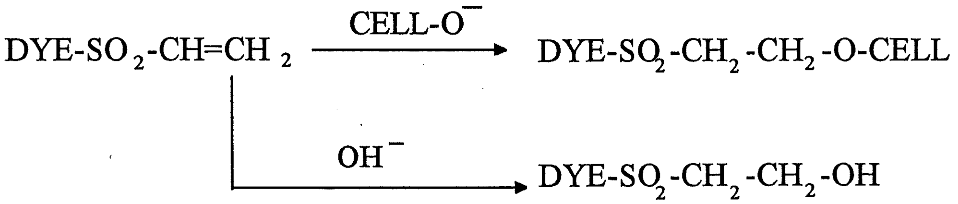


Figure 1.4 Fixation and hydrolysis of a dichloroquinoxaline reactive dye

$$\text{DYE-SO}_2\text{- CH}_2\text{-CH}_2\text{-O-SO}_3\text{Na +NaOH} \longrightarrow \text{DYE-SO}_2\text{-CH=CH}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$



$$\text{DYE-SO}_2\text{-CH=CH}_2 \xrightarrow{\text{CELL-O}^{-}} \text{DYE-SO}_2\text{-CH}_2\text{-CH}_2\text{-O-CELL}$$

$$\text{DYE-SO}_2\text{-CH=CH}_2 \xrightarrow{\text{OH}^{-}} \text{DYE-SO}_2\text{-CH}_2\text{-CH}_2\text{-OH}$$

Figure 1.5 Fixation and hydrolysis of a vinyl sulphone reactive dye

There are one primary and two secondary alcohol groups in each glucose unit of the cellulose. In the presence of an alkali, some of the hydroxyl groups along the cellulose polymer chains undergo acidic dissociation and anionic cellulosate ions are thus formed. This also breaks down interchain hydrogen bonding, causes charge repulsion between the polymer chains and leads to swelling. The process can be represented by Figure 1.3.

1.2.3 Reaction of fiber-reactive dyes

The reaction of cellulose with a reactive dye under alkaline conditions occurs by one of two mechanisms:

(1) Nucleophilic aromatic substitution of a reactive halogen atom in a heterocyclic group by a cellulosate ion.

Figure 1.4 shows a typical reaction by this mechanism. The characteristic features of this mechanism are that the most nucleophilic form of the cellulose (Cell-O^- group) attacks the heterocyclic carbon of the reactive group. In the dyeing the process, the pH value and hence the equilibrium concentration of cellulosate anions (Cell-O^-) have to be increased in order to promote the dye-fiber reaction. The alkaline conditions necessary for the dye-cotton reaction also cause hydrolysis of the reactive group and produce the hydrolysate which is unreactive towards cellulose. Hydrolysis is the same type of reaction as fixation to the fibre but with hydroxide ion as the nucleophile.

2) Nucleophilic Michael addition of a cellulosate ion to the activated C=C double bond of a vinyl sulphone.

A typical reaction by this mechanism is illustrated in Figure 1.5. The double bond of the reactive group is in most cases not present in the reactive dye, but is formed after addition of alkali by elimination of the sulphate ion from the sulphuric acid ester of a β-hydroxyethylsulphone.

The hydrolyzed dye remaining in the fabric after the dyeing process must be removed by washing, otherwise the optimal washing and rubbing fastness of the final fabric will not be realized (PRESTON, 1986). In general, excessive hydrolysis will not have taken place before the dye has had time to combine with the cellulose because the rate of reaction with water in the fiber is slower than with cellulose. Hydrolysis of reactive dyes results in decreased fixation yields and considerable quantities of dye in the effluent. Although this may not be overly toxic, some dyes resist biodegradation, and colored water streams are considered undesirable. In addition, because good dyebath exhaustion, and thus to some extent good fixation, depend upon the addition of large quantities of sodium chloride to the dyebath, the effluent has a high salt load which is also ecologically undesirable. Therefore, there is a real need for the development of new reactive dyeing processes which give high efficiency using no or a minimum of salt.

1.3 Dyeing methods for reactive dyes on cotton

Dyeing methods may be divided into pad impregnation and immersion exhaustion processes. Exhaustion dyeing is a batch process involving immersion of the fabric in the dyebath, transfer of the dye to, and its gradual diffusion into, the fiber, so that the bath concentration decreases. In the exhaust dyeing of cotton with reactive dyes, the first phase of dyeing is carried out under neutral conditions to allow dye diffusion into and migration among the fibers. This promotes uniform coloration. Fixation of the reactive dye is then achieved by addition of a suitable alkali to activate the cellulose by forming some cellulosate ion groups. The reaction phase of the dyeing occurs over 30-60 minutes at typical dyeing temperatures in the range from 30 to 90°C, depending upon the type of reactive group. Continuous pad impregnation is a process in which a piece of fabric is passed at full width through a small bath containing dye solution and then through the pad pressure rollers to express the excess liquid. For continuous dyeing, fixation must be relatively rapid (1-2 minutes) and usually involves heating the impregnated fabric. The exception to this is the cold pad-batch process, where the fabric is impregnated with dye and alkali and is then batched at room temperature for 6-24 hours.

In continuous thermofixation, the dye reacts with the cellulose during the heating phase. Heating is usually carried out in saturated steam or in hot air. During heating, rapid diffusion of dye molecules into the fibers is promoted followed by the reaction with the fiber. Uniform coloration depends upon uniform dye solution application with the padder. Steam and hot air heating are relatively inefficient as the rate of energy transfer into the fabric is quite slow. In addition, hot air heating can cause considerable migration of unfixed reactive dyes to the yarn surfaces where water is evaporating during the early stages of drying (SOMM and BUSER, 1985; ETTERS, 1990). This will be discussed in Chapter 5.

Microwave heating involves radiant energy transfer and is very efficient for drying. It provides internal heating, the radiant energy being partially transmitted into a wet material and appearing as thermal energy at the site of absorption. Microwave heating has been shown to be effective for fixation of reactive dyes (HAGGAG, 1990). However, the expense of microwave equipment, and the cost of electricity for its operation, limit the use of this method to the drying of thick packages. The ratio of the specific capital cost of infrared and microwave dryers to that of a convection dryer was estimated (DOSTIE, 1992), and is shown in Table 1.1.

TABLE 1.1 CAPITAL COST AND EFFICIENCY FOR DIFFERENT HEATING METHODS

Heating (fixation) method	Capital cost ($/kW) (installed)	Heating efficiency (%)
Convection (Hot air)	300	60
Infrared	500	80
Microwave	2000	100

Infrared heating involves transfer of radiant energy from a high-temperature radiator to a wet material without physical contact. It is ideal for drying when the surface of the dyed fabric is saturated with water because water has strong absorption of infrared radiation in the 3 μm wavelength region. Power densities (W/m^2) 6-10 times higher those obtained in convection drying with hot air, make it attractive for drying wet textiles (SINGLETON, 1980). Absorption of radiation by the material to be heated is gradual and takes place at a certain depth from the surface, according to a decreasing exponential (Bouguer's law). The penetration depth depends in particular upon the wavelength of the incident radiation, this increases as wavelength decreases below 3 μm. Under suitable conditions, the radiation produces rapid and uniform heating throughout a wet fabric exposed to it.

1.4 Literature review

A considerable amount of research on infrared drying and its control has been carried out in the textile laboratory at Université de Sherbrooke (CÔTÉ, 1988; CÔTÉ et al., 1990; FORGET, 1990; THERIEN et al., 1991; FORGET et al., 1993; BROADBENT et al., 1994a; DHIB, 1994; DHIB et al., 1994; SLITINE, 1995). The M.Sc.A. thesis of Hamoudi (HAMOUDI, 1990), however, is the only source of information on the fixation of reactive dyes by a pad/heat process using infrared radiation. Apart from this study, and some confidential reports on work carried out for Électricité de France at ENSITM in Mulhouse, there is no published work on the infrared fixation of reactive dyes.

Hamoudi (HAMOUDI, 1990) only carried out a very preliminary study but concluded that effective infrared thermofixation was possible with dyes of high reactivity towards cotton. No attempt was made to optimize the low and moderate fixation yields of the dyes examined. She did, however, establish that dye fixation yields increased using higher radiant power densities and longer heating times. Some of the results presented are questionable because of an emitter circuit problem which caused incorrect voltage readings. This was not recognized until her work had been completed (BROADBENT, 1991).

A considerable technical literature exists dealing with the thermofixation of reactive dyes on cotton by heating in saturated steam or in hot air. However, as Hamoudi points out, there are no published fundamental scientific studies of even these technologically important processes.

1.5 Objectives of present work

Because of the lack of fundamental work on the fixation of reactive dyes on cotton using infrared heating in a pad-dry-heat processes, this study was undertaken with the following initial objectives:

(1) To establish optimum conditions for the continuous dyeing of cotton with reactive dyes in a pad-dry-heat process using infrared heating.

(2) To compare the efficiency of infrared fixation of reactive dyes with that obtained in other dyeing processes.

2. EXPERIMENTAL TECHNIQUES

2.1 Introduction

The objective of this chapter is to describe:

1) Materials and reactive dyes used in the experimental work
2) Equipment used to carry out dyeings, particularly the infrared oven
3) Details of the dyeing and fixation procedures
4) Methods of analysis used to determine the cotton water content, the dye fixation yield and the corrected fixation yield.

2.2 Materials

Fabrics of scoured and bleached 100% cotton with superficial weights of 246 and 164 g/m^2 were cut 20 cm wide for the experimental trials. The reactive dyes used, with different structures and reactivities, are listed in Table 2.1. In the text, dyes are referred to by their color and code, e.g. Levafix Brilliant Red E-4B = Red E-4B, since not all the dyes have been assigned Colour Index generic names (SDC-AATCC, 1971-88). All other chemicals were reagent grade.

2.3 Equipment

The equipment consisted of a pad bath, vacuum extraction unit and an electric infrared oven, shown in Figure 2.1.

The pad-vacuum extraction unit and the infrared dryer have been described in a number of previous publications (COTÉ, 1988, COTÉ et al., 1990). The fabric passed through the dye solution in the pad bath and then over the vacuum slot. If required, vacuum extraction was used to remove excess dye solution from the fiber surfaces to prevent dye migration during the early stages of drying. A sample was cut after padding with the dye solution and mounted on a 24 x 38 cm pin frame which was then supported in an opening in the stainless steel mesh conveyer which continuously passed through the infrared dryer (Radiant Heat Inc., Coventry, RI). The treatment of small samples on the pin frame allowed study of the continuous drying and heating of samples without consuming large amounts of cotton material.

TABLE 2.1 DYES USED IN THE EXPERIMENTAL WORK

Reactive Dyes	Reference	Supplier	Reactive Group	Reactivity
Remazol Brilliant Black B	C.I. Reactive Black 5	Hoechst	Bisvinylsulphone	High
Levafix Brilliant Red E-4B	C.I. Reactive Red 40	Bayer	Dichloroquinoxaline	Medium
Drimarene Navy K-2B	C.I. Reactive Blue 193	Sandoz	Difluorochloro-pyrimidine	High
Remazol Brilliant Blue R	C.I. Reactive Blue 19	Hoechst	Vinylsulphone	Medium
Drimarene Red X-6BN	----------	Sandoz	Monochlorotriazine	Low
Cibacron Blue F-R	----------	Ciba	Monofluorotriazine	Medium-high
Basilen Yellow E-3R	C.I. Reactive Yellow 3	BASF	Monochlorotriazine	Low
Procion Turquoise MX-G	C.I. Reactive Blue 140	Zeneca	Dichlorotriazine	High

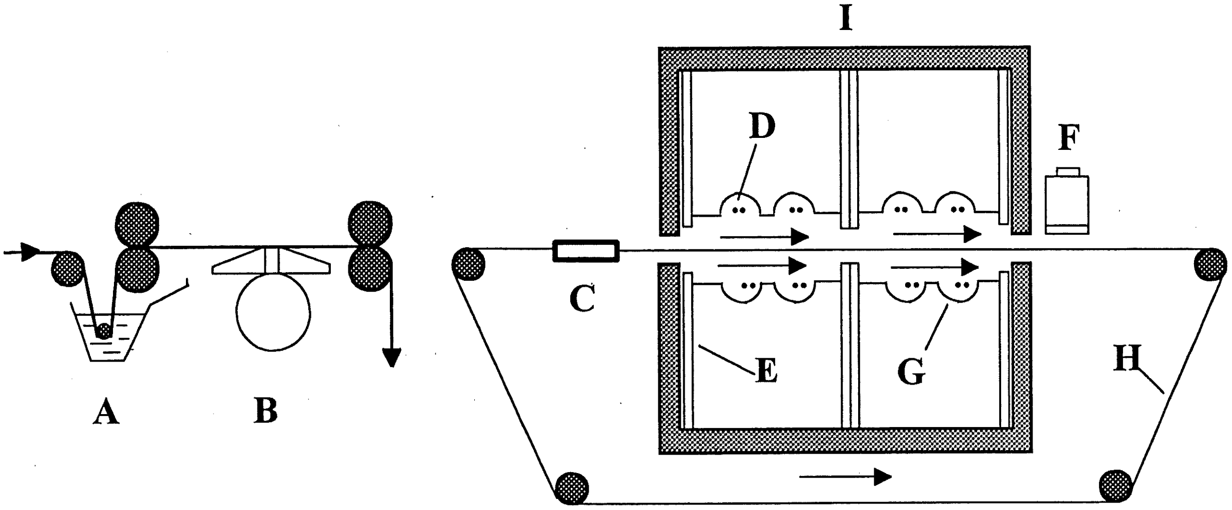


Figure 2.1 Scheme of padding and infrared fixation units

A. Pad bath	E. Air ducts
B. Vacuum slot extractor	F. Infrared pyrometer
C. Pin frame	G. Reflectors
D. Tubular sources	H. Mesh conveyor
I. Infrared oven	

Two types of tubular infrared source were used in the experimental work. The solid quartz T-3 tube sources, operating at a temperature of 2200°C at the maximum rated voltage of 450 V, give a short-wave infrared emission with maximum output at about 1 μm. The quartz tube sources (iron/aluminium filament inside a 67.5 cm transparent quartz envelope) give a medium-wave infrared emission, with maximum output around 3 μm, at a temperature of about 760°C for their maximum rated voltage of 450 V. The tubular sources were installed in four independently operated modules each with a maximum power of 5 kW per module. Two modules were situated over the mesh conveyer, and two below, to give uniform heating on both faces of the fabric. Each module had its own control unit but in all the tests the four modules were operated under the same conditions. They were placed at a distance of 5 cm from the fabric. Polished aluminum reflectors behind the tubes redirected as much radiation as possible towards the web. The effective heating zone in the oven was 1.44 m long.

The ventilation system allowed introduction and evacuation of air using transversely placed slots, the flow being directed along the upper and lower faces, as the fabric was moved horizontally in the same direction. The air introduced was at ambient temperature with a flow rate of 4 kg/min measured with a mass flow meter (COTÉ, 1988). This allowed effective removal of steam from the fabric surface.

The infrared oven had a variety of instruments for measuring the current and voltage supplied to each module, and for display of thermocouple readings. An infrared pyrometer with appropriate filter (Modline 4, Ircon Inc., Niles, IL, USA), situated at the exit of the infrared oven, was used to measure the temperature of the fabric surface as it left the oven. The maximum response of the pyrometer was recorded, which would be somewhat lower than the final fabric surface temperature. This is examined in more detail in Chapter 6.

2.4 Dyeing and fixation procedures

The dye solution for padding was freshly prepared by dissolving the reactive dye in water, followed, if necessary, by the sodium chloride and urea. It was well mixed with the appropriate alkali solution about one minute before padding and the mixture used immediately to minimize premature hydrolysis of the reactive group. The dye solution usually had a final concentration of 20 g/L but, if the padded fabric was to be vacuum extracted, this was increased to 30 g/L since the extractor removed about 30% of the applied solution. The NaCl concentration was usually 25 g/L. A piece of cotton was passed through the dye solution in the pad bath at room temperature at a speed of 5 m/min, and then through the pad rollers to express the excess padding liquid. The typical water content was 65-70% without vacuum extraction, and 35-40% after vacuum at a pressure drop of 54 kPa. The fabric left the unit via a pair of drive rollers which maintained the correct tension and alignment with the vacuum slot. Samples of padded fabric were then cut immediately, one for determination of water content (section 2.5.1), one for initial dye content (section 2.5.2), and the others ready for fixation. A sample of padded fabric was mounted on the pin frame, which was then placed in the hole on the mesh conveyer. It was passed through the infrared oven, which had been preheated for about 30 minutes at given settings, at a speed in the range 2-4 m/min. Each trial was repeated under the same conditions. The measurements of fixation yields presented in the text represent the average of two readings with good reproducibility (see Tables 4.3 and 4.4 in Chapter 4).

Fixation of the reactive dye on cotton was achieved not only by heating in the infrared oven, but also at room temperature, or by drying and heating in a hot air oven. For fixation at room temperature, a padded sample was sealed in a plastic bag and stored for 24 hours. For hot air fixation, a padded sample was dried in a hot air oven for 15 minutes at 110°C. Some samples were also heated under the same conditions after sealing in a plastic bag, so as to simulate steaming. Later in the research, fixation was carried out in a laboratory hot air impingement dryer. This is described in Chapter 6.

2.5 Analytical methods

2.5.1 Fabric water content

The water content of dyed fabrics after padding depends mainly on the pad roller pressure and the vacuum level of the extractor, if used. In order to measure the water content of the dyed cotton fabric, samples were cut after padding and again after fixation. They were immediately sealed in pre-weighed plastic bags and weighed before drying at 110°C for 90 minutes, cooling in a desiccator for 15 minutes and re-weighing (ASTM, 1991). The water content of padded fabric is given by equation 2-1, based on dried fabric (including dye, salts, and urea if used).

$$\%Water\,Content = \frac{M_w - M_d}{M_d} x100 \qquad (2\text{-}1)$$

Where:

%Water Content = Water content of the padded fabric (g water/100 g dried fabric)

M_w = Mass of wet padded fabric (including all water and chemicals) (g)

M_d = Mass of dried fabric (including chemicals) (g)

This is not a water content based on dry fiber alone but gives the amount of water per 100 g of cotton plus non-volatile solids. It is close to the water content per 100 g of dry cotton except when the dye solution contained urea. For example, using a dyebath solution containing 20 g/L of dye, 25 g/L NaCl, and 5 g/L NaOH, a water content of 70%, as determined above, would correspond to a true water content of 72.5% on a basis of dry cotton. This value increase to 78% if the dye solution also contains 100 g/L urea. This method avoided the time consuming extraction of cut samples necessary for the determination of the solution pick-up and gave an acceptable measure of the water content.

The water content after heating in the infrared oven was also determined by equation 2-1. The cut samples from the fabric after fixation were weighed, extracted in boiling water to remove unfixed dyes and salts, and then dried, cooled and reweighed. This gives a water content close to the value based on 100 g of dry cotton because the small amount of unextracted fixed dye is not very significant. In this case, the extraction technique was used because the same sample also served for measurement of the amount of unfixed dye which was removed from the cotton (section 2.5.2).

2.5.2 Determination of the dye fixation yield

The fixation yield of the reactive dye is the percentage of the dye originally present in the fabric which has reacted with the cellulose. In order to determine the dye fixation yield, the fabric samples were cut immediately after padding and after fixation in the dryer. Any unfixed dye on the samples was removed from these by two 5 min extraction with boiling water, the first containing a small amount of HCl to just neutralize the alkali in the fabric. The fixation yield was determined from the calculated quantities of unfixed dye per gram of dry fabric on the appropriately diluted aqueous extracts using spectrophotometric measurements.

A Diano Match Scan II spectrophotometer was used for measurement of the dye concentration in solution. This is an automatic double-beam reflection spectrophotometer with an integrating sphere, providing diffuse illumination and sample viewing at an angle of 6.5°. It can be used to measure percentage transmission (T%) of a dye solution at various wavelengths in the visible region from which absorbance values (A) can be calculated using Equation 2-2.

$$A = Log(\frac{100}{T\%}) = \varepsilon \times L \times C_d \qquad (2\text{-}2)$$

Where: A = Absorbance of the dye solution at a given wavelength

ε = Extinction coefficient of the dye solution at that wavelength $(g/L)^{-1}(cm)^{-1}$

L = Length of spectrophotometer cell (1.00 cm)

C_d = Concentration of the dye solution (g/L)

T% = Percentage transmission of the dye solution at the given wavelength

For each dye, a Beer-Lambert calibration graph of absorbance at the wavelength of maximum absorption (A) as a function of the dye solution concentration (C_d) was prepared. The dye solutions were prepared in phosphate buffer solution (QU and JAMSHIDI-BARZI, 1992). The extinction coefficient (ε) of the dye was obtained by linear regression of A on C_d according to equation 2-2. Figure 2.2 shows the Beer-Lambert calibration graphs and Table 2.2 gives the calculated extinction coefficients and the squares of the correlation coefficients (R^2).

The Beer-Lambert law (Equation 2-2) predicts a linear dependence of the absorbance of the solution on the concentration of the dye in solution provided that L and ε remain constant. The measurements were always performed using the same optical cell and the dye solutions were usually very dilute to avoid any deviations from Equation 2-2 resulting from dye aggregation. An unknown concentration of a dye can thus be obtained by measurement of the solution absorbance and subsequent calculation using the value of the slope found from the calibration.

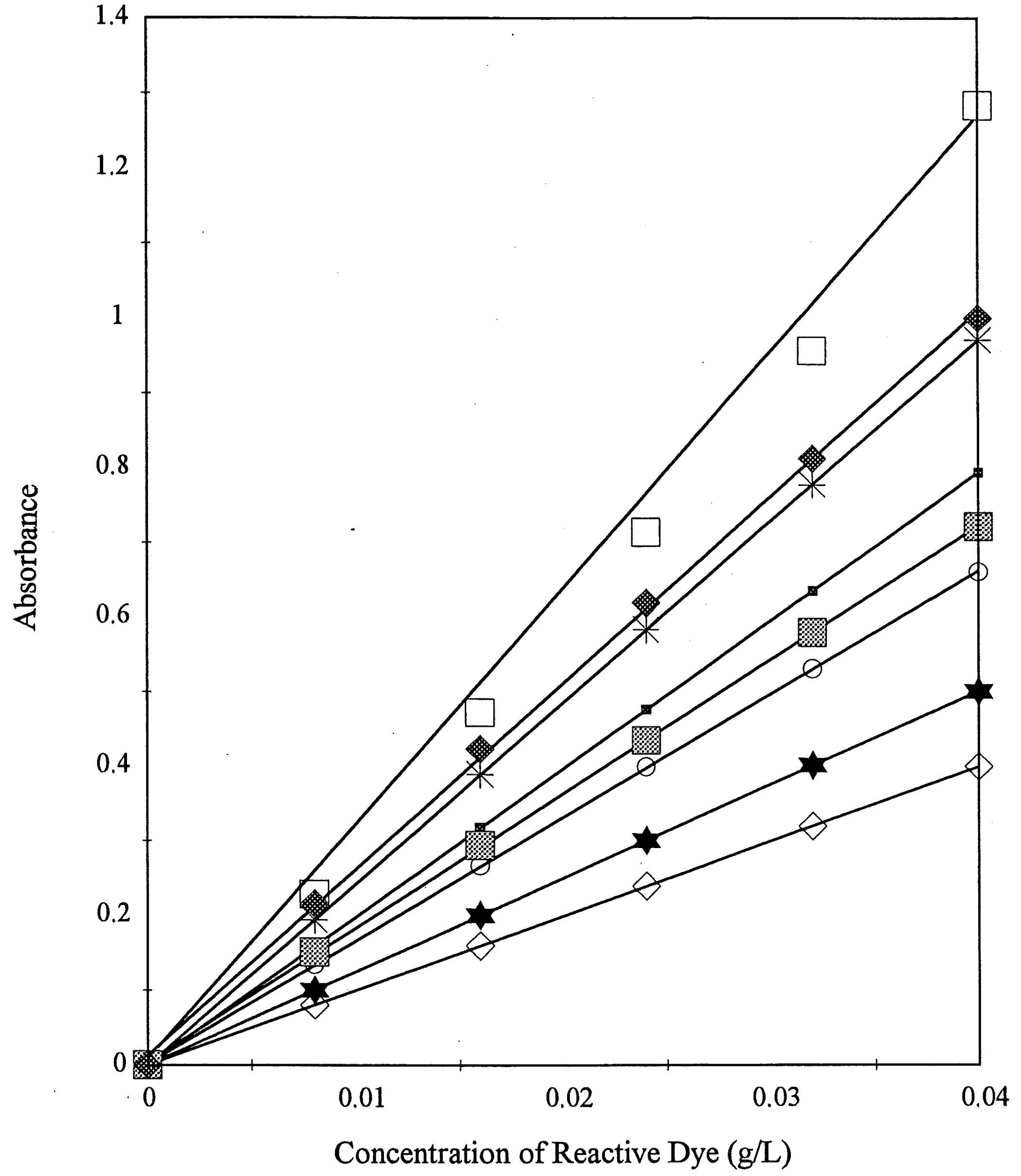


Figure 2.2 Beer-Lambert calibration curves of reactive dyes

TABLE 2.2 EXTINCTION COEFFICIENTS (ε) AND CORRELATION COEFFICIENTS (R^2)

Reactive dyes	λ_{max} (nm)	ε values ($(cm)^{-1}(g/L)^{-1}$)	R^2 values
Black B	600	24.29	1.0000
Red E-4B	520	16.47	0.9997
Navy K-2B	598	29.97	0.9964
Blue R	590	9.98	1.0000
Red X-6BN	518	19.84	1.0000
Blue F-R	610	12.52	0.9998
Yellow E-3R	390	18.03	0.9978
Turquoise MX-G	666	24.47	0.9969

The amount of dye in a fabric sample after padding is usually determined from the mass of solution retained by the fabric and the concentration of dye in it. This assumes that both components of the solution, the dye and the water, are absorbed in unchanged proportions, i.e., that there is no preferential absorption of either. This is often not the case when the dye has some substantivity for the fibre (BROADBENT et al., 1994b). The preferential absorption of the dye by the fibre gives more dye present in the fibre than calculated from the solution pick-up. For this reason, the following extraction method was used.

The dye in the fabric sample, cut immediately after padding, was quickly extracted with boiling water (100 mL) for 5 min in a beaker containing hydrochloric acid (2-3 drops of conc. HCl, to give a pH of 6-7), followed by a second extraction with boiling water in an another beaker. Hydrochloric acid neutralizes the alkali in the cotton and stops its reaction with the dye. An approximately neutral solution is necessary to prevent acid- or base-catalysed hydrolysis of the dye-fibre bond and thus removal of fixed dye from the fabric. After the two extractions, the fabric was dried at 110°C in a hot air oven for 90 minutes, cooled in a desiccator for 15 minutes and then weighed.

The extracts were diluted to a known volume (V_f) containing buffer solution (20 mL buffer solution composed of $Na_2HPO_4{\cdot}7H_2O$ (0.1 M) and KH_2PO_4 (0.1 M) per 100 mL dilute dye solution) for measurement of transmission using the spectrophotometer as recommended by Qu and Barzi (QU and JAMSHIDI-BARZI, 1992). The use of a buffer solution minimizes any problems of varying dye extinction coefficient arising from variations in the solution environment. The dye concentration in the diluted extraction solution (C_d) was determined from the known value of the extinction coefficient using Equation 2-2. The mass of the reactive dye extracted from the initial fabric sample ($M_{i,dye}$) was calculated from

$$M_{i,dye} = V_f \times C_d \qquad (2\text{-}3)$$

Therefore, the dye concentration of per unit mass of dried sample (D_i, g dye/100 g fabric) may be determined by:

$$D_i = \frac{M_{i,dye}}{M_{i,fabric}} \times 100 \qquad (2\text{-}4)$$

where $M_{i,fabric}$ is mass of the dried sample after extraction

The same procedure was used to determine the amount of unfixed dye remaining in the fabric after thermal fixation in the infrared oven (D_u, g dye/100 g fabric), as shown by:

$$D_u = \frac{M_{u,dye}}{M_{f,fabric}} \times 100 \qquad (2\text{-}5)$$

where $M_{f,fabric}$ is mass of the dried sample including all fixed dyes after extraction, given by:

$$M_{f,fabric} = M_{i,fabric} + (M_{i,dye} - M_{u,dye}) \qquad (2\text{-}6)$$

Usually, the weight of the cotton sample ($M_{i,fabric}$) was about 3 g. The amount of dye on 3 g of fabric is about 0.042 g (1.4% x 3). Therefore, $M_{i,fabric} >> (M_{i,dye} - M_{u,dye})$, and $M_{f,fabric}$ is approximately equal to $M_{i,fabric}$. Hence, the fixation yield (F1) of the reactive dye may be determined by:

$$F_1 = \frac{D_i - D_u}{D_i} \qquad (2\text{-}7)$$

2.5.3 Correction of the dye fixation yield

In the short time between padding, cutting of the sample, and its extraction (within 10 s), a small proportion of the dye invariably reacted with the cotton and all the initially absorbed dye in the fabric could not always be removed immediately after padding. The extracted cotton was thus weakly coloured rather than being white. What is the influence on D_i of this initially fixed dye? The measured value of D_i would be too low, so that the fixation yield would also be too low. Fixation yields were therefore corrected by a method based on measurement of the reflectance spectra and calculation of the Kubelka-Munk K/S values of the extracted and dried initial and final fabric samples.

The corrections always increased the fixation yield but usually by less than 3% depending on the reactivity of the dye. The fixation yields were corrected using a method based on a simplified form of the Kubelka-Munk equation 2-8.

$$K/S = \frac{(1 - R_\infty)^2}{2R_\infty} \qquad (2\text{-}8)$$

where R_∞ is the reflectance of light of a given wavelength by a sample of infinite thickness, expressed in fractional form (MCDONALD, 1987), K is the Kubelka-Munk absorption coefficient of dyed fabric, and S the Kubelka-Munk scattering coefficient of dyed fabric.

K/S values were determined at the wavelength of minimum reflectance using the Match Scan II spectrophotometer for the fabric samples extracted both immediately after padding and after fixation, and the corresponding K/S value of the original white fabric was subtracted from these.

Because the amount of dye on the fabric was fairly low, a linear relationship between the K/S value and dye concentration on the cotton fabric was assumed. The appropriate equations for extracted samples obtained after padding and after fixation are:

$$(K/S)_i = k \times D^* \qquad (2\text{-}9)$$

$$(K/S)_f = k \times [(D_i - D_u) + D^*] \qquad (2\text{-}10)$$

where D* is the amount of dye remaining in a dried sample of fabric (g /100 g fabric) which had reacted before it could be extracted from the initial sample. Ideally this should be zero. $(K/S)_i$ and $(K/S)_f$ are the K/S values of the extracted samples obtained after padding and after fixation, respectively, and k is a proportionality constant.

Figure 2.3 illustrates the various amounts of dye in the fabric samples and the extraction solutions.

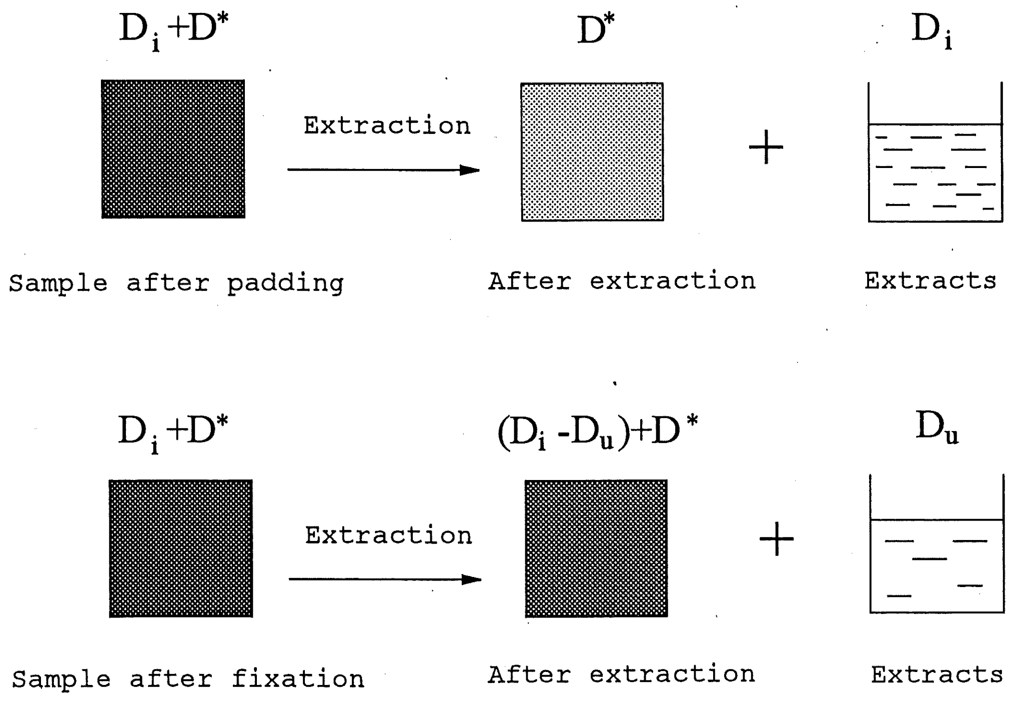


Figure 2.3 Scheme illustrating the distribution of dye in the fabric and solution after extraction

Division of equation 2-9 into 2-10 gives

$$\frac{(K/S)_f}{(K/S)_i} = \frac{(D_i + D^*) - D_u}{D^*} = 1 + \frac{D_i - D_u}{D^*} = 1 + \frac{1}{\alpha} \qquad \text{(2-11)}$$

Where:

$$\alpha = \frac{D^*}{D_i - D_u} = \frac{(K/S)_i}{(K/S)_f - (K/S)_i} \qquad \text{(2-12)}$$

Therefore,

$$D^* = \alpha(D_i - D_u) = \frac{(D_i - D_u) \times (K/S)_i}{(K/S) - (K/S)_i} \qquad \text{(2-13)}$$

The corrected fixation yield (F_2) of the reactive dye on cotton is given by equation 2-14.

$$F_2 = \frac{(D_i - D_u) + D^*}{D_i + D^*} = \frac{(1 + \alpha)F_1}{1 + \alpha F_1} \qquad \text{(2-14)}$$

where F_1 is the uncorrected fractional fixation yield (equation 2-7). In all cases, the correction was small, rarely exceeding +3%. This is new technique for correction of the fixation yields.

The influence of the value of α on the correction of the fixation yield (F_2 - F_1), was greater for the lower values of the fixation yield. The value of α was always greater for dyes of high reactivity and for the more strongly alkaline dye solutions, which activated the cotton more strongly. In most cases, values of α were in the range of 0 to 0.3. The value of (F_2 - F_1)% can be obtained from Equation (2-14) and given by:

$$(F_2 - F_1)\% = \frac{\alpha F_1(1 - F_1)}{1 + \alpha F_1} \times 100 \qquad \text{(2-15)}$$

Figure 2.4 shows the dependence of (F_2 - F_1)% on α according to equation 2-15.

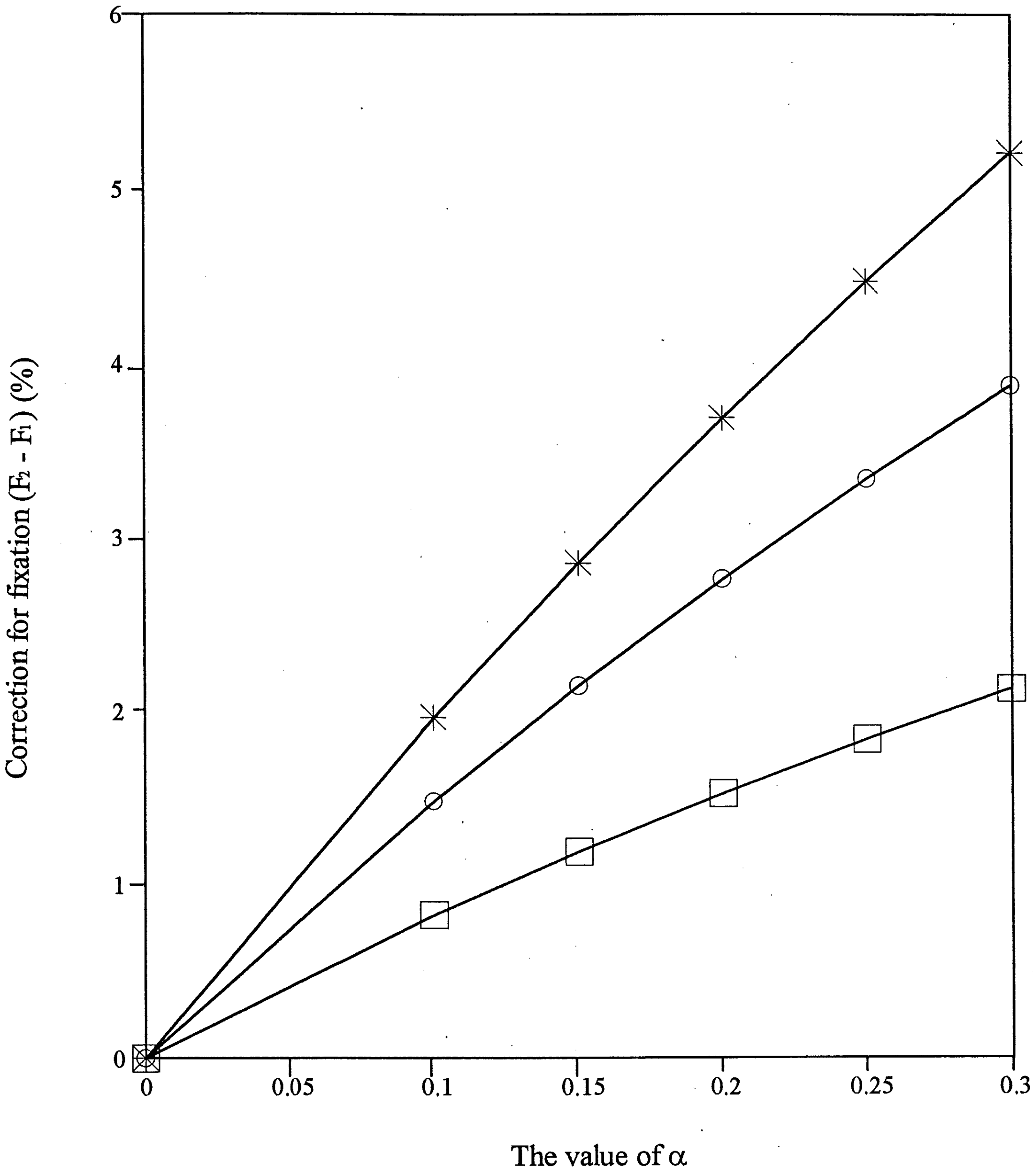


Figure 2.4 Influence of α value on correction for fixation yield

3. INFLUENCE OF PROCESS VARIABLES ON DYE FIXATION

3.1 Initial objectives

The first objective of the research was to study the influence of the process variables for the fixation of reactive dyes on cotton using infrared heating in a pad-thermofixation process. Hamoudi's work (HAMOUDI, 1990) had indicated that the two most important variables were the fabric speed through the infrared dryer, which determines the residence time, and the infrared emitter power. In addition, the following variables were also considered in this study:

1) The reactivity of the reactive dye towards cotton.

2) The type and concentration of alkali used in the dye solution. This would alter the degree of activation of the cellulose.

3) The concentration of sodium chloride and urea added to the dye solution. Addition of salt increases the substantivity of the dye for the cotton thus increasing the possibility of reaction with the fiber. Urea promotes dye solubility, decreases the rate of drying and has been claimed to provide a medium for dye diffusion once drying is complete (BIRD, 1975).

4) The use of vacuum extraction of the wet fabric after padding with the dye solution. This technique has been shown to increase the degree of fixation of the dye remaining in the fabric after extraction (FORTIN et al., 1988).

The trials described in this section also served to provide experience in the use of the equipment, to test the analytical procedures, and to confirm and extend the results of Safia Hamoudi (HAMOUDI, 1990). The objective was to examine reactive dyes of varying reactivity and the influence of each process variable on the fixation of the dye on cotton fabric, which was padded with alkaline dye solution, dried and heated in the infrared oven. These variables were the fabric speed through the infrared oven, the emitter power, the nature and concentration of the alkali, the concentration of salt and urea in the dyebath, and the amount of dye solution retained by the fabric. The latter was either that obtained after padding or the much lower level remaining after vacuum extraction of the wet fabric.

3.2 Results and discussion

3.2.1 Influence of emitter power and fabric speed on fixation

The power supplied to the quartz tube emitters and the fabric speed through the oven were the first variables examined based on the results of Hamoudi (HAMOUDI, 1990). The results are given in Table 3.1. The dye fixation yield increased with increasing emitter power and residence time, but there are critical limits for these to avoid burn marks on the fabric. The emitter power and fabric speed should therefore be controlled properly, so that the maximum fixation yield can be obtained without thermal damage to the cotton. All the trials described in this chapter were carried out using the medium-wave quartz tube sources.

The results in Table 3.1 show that a dye of high reactivity, such as Black B, gives higher fixation yields at lower temperatures than a dye of lesser reactivity, such as Red X-6BN. For dyes of low reactivity, the highest fixation yield of the dye can only be obtained by heating the fabric to the highest final temperature around 140°C. In fact, the more reactive Black B is almost completely fixed on the fabric before the end of the constant drying rate period (temperature 42-45°C). Table 3.1 also shows the importance of longer residence in the oven, or lower fabric speed, for Red E-4B and Red X-6BN, respectively. Note from Table 3.1 that the fixation yield for Red X-6BN increases from 78 to 82 to 84% as the power supplied to the sources was decreased but offset by an increased residence time in the oven. The highest yield was obtained at lower power and fabric speed even though the final fabric temperature was lower than in the other cases. Thus, in the case of a dye of low reactivity, the residence time may be the more important variable influencing the fixation yield. The difference in residence times between Red E-4B and Red X-6BN are only about 5 and 2 s, respectively, clearly illustrating the sensitivity of the fixation yield to this variable.

3.2.2 Influence of the nature and concentration of alkali on dye fixation

Table 3.2 shows the influence of the nature of the alkali in the dyebath and its concentration on the dye fixation yield. All samples were heated to the maximum permissible fabric temperature (about 140°C) without fabric burning.

TABLE 3.1 INFLUENCE OF EMITTER POWER AND FABRIC SPEED ON FIXATION

Reactive dye	Initial water content (%)	Fabric speed (m/min)	Emitter power (kW)	Fabric temp. (°C)	Water content after drying (%)	Fixation yield (%)
Remazol Black B	70	2.5	10.01	43	10.6	80
	70	2.5	13.12	72	2.5	95
	69	3.5	10.01	42	26.9	68
	69	3.5	13.12	45	10.17	90
Levafix Red E-4B	69	2.2	13.12	132	1.97	78
	69	2.25	13.12	125	2.08	76
	69	2.3	13.12	109	2.13	74
	69	2.4	13.12	96	2.13	70
	69	2.5	13.12	82	2.55	67
Drimarene Red X-6BN	60	2.9	10.01	124	2.4	84
	60	3.0	10.01	118	2.5	77
	60	3.15	10.01	113	2.8	71
	65	3.1	13.12	136	1.0	82
	65	4.2	16.18	136	1.0	78
	64	5.9	10.01	45	15.3	26
	64	5.9	13.12	51	8.1	35
	64	5.9	16.18	109	3.7	61

Fabric density: 246g/m^2 for Black B and Red E-4B, and 164 g/m^2 for Red X-6BN

NaOH concentration: 5 g/L, Salt concentration: 25 g/L

TABLE 3.2 INFLUENCE OF NATURE AND CONCENTRATION OF ALKALI ON FIXATION YIELD

Reactive dye	Nature of alkali	Concentration of alkali (g/L)	Fixation yield (%)
Remazol Black B	NaOH	2	71*
		5	95*
	Na_2CO_3	5	71
		10	85
Levafix Red E-4B	NaOH	5	80*
	Na_2CO_3	10	75*
Remazol Blue R	NaOH	0.5	30
		5	74
Drimarene Navy K-2B	NaOH	2	90
		5	89
	Na_2CO_3	5	87
		10	88
Drimarene Red X-6BN	NaOH	5	82
	Na_2CO_3	5	57
Basilen Yellow E-3R	Na_2CO_3	5	48
		10	52
Procion Turquoise MX-G	NaOH	2	40
		5	39

Fabric density: 164 g/m^2, emitter power: 13.12 kW, Fabric speed: 3.3 m/min

* Fabric density: 246 g/m^2, emitter power: 13.12 kW, Fabric speed: 2.5 m/min

Salt concentration for all dye solutions: 25 g/L

It is clear from Table 3.2 that usually the stronger the alkali, and the higher its concentration, the higher the reactivity of the cellulose towards dye. Although the use of a stronger alkali such as NaOH, at higher concentration, would increase the rate of dye hydrolysis, the effect on the rate of fixation is even more pronounced. The optimum conditions will also depend upon the reactivity of the dye and other factors such as its substantivity for the cotton. For four of the seven dyes, the best fixation was obtained using an NaOH concentration of 5 g/L, which produces a considerably higher pH than usually recommended. At NaOH concentrations of 5 g/L, any premature hydrolysis of the dye's reactive group could be avoided by mixing the alkali, from a metering pump, with the dye solution as they enter the pad bath. Alternatively, a two pad system could be used to separate the dye and alkali solution.

Only two dyes gave fixation yields below 80%. The dichlorotriazine reactive dye, Procion Turquoise MX-G, would be the most rapidly hydrolyzed in the presence of alkali, which may explain the low fixation yield obtained. The dye was not, however, a new sample and there is a real possibility that some hydrolysis had occurred on storage. The recommended shelf life is 6-12 months but the sample used was at least 2-3 years old. It is also possible that such a highly reactive dye would undergo rapid hydrolytic deactivation on heating in the fabric in NaOH solutions with concentrations of 2 and 5 g/L. No further tests were conducted with this dye. The reasons for the low fixation yields of Yellow E-3R are not clear. In the presence of urea, the fixation yield was 83% (Table 3.4). Again, it is possible that 5 g/L NaOH does not provide the optimum pH for fixation of this dye. Vinyl sulphone reactive dyes such as Black B and Blue R may be less sensitive to deactivation by alkali in a pad-heat system. Although they will undergo hydrolysis to the β-hydroxyethyl sulphone, this can re-eliminate hydroxide ion to give back the reactive vinyl sulphone under hot alkaline conditions. The problem of dye hydrolysis will be discussed in a later section. These initial results indicated that, for dyes of medium and low reactivity, high fixation yields are possible provided that the reaction conditions promote maximum fiber and dye activation, i.e., high temperatures and high NaOH concentrations.

3.2.3 Influence of salt and urea on fixation

Addition of salt to the pad solution would be expected to increase the proportion of dye absorbed by the fabric, since salt increases the substantivity of the dye for the cotton. Apart from the Yellow E-3R, there were no particularly significant influences of salt concentration on the dye fixation yields. The effect of increasing the salt concentration was far less than that for the alkali. It is known that the effect of salt concentration on the fixation yield decreases as dyeing is carried out at lower and lower liquor ratios (WOLFF and HENK, 1990). The results of the trials are shown in Table 3.3. As before, all samples were heated to the maximum fabric temperature of about 140°C. The low fixation yields for Blue F-R and Yellow E-3R may be a consequence of too high a bath pH (See Red F-R in Table 3.8) and a low fabric temperature. The final temperature for Blue R was only about 109°C.

The results of the trials showing the influence of urea concentration on fixation yields are presented in Table 3.4. All samples were dried to the maximum fabric temperature (about 140°C) without fabric burning. In general, the addition of urea to the pad solution at a concentration of 100 g/L is often claimed to give a significant increase of the fixation yield, particularly for low or medium reactivity dyes such as Levafix Red E-4B, Drimarene Red X-6BN and Basilen Yellow E-3R. This was, in fact, observed. Urea promotes dye solubility, retards water removal during drying, acts as a fiber swelling agent and is believed to combine with water to provide a diffusion medium in the dried fabric. The achieved effect, however, depended upon which dye was used, in agreement with recent German work (HERLINGER et al., 1990). The vinylsulphone reactive dyes, which react with cellulose by nucleophilic addition, also react with urea, so that the dye has less reactive capability, as shown below. This type of reaction would explain the decreased fixation yields for the dye Black B in the presence of urea.

$$Dye - SO_2CH = CH_2 + NH_2 - CO - NH_2 \rightarrow Dye - SO_2CH_2CH_2NHCONH_2$$

Figure 3.1 also shows the influence of addition of urea on the fixation yield at the different fabric speeds for Red E-4B.

TABLE 3.3 INFLUENCE OF SALT CONCENTRATION ON FIXATION YIELD

Reactive dye	Salt conc. (g/L)	NaOH conc. (g/L)	Fixation yield (%)
Drimarene	10	0.5	62
Red X-6BN		5	81
	40	0.5	64
		5	87
Remazol	10	5	61*
Blue R	40	5	58*
Levafix	10	5	77
Red E-4B	40	5	76
Cibacron	10	5	53
Blue F-R	40	5	52
Basilen	10	5	49
Yellow E-3R	25	5	56
	40	5	64

Fabric density: 164 g/m^2, emitter power: 13.12 kW , * fabric temperature only 109°C

Fabric speed was usually 3.3 m/min for fabric density of 164 g/m^2

TABLE 3.4 INFLUENCE OF UREA ON FIXATION

Reactive dye	Nature of alkali	Conc. of alkali (g/L)	Fixation yield (%)	
			No urea	With urea
Remazol Black B	NaOH	5	95*	90
	Na_2CO_3	5	71	50
		10	85	80
Levafix Red E-4B	NaOH	5	80*	89*
	Na_2CO_3	10	75*	94*
Drimarene Navy K-2B	Na_2CO_3	10	88	93
Drimarene Red X-6BN	NaOH	5	82	92
	Na_2CO_3	5	57	63
Basilen Yellow E-3R	NaOH	5	56	83
	Na_2CO_3	10	52	70

No urea:

Fabric density: 164 g/m^2, emitter power: 13.12 kW, Fabric speed: 3.3 m/min

* Fabric density: 246 g/m^2, emitter power: 13.12 kW, Fabric speed: 2.5 m/min

With urea:

Fabric density: 164 g/m^2, emitter power: 13.12 kW, Fabric speed: 3.0 m/min

* Fabric density: 246 g/m^2, emitter power: 13.12 kW, Fabric speed: 2.2 m/min

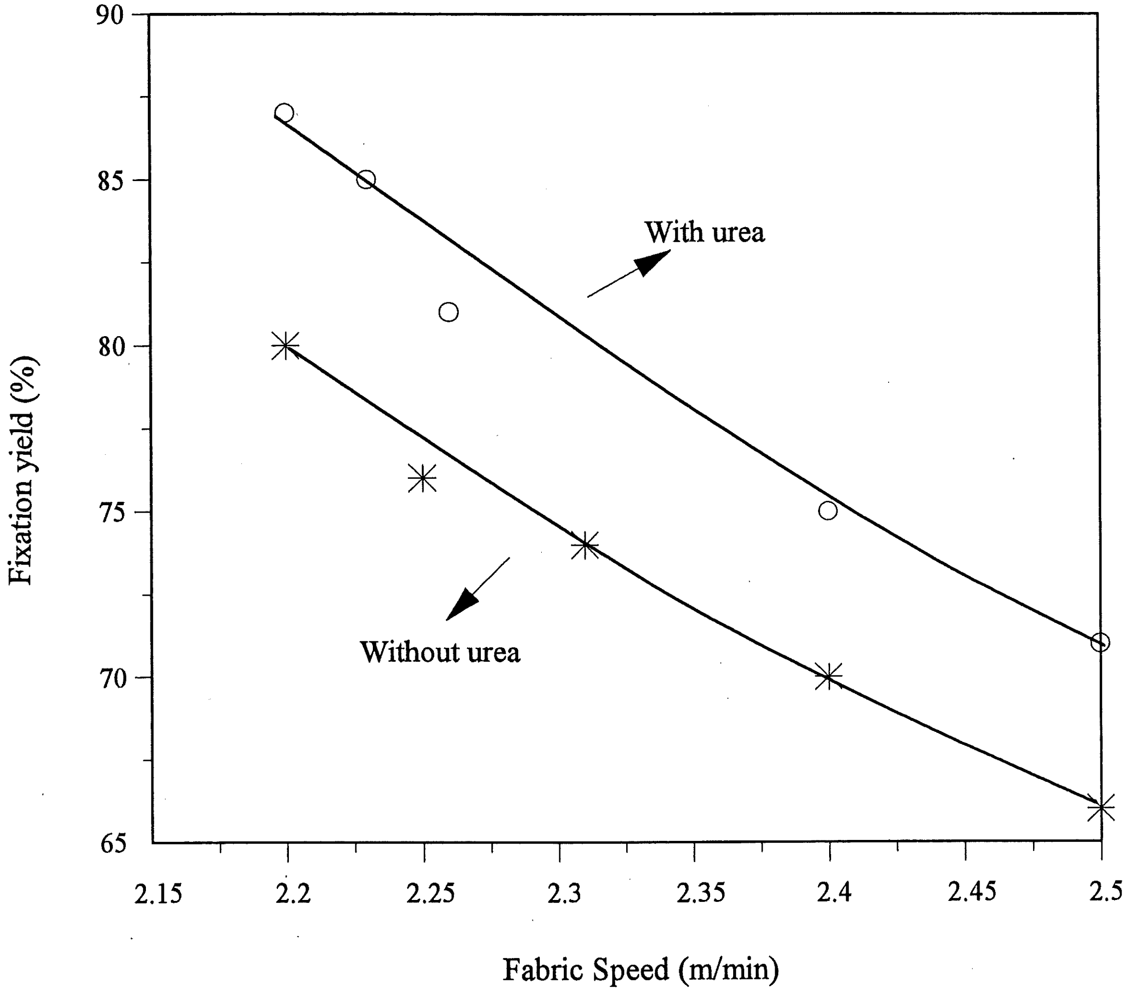


Figure 3.1 Influence of urea on fixation yield for Red E-4B

Emitter power: 13 kW, fabric density: 246 g/m^2

NaOH concentration: 5 g/L, salt concentration: 25 g/L

3.2.4 Influence of vacuum extraction on fixation

The dye in solution on the fiber surface is much more likely to undergo hydrolysis unless it can diffuse rapidly into the cotton fiber. Since vacuum extraction removes the bulk of the unbound liquid on the fiber surface, it should increase the fixation yield of the dye remaining in the fabric (FORTIN et al., 1988). Migration of unfixed dyes and chemicals during the initial phase of drying is suppressed by vacuum extraction after padding so that poor washing and rubbing fastness, may be avoided, particularly for deep shades. Since the water content of the fabric is lower after vacuum extraction, the color of the dyed fabric is paler, so the dye concentration in the pad bath was increased from 20 to 30 g/L.

Some trials showing the effects of vacuum extraction after padding on dye fixation were carried out. This was done for dye solutions without added urea. The water content of the fabric after padding alone was about 65%, dropping to around 35% after vacuum extraction. The fixation yields obtained by infrared heating for Red E-4B and Navy K-2B were already quite high and the improvement obtained by application of vacuum was only marginal, as shown in Table 3.5. In these cases, the fabric was heated to about the same final temperature of about 135-140°C. The lower fixation yield of the dye Red E-4B was substantially increased by the use of vacuum extraction prior to fixation, particularly for the dye solution containing Na_2CO_3. Table 3.5 agrees with previous results (FORTIN et al., 1988).

For dyes of lower reactivity, the degree of fixation could be increased by vacuum extraction after padding provided the fabric was strongly heated. The dye fixation yields were significantly improved by application of vacuum, when using the same power and fabric speed as for fabric which had been padded but not vacuum extracted, as shown in Table 3.6. The water content after vacuum was significantly reduced so the wet fabric was dried and heated to 135-140°C more rapidly than when vacuum was not used.

3.2.5 Comparison of infrared fixation with other methods

In the textile industry, reactive dyes are applied to cotton fabrics by pad-batch, pad-dry, pad-dry-cure and pad-steam processes. Dyeings obtained by infrared fixation were compared with those from pad-batch and simulated pad-dry and pad-steam processes. The results of the trials are shown in Table 3.7. Infrared fixation is a very fast heat transfer process due to its high surface power density. Infrared fixation gave a higher fixation yield than hot air or cold fixation, particular for the less reactive dyes, such as Drimarene Red X-6BN. Hot air and cold fixation were carried out, however, on fabric padded with alkaline dye solution in preparation for infrared fixation (mainly 5 g/L NaOH) and not by the recommended procedure of the dye manufacturers. In general, use of the recommended weaker alkalis such as sodium carbonate gave lower fixation yields.

The most widespread use of infrared in textiles is in pre-drying fabrics to minimize migration and eliminate pick-off of chemicals onto hot cylinder surfaces. Migration occurs during the constant rate period in drying process because the liquid, moving to the yarn surface where evaporation takes place, carries the dissolved solids with it. When the liquid evaporates, it leaves the solids behind. Thus, the concentrations of dyes or chemicals are much greater at the yarn surface than inside. Once the constant rate period terminates, migration will stop and the water content of the dyed fabric is normally about 15% (see Figure 6.3). With infrared, evaporation takes place both at and below the yarn surface, and there is a smaller temperature gradient between the interior and the surface because of the penetration of some wavelengths of the radiation. Migration is thus suppressed and less solids are transported right to the yarn surface. Since dye which migrates to the yarn surface is less likely to react with the cotton, the fixation yield should be improved by application of infrared predrying. Based on the above reason, hot air fixation with infrared predrying in which the water content reach 13.9% can increase the fixation yield to about 74% , as shown in Figure 3.2, whereas the hot air fixation without infrared predrying only give a about 45% fixation yield (Figure 3.3) because of high migration. The results of Figure 3.4 shows the influence of fixation methods on fixation for Red X-6BN.

Heating a padded sample in a sealed plastic bag, a process analogous to steam fixation in industry, gave a higher fixation than when drying and heating using hot air. Steaming allows better dye penetration into the initially wet fibers. More detailed migration principles and experimental results on the comparison of infrared fixation with cold batch and hot air fixation will be presented in Chapters 5 and 6.

TABLE 3.5 INFLUENCE OF VACUUM EXTRACTION ON FIXATION

Reactive dye	Nature of alkali	Conc. of alkali (g/L)	Fixation yield (%)	
			No vacuum	With vacuum
Levafix Red E-4B	NaOH	5	84	90
	Na_2CO_3	10	67	94
Drimarene Navy K-2B	Na_2CO_3	10	88	91

Fabric density: 164 g/m^2, emitter power: 13.12 kW, Fabric speed: 5.1 m/min, dye solution 30 g/L with vacuum

*The fixation yield (84%) for Red E-4B is different from that in TABLE 3.2 because of different fabric density.

TABLE 3.6 INFLUENCE OF VACUUM EXTRACTION ON FIXATION FOR RED X-6BN

Fabric speed (m/min)	Emitter power (kW)	Fabric temperature (°C)		Fixation yield (%)	
		No vacuum	With vacuum	No vacuum	With vacuum
3.8	10.6	48	137	13	84
3.8	7.8	40	69	8	27
4.6	10.6	46	103	9	46
4.6	7.8	40	53	5	14

* NaOH concentration: 5 g/L, NaCl concentration: 10 g/L, Vacuum level: 54 kPa

TABLE 3.7 INFLUENCE OF FIXATION METHOD ON FIXATION

Reactive dye	Nature of alkali	Conc. of alkali (g/L)	Fixation yield (%)		
			IR fixation	Hot fixation	Cold fixation
Remazol Black B	NaOH	5	95*	93*	95*
Levafix Red E-4B	NaOH	5	80*	70*	73*
Drimarene Navy K-2B**	Na_2CO_3	10	93	89	92
Remazol Blue R	NaOH	5	74	40	-----
Drimarene Red X-6BN	NaOH	5	82	63	60
Baselin Yellow E-3R	NaOH	5	56	30	70
Cibacron Blue F-R	NaOH	5	53	48	59

Fabric density: 164 g/m^2, emitter power: 13.12 kW, Fabric speed: 3.1 m/min

* Fabric density: 246 g/m^2, emitter power: 13.12 kW, Fabric speed: 2.5 m/min

Salt concentration: 25 g/L, ** Dye solution include urea 100 g/L

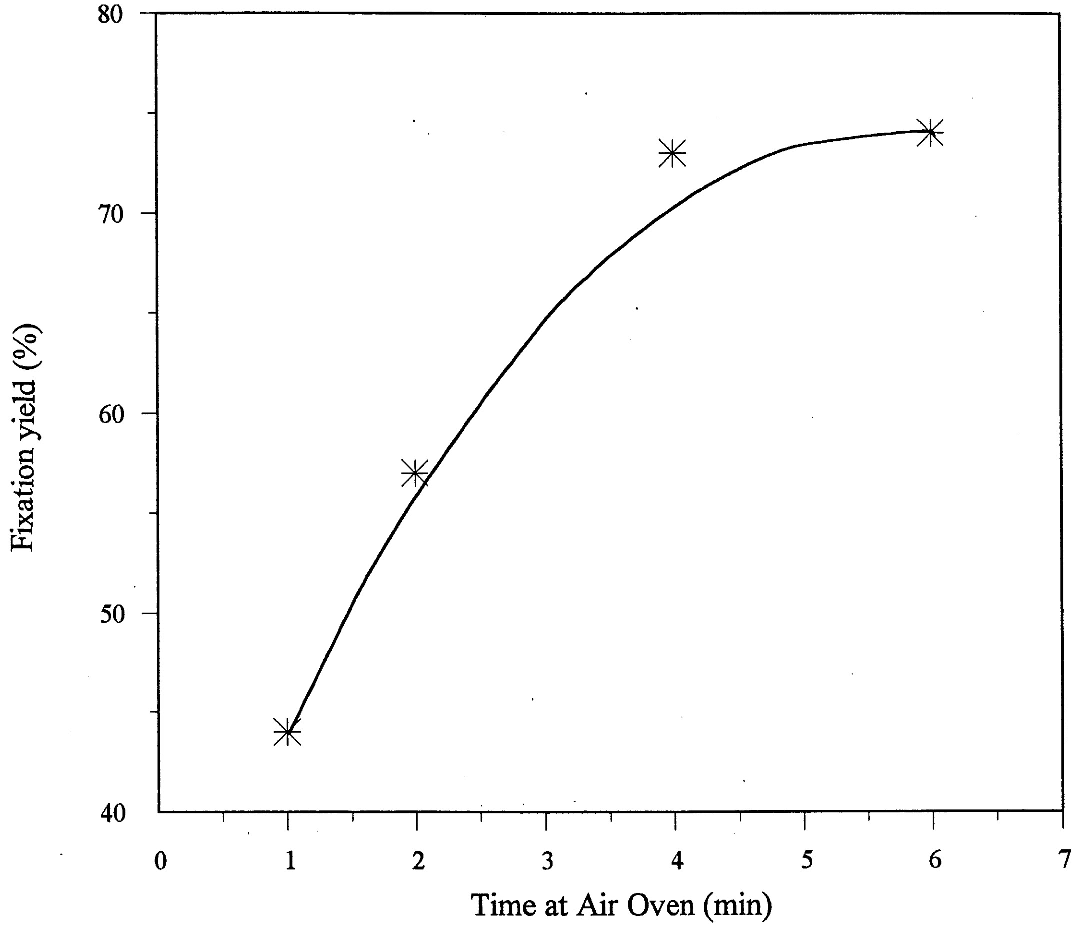


Figure 3.2 Influence of time in oven on fixation for Red X-6BN

IR preheating at 60°C by three passes at a fabric speed of 1.5 m/min until the water content was reduced to 13.9%, fixation temperature at air oven: 140°C, fabric density: 164 g/m²

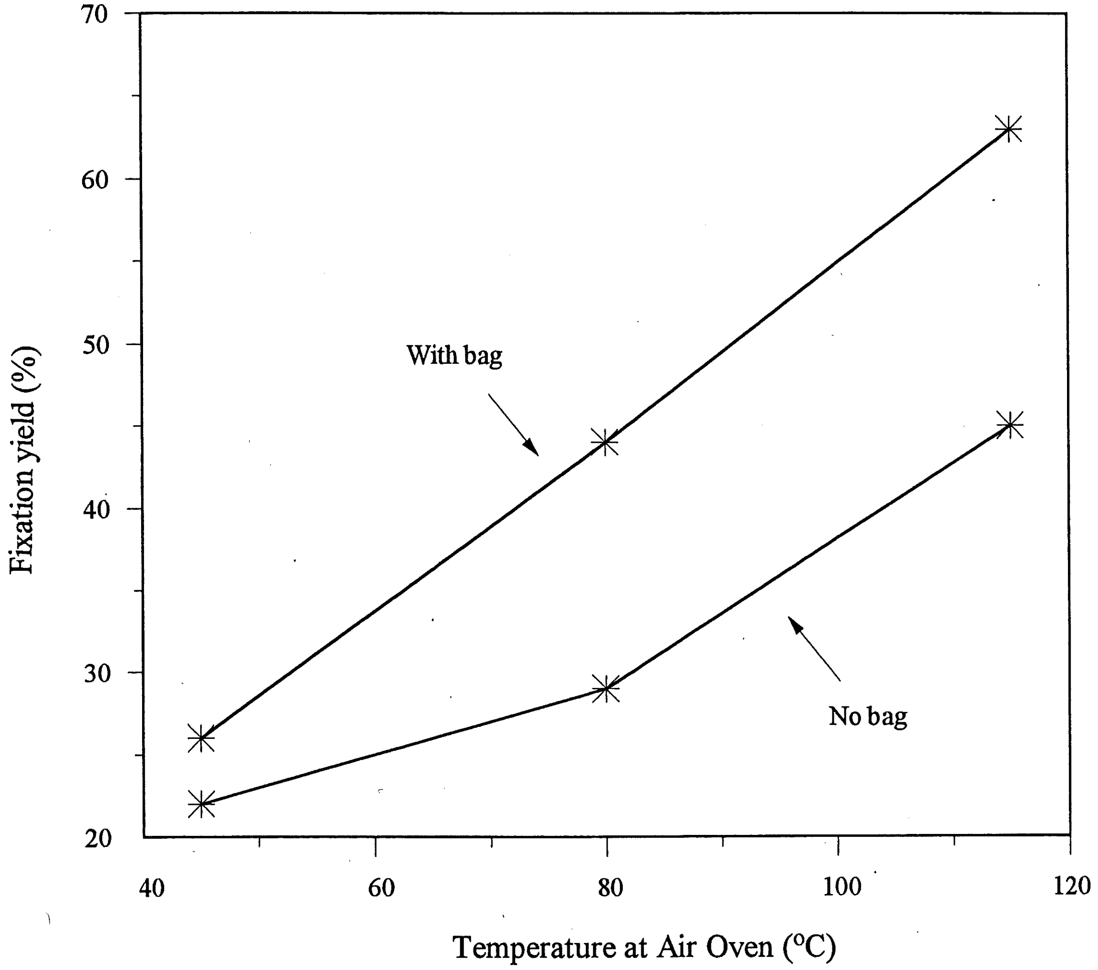


Figure 3.3 Influence of temperature in hot air oven on fixation for Red X-6BN

Fabric density: 164 g/m², NaOH concentration: 5 g/L, salt concentration: 25 g/L, all samples were heated at hot air oven for 10 minutes

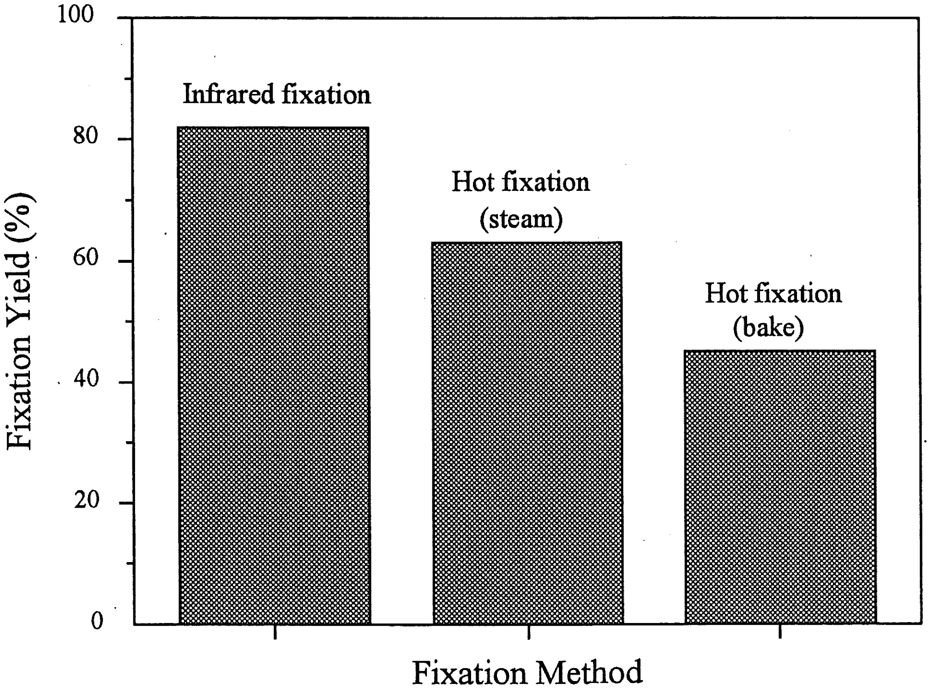


Figure 3.4 Influence of fixation methods on fixation for Red X-6BN

Fabric density: 164 g/m^2

#1 Method: infrared emitter power: 13 kW, fabric speed: 3.1 m/min

#2 Method: hot air temp.: 115°C, heating time: 10 min in a sealed plastic bag

#3 Method: hot air temp.: 115°C, heating time: 10 min dried without a bag

3.3 Conclusions and postscript

This preliminary work provided useful information on the influence of the various operational parameters on the fixation of the dyes. In general, the results showed, as expected, that the higher the reactivity of the dye, the higher the fixation yield. The latter increased significantly with decrease in fabric speed and increase in emitter power, within the limits of fabric temperature required to avoid thermal damage to the cotton. The fixation yield was quite sensitive to changes in these two variables.

The fixation yields of some dyes were quite sensitive to the type and concentration of the alkali used for the fixation reaction. The weaker alkali Na_2CO_3 was suitable for fixation of high reactivity dyes, but for dyes of low reactivity, the stronger NaOH was necessary to achieve high fixation. Despite the fact that the alkali type and concentration were not optimized, it was possible to obtain fixation yields over 85% for most dyes, and in some cases over 90%. The effects of alkali have been confirmed recently in this laboratory (SANDIE and BROADBENT, 1996). Their results are in line with those presented in this chapter, but show the importance of optimization of the alkali in the dyebath. Table 3.8 shows the effect of alkali on the fixation yields for various reactive dyes using infrared heating up to a fabric temperature of 140°C. In these trials there was no added salt in the dye solution (SANDIE and BROADBENT, 1996).

The effect of increasing the salt concentration in the pad solution was not very significant in agreement with the generalization that salt is much less effective at low liquor to goods ratios (WOLFF and HENK, 1990). Addition of urea to the dye solution had variable effects on the fixation yields obtained using infrared heating. It was effective in increasing the yields of some dyes of lower reactivity.

The fixation yield of the reactive dye to cotton can be improved to a certain extent by vacuum extraction, but the effect was not significant for some reactive dyes studied when the final fabric temperatures were the same. Vacuum extraction significantly improves the performance of the operation because the fabric can be dried much more quickly.

TABLE 3.8 THE EFFECT OF ALKALI ON FIXATION YIELD (SANDIE AND BROADBENT, 1996)

Reactive dye	Dye type	Alkali	Fixation yield %
Red X-6BN	MCT	5 g/L NaOH	82
Cibacron Red F-B	MFT	5 g/L NaOH	33
		2 g/L NaOH	53
		12 g/L Na_2CO_3	63
		6 g/L $NaHCO_3$ 1 g/L NaOH	78
Cibacron Red C-R	MCT-VS	5 g/L NaOH	63
		20 g/L Na_2CO_3	85
Remazol Brilliant Red 3BS	VS	5 g/L NaOH	84
		20 g/L Na_2CO_3	84

These early trials also allowed verification of the validity and reliability of the analytical techniques used. A comparison of the fixation yields in Tables 3.1, 3.2 and 3.5, for dyeing carried out with the dyes Black B, Red E-4B and Navy K-2B, under identical conditions for each dye, showed differences in the dye fixation yields mainly ranging from 2-4%. A new method for determining the amount of dye present initially in a sample of padded fabric was developed with a correction for the small amount which could not be extracted because it had reacted. Considering the numerous uncontrolled variables in this type of textile processing, and all the possible irregularities in the determination of dye concentrations by absorption spectrophotometry (QU and JAMSHIDI-BARZI, 1992), the reproducibility of the fixation yields for a number of dyes was encouraging.

In infrared fixation, the most important parameters influencing the fixation yield were the reactivity of the dye, the fabric speed through the oven, the emitter power and the concentration and nature of the alkali. In Chapter 4, a quantitative examination of the effects of the process variables in infrared fixation using a factorial plan will be presented. The key conclusion from this preliminary study was that infrared fixation can give remarkably high fixation yields, even for dyes of low inherent reactivity towards the cotton. The yields obtained were higher than those obtained by conventional thermofixation using hot air. The more detailed study of this effect will be discussed in Chapter 6. The results clearly showed the potential for developing a pad-thermofixation dyeing process for cotton with reactive dyes, using infrared heating, that would allow high fixation yields without salt additions to the dyebath, and possibly without addition of high concentrations of urea. Such a process would reduce the color of effluent from the post-dyeing washing process and its overall pollution load.

4. FACTORIAL ANALYSIS OF PROCESS VARIABLES FOR INFRARED FIXATION OF REACTIVE DYES TO COTTON

4.1 Introduction

In Chapter 3, we described some preliminary results of the application of various reactive dyes to cotton fabric by means of impregnation with an alkaline dye solution (padding) followed by infrared drying and heating. Even though the process was not optimized, the dye fixation yields obtained were very encouraging and were higher than when the impregnated fabric was dried in a hot air unit (See Table 3.7). In addition, we established that the best fixation yields required rather forceful conditions, i.e., high dyebath pH, and drying and heating the fabric to temperatures around 140°C, using longer residence times in the dryer and higher emitter power settings.

This section analyses, in a systematic manner, the dependence of the dye fixation yield, and also of the final sheet temperature and water content, on fixation conditions and the controllable process variables. This was achieved using two factorial plans of experiments and statistical analysis of the results. The dye selected for study, Drimarene Red X-6BN was of low reactivity and would not usually be recommended for application in such a pad/heat process (FOX AND SUMNER, 1986). As initially hoped, the low reactivity of this dye gave a large variation in the fixation yield for the selected changes in the controllable process variables. The objective was to determine the optimum conditions for application of this dye to cotton using infrared heating of the cotton fabric impregnated with the alkaline dye solution.

4.2 Experimental

4.2.1 Materials and equipment

The equipment used for the padding and infrared fixation process is shown in Figure 2.1 and is fully described in Chapter 2. The trials in this experiment were carried out using the medium-wave quartz tube sources. A bleached cotton fabric (plain weave, superficial density = 164 g/m^2) was used for all the trials. The dyebath for padding contained the reactive dye (Drimarene Red X-6BN, Sandoz Canada Inc.), NaCl, NaOH and possibly urea.

4.2.2 Experimental procedures and analysis

The dyeing and fixation processes, and analysis methods for water content and fixation yield were described in detail in Chapter 2.

4.3 Two-level factorial design

4.3.1 General Features

Factorial designs permit estimation of the effects of several process variables (factors) simultaneously. Main effects of variables and interactions of variables are estimated. This is accomplished by making experimental trials with all combinations of the p-factors, with q levels per factor. The number of experimental runs required is $n = q^p$. In particular, for $q = 2$ the number of runs is $n = 2^p$. These two-level factorial designs are highly useful for a wide variety of problems. They are easy to plan and analyze, readily adaptable to both continuous and discrete factors, and provide adequate prediction models for responses that have no strong curvature in the experimental region.

4.3.2 Factors and predicted responses

The predicted responses which depend on the main factors and their interaction have been described in several books (MONTGOMERY, 1991). Two-level factorial designs were used in our plans for examining the effects of both continuous and discrete variables (such as two levels of temperature). The higher and lower levels are coded "+1" and "-1", respectively. The (+1) and (-1) levels should be far enough apart so that the "effect" of a factor is clearly larger than the experimental error. Coding of the factors in this way is simply a convenient linear transformation that converts the various natural scales of the all factors into the same numerical range (-1 to +1).

4.4 Factorial analysis and results

4.4.1 Experimental results and discussion

For trials in which the padded fabric was not vacuum extracted prior to heating, the five independent controllable process variables whose effects were examined were infrared emitter power (P), fabric speed (S), and the alkali NaOH (A), urea (U), and electrolyte NaCl (E) concentrations. All the remaining operational parameters such as the dye solution concentration (20 g/L), the initial temperature and water content of the padded fabric (65 %), the initial temperature, humidity and flow rate of the ventilating air, and the source/web distance (5.1 cm) were held, or were assumed, constant.

Because there was a considerable reduction of the water content of the impregnated wet fabric after vacuum extraction (65 to 45% water), the key operational parameters for infrared drying and heating (P and S) had to be significantly different when vacuum extraction was used. Its effect was therefore studied in a separate factorial plan. For this, only three controllable variables were studied, namely, emitter power (P), fabric speed (S) and vacuum level (V). All chemical concentrations were held constant for this second series of trials with dye at 30, NaCl at 10 and NaOH at 5 g/L.

For each factorial plan, two levels of operation were selected for each controllable variable (Tables 4.1 and 4.2). Thus 32 (2^5) trials without prior vacuum extraction and 8 (2^3) with vacuum were carried out, each trial being duplicated (MONTGOMERY, 1991). The measured process output responses were the fabric water content (R_W) and temperature (R_T) on leaving the dryer, and the dye fixation yield (R_F).

The coded values of the controlled variables, the process responses (R) and the variance (σ^2) of a single response observation are given in Tables 4.3 and 4.4. In order to evaluate the precision of experimental measurements and results, the pooled standard deviation (σ_{PSD}) for each response observation in different processes were calculated by Equations 4-1 and 4-2, and presented in Table 4.5. It is clear that the reproducibility of the repeat trials was very good. The dye fixation yields showed the desired wide range of values clearly indicating the process conditions for obtaining optimum fixation (> 90% yield).

TABLE 4.1 VALUES OF CONTROLLED VARIABLES FOR INFRARED DYE FIXATION WITHOUT PRIOR VACUUM EXTRACTION

Variable	Symbol	Units	Lower limit	Upper limit
Fabric speed	S	m/min	3.1	4.0
Emitter power	P	kW	10.03	13.06
NaCl conc.	E	g/L	10	40
NaOH conc.	A	g/L	0.5	5.0
Urea conc.	U	g/L	0	100

TABLE 4.2 VALUES OF CONTROLLED VARIABLES FOR INFRARED DYE FIXATION WITH PRIOR VACUUM EXTRACTION

Variable	Symbol	Units	Lower limit	Upper limit
Fabric speed	S	m/min	3.8	4.6
Emitter power	P	kW	7.84	10.55
Vacuum level	V	kPa	0	39

TABLE 4.3 TWO LEVEL FACTORIAL PLAN - PROCESS RESPONSES AND VARIANCE WITHOUT PRIOR VACUUM EXTRACTION

Coded values of input variables					Fixation yield				Fabric water content				Fabric temperature			
S	P	E	A	U	R_F (%)		R_{FM}	σ^2	R_W(%)		R_{WM}	σ^2	R_T(°C)		R_{TM}	σ^2
-1	-1	-1	-1	-1	3.2	4.0	3.6	0.32	3.8	3.8	3.8	0	60	59	59.5	0.5
1	-1	-1	-1	-1	2.0	2.5	2.25	0.13	16.6	15.6	16.1	0.5	43	43	43	0
-1	1	-1	-1	-1	62.1	62.3	62.2	0.02	0.9	0.8	0.85	0.01	144	148	146	8
1	1	-1	-1	-1	6.2	6.1	6.15	0.01	2.7	2.5	2.6	0.02	72	76	74	8
-1	-1	1	-1	-1	4.4	4.6	4.5	0.02	6.9	8.0	7.45	0.61	57	54	55.5	4.5
1	-1	1	-1	-1	2.6	2.2	2.4	0.08	19.5	18.8	19.15	0.25	44	43	43.5	0.5
-1	1	1	-1	-1	63.3	63.9	63.6	0.18	2.9	2.5	2.7	0.08	155	151	153	8
1	1	1	-1	-1	6.6	6.5	6.55	0.01	6.1	6.1	6.1	0	72	69	70.5	4.5
-1	-1	-1	1	-1	18	18.5	18.25	0.13	4.4	4.4	4.4	0	55	52	53.5	4.5
1	-1	-1	1	-1	3.5	4.8	4.15	0.85	17.1	15.3	16.2	1.62	44	43	43.5	0.5
-1	1	-1	1	-1	81.3	81.5	81.4	0.02	0.6	0.7	0.65	0.01	142	145	143.5	4.5
1	1	-1	1	-1	31.6	31.4	31.5	0.02	2.7	2.6	2.65	0.01	77	73	75	8
-1	-1	1	1	-1	24.8	27.1	25.95	2.65	7.2	6.0	6.6	0.72	55	58	56.5	4.5
1	-1	1	1	-1	11.1	11.2	11.15	0.01	18.2	19.3	18.75	0.61	44	44	44	0
-1	1	1	1	-1	86.4	86.8	86.6	0.08	1.4	0.9	1.15	0.13	148	151	149.5	4.5
1	1	1	1	-1	40.4	40.3	40.35	0.01	4.8	4.6	4.7	0.02	74	78	76	8
-1	-1	-1	-1	1	3.1	3.2	3.15	0.01	9.2	8.3	8.75	0.41	72	72	72	0
1	-1	-1	-1	1	2.3	2.5	2.4	0.02	18.1	17.3	17.7	0.32	45	46	45.5	0.5
-1	1	-1	-1	1	36.4	35	35.7	0.98	3.1	2.4	2.75	0.25	153	155	154	2
1	1	-1	-1	1	6.8	7.4	7.1	0.18	8.2	7.6	7.9	0.18	107	103	105	8
-1	-1	1	-1	1	5.6	6.7	6.15	0.61	11.3	10.9	11.1	0.08	77	77	77	0
1	-1	1	-1	1	4.0	3.7	3.85	0.05	19.8	19.2	19.5	0.18	47	47	47	0
-1	1	1	-1	1	39.1	37.5	38.3	1.28	4.4	4.4	4.4	0	159	157	158	2
1	1	1	-1	1	8.5	8.3	8.4	0.02	10.6	10.6	10.6	0	110	105	107.5	12.5
-1	-1	-1	1	1	22	20.6	21.3	0.98	9.2	9.4	9.3	0.02	78	76	77	2
1	-1	-1	1	1	5.6	6.4	6	0.32	18.4	17.9	18.15	0.13	45	45	45	0
-1	1	-1	1	1	90.9	90.8	90.85	0.01	3.1	2.4	2.75	0.25	157	158	157.5	0.5
1	1	-1	1	1	52.1	54.2	53.15	2.21	8.6	8.5	8.55	0.01	108	108	108	0
-1	-1	1	1	1	30.3	29.3	29.8	0.5	11.2	11.6	11.4	0.08	81	78	79.5	4.5
1	-1	1	1	1	13.8	11.8	12.8	2	20.4	19.9	20.15	0.13	46	47	46.5	0.5
-1	1	1	1	1	92.1	92.2	92.15	0.01	4.4	4.0	4.2	0.08	158	158	158	0
1	1	1	1	1	54.8	54.4	54.6	0.08	10.6	10.4	10.5	0.02	107	110	108.5	4.5

* R_{FM} - average value of fixation yield response
R_{WM} - average value of fabric water content response
R_{TM} - average value of fabric temperature
σ^2 - variance of a single response observation

TABLE 4.4 TWO LEVEL FACTORIAL PLAN - PROCESS RESPONSES AND VARIANCE PRECEDED BY VACUUM EXTRACTION

Coded Values of Input Variables			Fixation yield				Fabric water content				Fabric temperature			
S	P	V	R_F (%)		R_{FM}	σ^2	R_W(%)		R_{WM}	σ^2	R_T (°C)		R_{TM}	σ^2
-1	-1	-1	7.6	8.2	7.900	0.180	14.5	15.4	14.95	0.41	40	40	40	0
1	-1	-1	4.5	4.9	4.7	0.08	20.5	19.2	19.85	0.85	40	40	40	0
-1	1	-1	12.9	12.9	12.9	0	4.9	6.7	5.8	1.62	49	47	48	2
1	1	-1	8.8	9.8	9.3	0.5	11	9.6	10.3	0.98	45	46	45.5	0.5
-1	-1	1	25.1	28.1	26.6	4.5	1.0	1.0	1	0	68	69	68.5	0.5
1	-1	1	14	13.8	13.9	0.02	2.5	2.3	2.4	0.02	52	54	53	2
-1	1	1	83.6	85.1	84.35	1.13	0.3	0.2	0.25	0.01	136	138	137	2
1	1	1	48.8	44.1	46.45	11.05	0.6	0.6	0.6	0	105	100	102.5	12.5

* R_{FM} - average value of fixation yield response

R_{WM} - average value of fabric water content response
R_{TM} - average value of fabric temperature

σ^2 - variance of a single response observation

TABLE 4.5 POOLED STANDARD DEVIATIONS OF EXPERIMENTAL RESULTS

Responses in infrared fixation processes		Pooled standard deviation (σ_{PSD})
Without vacuum	Fixation yield (R_F)	0.670
	Fabric water content (R_W)	0.460
	Fabric temperature (R_T)	1.840
With vacuum	Fixation yield (R_F)	1.580
	Fabric water content (R_W)	0.750
	Fabric temperature (R_T)	1.670

$$\sigma^2 = \frac{\sum_{i}^{k} (R_i - R_M)^2}{k-1} \tag{4-1}$$

where k - the number of replicates of each trial

R_i - response of replicates of each trial

R_M - average response of replicates of all trials

σ^2 - variance of a single response observation

$$\sigma_{PSD} = \sqrt{\frac{1}{n} \times \sum_{j}^{n} (\sigma_j)^2} \tag{4-2}$$

where n - the number of experiments (2^p)

σ_{PSD} - pooled standard deviation

The effects of final water content, and of final fabric temperature, on the fixation yield are shown in Figures 4.1 and 4.2. In most processes without urea added to the dyebath, the highest fixation yields were only obtained if the final water content was below about 1-2%, or if the final fabric temperature was more than 120-130°C. The highest fixation yields were obtained for dye solutions containing 100 g/L urea and 5 g/L NaOH. Urea promotes dye solubility, retards water removal during drying (Figure 4.1), acts as a fiber swelling agent and is believed to combine with water to provide a diffusion medium in the dried fabric (TROTMAN, 1984). At an alkali concentration of 5 g/L NaOH, the urea clearly retards initial drying and promotes slightly higher fixation yields. The points along the line in Figure 4.2 indicate that the major effect of added urea, and of vacuum extraction, is to allow the attainment of somewhat higher fabric temperatures and thus higher fixation towards the end of process.

The middle curve in Figure 4.2 clearly illustrates how the lower NaOH concentration of 0.5 g/L results in a decreased fixation yield. The effect of urea at this lower NaOH concentration was not as anticipated but was reproducible. Again, the presence of urea in the dye solution retards drying somewhat and allows attainment of higher final fabric temperatures once drying is complete.

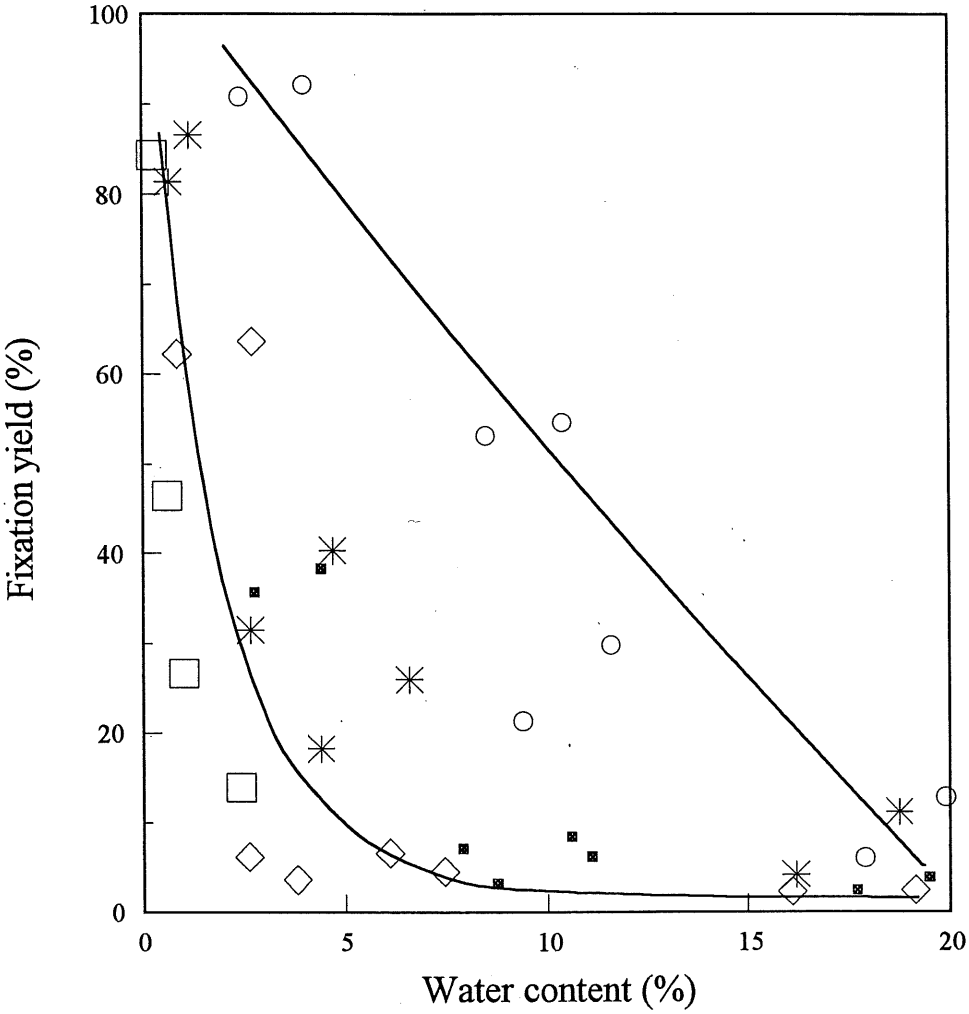


Figure 4.1 Effect of final water content on fixation yield

No urea, 5 g/L	With urea, 5 g/L	Vacuum, 5 g/L
—✳—	—○—	—□—
No urea, 0.5 g/L	With urea, 0.5 g/L	
—◇—	—▪—	

* The lines only illustrate the limiting values

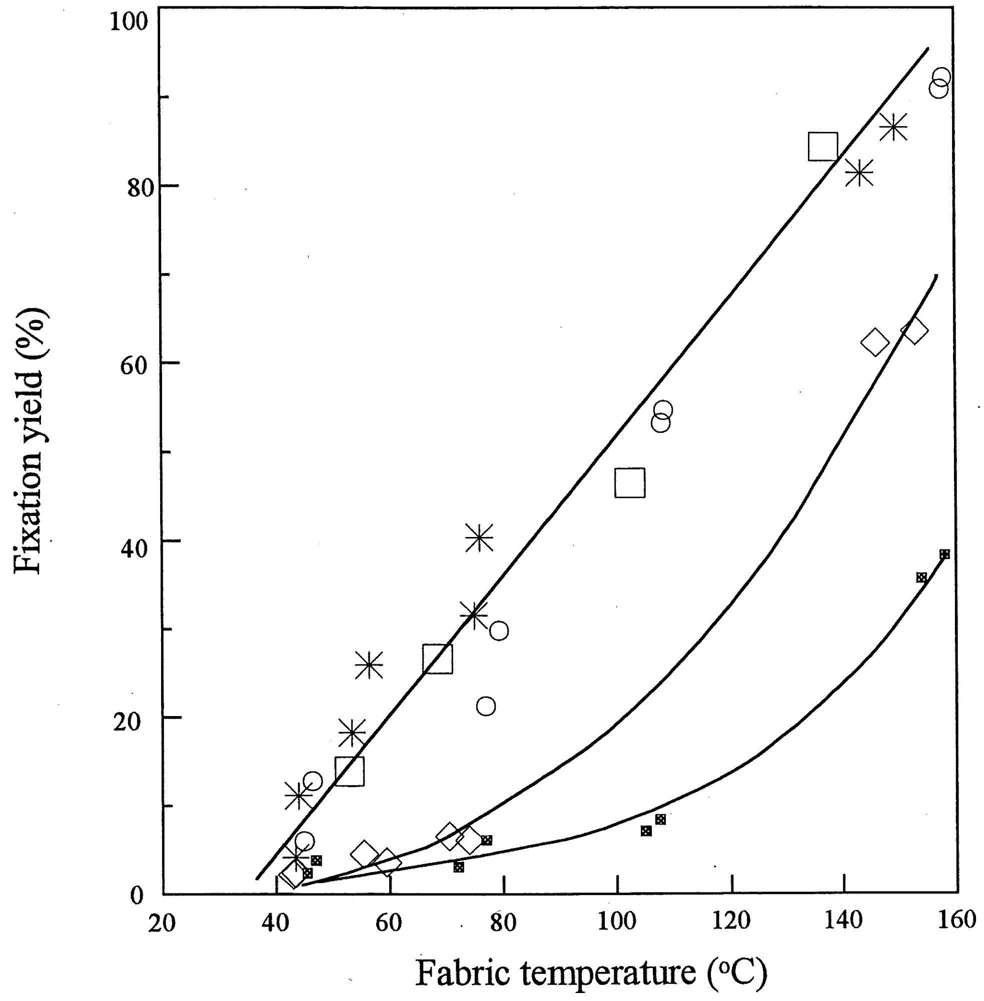


Figure 4.2 Effect of final temperature on fixation yield

However, at the lower alkali concentration, the presence of urea suppressed the fixation yield even though the dyed fabric was heated to almost 160°C. This is the opposite effect to that found for urea with 5 g/L NaOH. One possible explanation might be that reaction of the urea with the NaOH during the heating phase reduces the alkali concentration leading to less activation of the cellulose and thus lower fixation. One possible reaction might be

$$NH_2CONH_2 + 2HO^- \rightarrow 2NH_3 + CO_3^{2-}$$

The urea is present in large excess (100 g/L) so even a reaction with the NaOH at a urea conversion as low as 0.25% (2.5% x 100 g/L = 0.25 g/L) could reduce the original 0.5 g/L NaOH concentration. Thus addition of urea could reduce the activation of the cotton for the lower NaOH concentration. But there is no significant reduction of NaOH concentration at 5.0 g/L value.

4.4.2 Factorial analysis of experimental results

The model for a given process response R_i was written in terms of coded values of the controlled variables and coefficients describing the magnitude of their individual effects and 2nd and higher order interactions (MONTGOMERY, 1991). These have the form

$$\begin{aligned} R_i = {} & \beta_0 + \beta_1 S + \beta_2 P + \beta_3 E + \beta_4 A + \beta_5 U + \beta_{15} SU + \ldots\ldots \\ & + \beta_{23} PE + \beta_{24} PA + \beta_{25} PU + \ldots\ldots + \beta_{34} EA + \ldots\ldots \beta_{45} AU \\ & + \beta_{123} SPE + \beta_{124} SPA + \beta_{125} SPU + \ldots\ldots\ldots \\ & + \text{other high order interactions} \qquad (4\text{-}3) \end{aligned}$$

R_i = process response (fixation yield R_F, water content R_W, or fabric temperature R_T)
β_0 = average value of the process response
β_i = coefficient determining the principal effect of each variable
β_{ij} = coefficient describing the effect of interactions of variables, i and j
S = coded value of the fabric speed, +1 (upper limit) to -1 (lower limit).
P = coded value of the total emitter power
E = coded value of the NaCl concentration

A = coded value of the NaOH concentration

U = coded value of the urea concentration

$$\text{Coded value of variable} = \frac{V-(H_i+L_o)/2}{(H_i-L_o)/2} \qquad (4\text{-}4)$$

where: Hi = value of the upper limit of the particular variable

Lo = value of the lower limit of the particular variable

V = actual value of the variable

Multiple linear regression according to least squares estimation of the parameters, was used to calculate the values of the coefficients ($\beta_0, \beta_i, \beta_{ij}$) for the principal effects and 2nd and higher order interactions (equation 4-3) for the three responses dye fixation yield (R_F), final fabric water content (R_W) and temperature (R_T). Equations such as equation 4-3, but including many 3rd and higher order interactions, obviously gave higher values for the correlation coefficients, but become rather cumbersome. We therefore performed regressions using only significant coefficients having values above a certain level (Table 4.6). This allowed equations with good predictive capability which were easy to manipulate.

Table 4.6 shows that the most important variables influencing the dye fixation yield were fabric speed, emitter power and NaOH concentration. In our experimental range, the lower the fabric speed, the higher the emitter power and NaOH concentration, the larger the fixation yield. The results obtained using the model are in agreement with the results in Chapter 3. We had previously established that higher fixation yields were obtained using NaOH as the cellulose-activating alkali rather than a weaker one such as Na_2CO_3 (ZHAO and BROADBENT, 1993). The effect of NaCl concentrations was much less significant. Addition of NaCl to the dyebath increases the value of the concentration ratio [Cell-O$^-$]/[OH$^-$] which increase the rate of dye fixation (PRESTON, 1986). It was expected to improve the fixation yield, as it also increases the substantivity of the reactive dye for the cotton. Its effect, however, was not particularly significant, even its effect coefficient could be neglected. The effect of urea addition was also less significant on fixation yield. The fabric speed and emitter power were also the principal variables influencing the final fabric temperature and water content. As expected, these responses were barely affected by the NaOH concentration but were both somewhat greater in the presence of urea, which retards loss of water during drying. In fact, the enhancement of the fixation yield in the presence of urea appears to be its effect on the final fabric temperature (Figure 4.2).

When the cotton fabric was padded with dye solution, and then vacuum extracted to remove the bulk of the interstitial solution, the falling rate drying period began almost as soon as the fabric entered the dryer and R_T was higher. The reaction of the dye with cellulose under alkaline conditions occurred mainly at temperatures above 100°C, which were easier to attain if the impregnated fabric had been vacuum extracted. In the simpler factorial plan for evaluation of the effect of prior vacuum extraction, the emitter power and fabric speed were the only other parameters varied. The principal effects and interactions are shown in Table 4.7. Again, only significant effects were used in the regression so that simple relationships could be derived. The pronounced effect of prior vacuum extraction of the padded fabric on the dye fixation yield, confirmed previous results from our laboratory for fixation with radiant heat and steam (FORTIN et al., 1988). It is easy to heat a vacuum extracted fabric to a higher temperature because it dries more rapidly. Clearly, the alkaline solution of the dye adhering to the fiber surfaces is a major source of hydrolyzed dye. If this is extracted before heating, higher fixation yields for the dye remaining in the cotton would be expected. If the operating conditions were such that a high fabric temperature was achieved without prior vacuum extraction (higher power and low speed), the already high dye fixation yield was only slightly increased using vacuum.

To evaluate the adequacy of the model relationships for the process responses for values of the controlled variables other than at the extremes of the ranges, we performed two trials, with and without vacuum extraction before drying, in which the controlled variables had values mid-way between their upper and lower limits (coded values = 0). For the trial with prior vacuum extraction, the vacuum level was 24 kPa (coded value = + 0.22). The results (Table 4.8) showed good agreement with the predicted responses using equation 4-1 and the coefficients in Tables 4.6 and 4.7. There was no significant curvature over the range of input parameters used in these trials.

TABLE 4.6 COEFFICIENTS FOR EMPIRICAL RELATIONSHIPS BETWEEN THE PROCESS RESPONSES AND CONTROLLED VARIABLES WITHOUT PRIOR VACUUM EXTRACTION

Coefficients	Estimates of coefficients		
	R_F(%)	R_W(%)	R_T(°C)
β_0(intercept)	28.6	8.7	88.5
β_1(S)	-12.8	3.8	-20.9
β_2(P)	18.8	-4.1	33
β_3(E)	-	1.2	-
β_4(A)	12.6	-	-
β_5(U)	-	1.6	8.1
β_{12}(S.P)	-8.6	-1.6	-10.1
β_{15}(S.U)	2.3	-	-
β_{24}(P.A)	6.3	-	-
β_{25}(P.U)	-	-	2.5
β_{45}(A.U)	3.4	-	-
$\beta_{12}5$(S.P.U)	2.5	-	5.3
β_{245}(P.A.U)	2.9	-	-
Correlation, R^2	0.983	0.969	0.997
Std. dev. of estimate of response	4.5	1.2	2.5
Coefficients neglected	< 2.0	< 1.0	< 2.0

TABLE 4.7 COEFFICIENTS FOR EMPIRICAL RELATIONSHIPS BETWEEN THE PROCESS RESPONSES AND CONTROLLED VARIABLES WITH VACUUM EXTRACTION BEFORE FIXATION

Coefficients	Estimates of coefficients		
	R_F(%)	R_W(%)	R_T(°C)
β_0(intercept)	25.7	6.9	66.8
β_1(S)	-7.2	1.4	-6.6
β_2(P)	12.5	-2.7	16.4
β_3(V)	17.1	-5.8	23.4
β_{12}(S.P)	-3.2	-	2.7
β_{13}(S.V)	-5.5	-	-5.9
β_{23}(P.V)	10.1	2	13.1
β_{123}(S.P.V)	-3.1	-	-2.06
Correlation, R^2	0.987	0.980	0.989
Std. dev. of estimate of response	4.7	1.6	3.8
Coefficients neglected	< 2.0	< 1.0	< 2.0

TABLE 4.8 PROCESS RESPONSES FOR INFRARED DYE FIXATION WITH AND WITHOUT PRIOR VACUUM EXTRACTION USING MID-POINT VALUES FOR THE PROCESS VARIABLES (MODEL PREDICTIONS IN PARENTHESES)

Coded Values of Input Variables						R_F (%)		R_W (%)		R_T (°C)	
S	P	E	A	U	V	Observed	Model	Observed	Model	Observed	Model
0	0	0	0	0	-	29.8	(28.6)	8.4	(8.7)	93	(89)
0	0	-	-	-	0.22	28	(29.5)	5.5	(5.6)	73	(72)

4.5 Conclusions

Relatively simple relationships between controlled process variables and output responses were obtained for the fixation of a reactive dye on cotton using two factorial experimental designs. These indicated that the fabric speed, emitter power and NaOH concentration were the most important variables influencing the dye fixation yield. The fabric speed and emitter power also significantly affected the final fabric temperature and water content. Vacuum extraction prior to drying was one means of obtaining a higher final fabric temperature. It significantly increased the dye fixation yield, but not in those cases where reaction conditions already favored a high degree of fixation.

The possibility of obtaining high fixation yields (> 90%) using infrared heat makes this a technologically attractive process for several reasons. Such high yields are possible with dyes of high, medium, and low reactivity, in short processing times, with little migration of the dye to the yarn surfaces during initial drying. Most importantly, very little unfixed dye remains in the cotton fabric so the washing effluent is only slightly colored. This is a current environmental problem for dyehouses using reactive dyes. Two problems, however, must be considered. The high fabric temperatures required for good dye fixation increase the risk of fabric scorching and the emitter power and fabric speed should be automatically controlled (DHIB et al., 1994). Also, at the high NaOH concentration necessary for optimum dye fixation, the dye in the bath is more likely to undergo premature hydrolysis. To avoid this, it would be necessary to mix the dye and NaOH solutions just prior to impregnation, which would require the use of metering pumps as in the cold pad-batch process (FOX and SUMNER, 1986). The dyeing obtained by heating with infrared radiation showed very high fixation yields and were of uniform color provided that the initial application of the reactive dye solution was uniform. The fixation yields were considerably higher than those obtained by heating in forced hot air where the significant migration of the dye in solution to the yarn surfaces in the initial stages of drying interferes with its ability to react with the cellulose. We will investigate this phenomenon in Section 6.

5. PRINCIPLES AND ANALYSIS OF DRYING FOR HOT AIR AND INFRARED FIXATION PROCESSES

5.1 Introduction

Three types of fixation processes for reactive dyes on cotton were used in our experiments: hot air fixation, infrared fixation and cold batch fixation. In fact, dye fixation is a combination of drying and chemical reaction processes, except for cold batch fixation. The chemical reaction of the dye with the cotton and its conditions were described in Chapters 2 and 3. In this chapter, some basic principles and analysis of textile drying are introduced as well as the problem of the migration of dyes in solution to the fiber and yarn surfaces during the initial stages of drying. This precedes the discussion of the influence of the fixation method on the reactive dye fixation yield, and on the color yield obtained, so as to facilitate the interpretation of the results.

The process of drying is probably the most common process to which textile materials are subjected. Drying, defined as the removal of moisture or other liquid from the textile web by the use of heat, may be carried out at the fiber, yarn or fabric stages and frequently is carried out more than once in the production process (LYONS et al., 1971). The development of improved drying processes requires an understanding of the mechanisms of drying, and the associated mass and heat transfer. It is the objective of this chapter to explain the process of drying textile materials as the basis for understanding the thermofixation processes of reactive dyes. A fibrous material consists of an irregular array of interlocking fibers of varying length and orientation. The material consists essentially of interconnected cavities or capillaries of irregular shapes and sizes (MILES, 1985). The microscopic model for the study of drying of capillary porous media was established by Plumb (PLUMB et al., 1992). When the material is wet, these cavities are filled to varying degrees with the liquid to be removed. Since water is almost exclusively the solvent used during the processing of textile materials, the entrained fluid will be referred to as simply water.

The mechanism of the drying of textile materials is a combination of mass and heat transfer processes. Many analyses of the drying process in fibrous materials have been published (WOO et al., 1994; AKAOUI., 1983; KEEY, 1993; BROADBENT, 1990c; KUANG et al, 1994; LAMPINEN et al., 1991). For hot air drying, a mathematical model based on the mass and energy balances for the fabric was developed for the steady-state operation of a tenter (dryer) frame (BEARD, 1976). The model consists of a set of algebraic and differential equations which are solved simultaneously, to obtain fabric temperature and moisture content profiles along the length of the tenter (dryer). Heat is transferred from the hot air in the dryer to the exterior surface of the fabric, then conducted through the fabric where vaporization of the moisture takes place. Spirnek also developed a mathematical model (SPIRNEK, 1978) for the non-steady state operation of a hot air dryer. For infrared radiation drying, a complete mathematical model, also based on the mass and energy balances for the fabric and the air, was developed for the steady state operation of the dryer (CÔTÉ et al., 1990). The model consists of four differential equations which must be solved simultaneously, to obtain the temperature and moisture distribution along the infrared oven length. Dhib modified this model for non-steady state operation of the dryer (DHIB, 1994).

However, all the above models for hot air and infrared drying assumed that there was no temperature or moisture distribution within the fabric thickness. In fact, for hot air drying of dyed fabrics, there are temperature and moisture distributions within the fabric which result in moisture migration from the interior to the surface of the fabric. Pounder developed a mathematical model of high intensity paper drying based on moisture and energy balances, and analyzed the temperature and moisture distribution within the paper (POUNDER, 1986). Chen established a model for drying sheet materials and described moisture and temperature profiles within the sheet materials (CHEN, 1996). For infrared radiation, because of infrared penetration (ORFEUIL, 1987), there is not only heat conduction within the fabric, but also the infrared radiation energy may be absorbed within the fabric, giving a more uniform temperature profile across the fabric thickness than when using hot air. Navarri studied the infrared and convective drying of non hygroscopic solids and developed a heat and mass transfer model which described the moisture and temperature distributions within the solid (NAVARRI, et al., 1992). Parrouffe performed an experimental study of combined infrared and convection drying to investigate the characteristics of this drying process and examine the interaction between the infrared radiation and the flow transport properties (PARROUFFE, 1992a and 1992b).

In this chapter, we are going to demonstrate the basic principles and mechanisms of textile fabric drying during hot air and infrared fixation processes, and analyze and discuss:

1. Mass and heat transport phenomena between the fabric and drying air (external conditions), and in the drying fabric (internal conditions)
2. Temperature and moisture profiles within the fabric in hot air drying
3. Effect of absorption of the infrared radiation within the fabric on the temperature and moisture distribution throughout the fabric
4. Dye migration during hot air and infrared drying processes.

The following analysis and discussion will be based on Figures 5.1 and 5.2 which describe the configurations of the moisture and heat transfer in hot air and infrared drying processes. In Figures 5.1 and 5.2, the nomenclature and subscripts are:

Nomenclature:

L/2 - half fabric thickness

P_a - air pressure (kN/m^2)

Y_a - humidity of the air (kg vapor/kg air)

V_a - flow speed of air past the fabric (m/s)

T_a - air temperature (°C)

Q_{af} - energy by convection from hot air to fabric (W)

Q_{evap} - energy by evaporation (W)

Q_{fa} - energy by convection from fabric to air (W)

Q_{rf}- energy by radiation from infrared emitter to fabric (W)

T(x,t) - temperature distribution as a function of distance into the fabric and time

X(x,t) - moisture distribution as a function of distance into the fabric and time

Subscripts:

a - air

f - fabric

r - radiation emitter

evap - evaporation

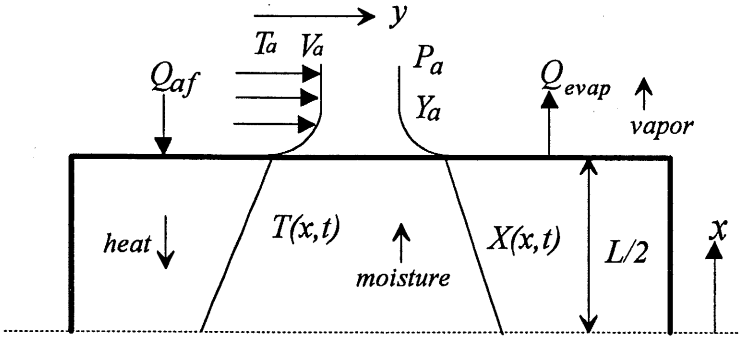


Figure 5.1 Configuration of moisture and heat transfer in hot air drying

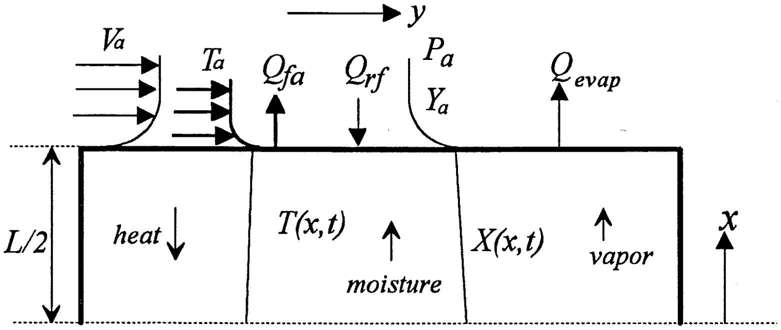


Figure 5.2 Configuration of moisture and heat transfer in infrared drying

5.2 Humidity - Moisture - Textile Fabric Relationships

5.2.1 Humidity in air and moisture content in fabric

In hot air drying processes, preheated air is used as a drying agent. This air-water vapour mixture transmits heat to the wet material and simultaneously absorbs moisture from the material. In infrared drying processes, on the other hand, the radiation is absorbed directly by the wet material, and the dry air absorbs moisture and heat from the material.

The gas above a wet solid will be damp and the humidity of the air is expressed on a mass-ratio basis which is the ratio of the mass of water vapour A to the mass of completely dry air B.

$$Y = \frac{m_A}{m_B} \qquad (5\text{-}1)$$

The water in a wet solid will evaporate until, at equilibrium, its partial pressure in the vapour-air mixture reaches the saturation vapour pressure p_A^* of the water at the prevailing temperature, which can be calculated from the Clausius-Clapeyron equation. At saturation, the molar ratio of vapour to dry air is $p_A^*/(P - p_A^*)$, where P is the total pressure. Since a moist gas at atmospheric pressure is usually described by the Ideal-gas law with sufficient accuracy in engineering calculations, we obtain:

$$p_A V = m_A R_A T \qquad (5\text{-}2)$$

and

$$p_B V = m_B R_B T \qquad (5\text{-}3)$$

where

R_A = 461.5 J/kg.K -- water vapour gas constant

R_B = 287 J/kg.K -- air gas constant

Hence, the humidity of air, a mass ratio, is given by

$$Y = \frac{m_A}{m_B} = \frac{p_A R_B}{p_B R_A} = 0.622 \frac{p_A}{P - p_A} \qquad (5\text{-}4)$$

and the humidity at saturation is

$$Y_s = 0.622\frac{p_A^*}{P - p_A^*} \tag{5-5}$$

By convention, the relative humidity ψ may be defined as the ratio of the actual pressure in the water-air mixture with respect to the saturation vapour pressure of water at the same temperature.

$$\psi = \frac{p_A}{p_A^*} \tag{5-6}$$

The amount of moisture held by a wet material (textile fabric) may be expressed in terms of either the whole mass (wet basis) or the bone-dry mass of solid (dry basis). Normally, the moisture content of a wet material is defined by the ratio of the mass of moisture (m_M) to the mass of bone-dry solid (m_d) and described by:

$$X = \frac{m_M}{m_d} \tag{5-7}$$

5.2.2 Moisture and textile fabric

The type of moisture in the fabric and the material-moisture bonding are very important in drying. The moisture in or on the textile material may be divided into unbound moisture, bound moisture, free moisture and equilibrium moisture. The types of moisture may be expressed as in Figure 5.3, where moisture X is plotted against the relative humidity ψ. The relation between the equilibrium material moisture content and air humidity is determined experimentally by allowing sufficiently long contact of the dry material with air at constant temperature and relative humidity.

Bound moisture (hygroscopic moisture) is the moisture associated with the material which exerts an equilibrium vapour pressure less than that of the pure liquid. This moisture is present in the cell walls, crevices, pores and fine capillaries of porous fibrous materials such as cotton, or in weak chemical combination with the cellulose. Sometimes, this moisture is absorbed on the solid surface.

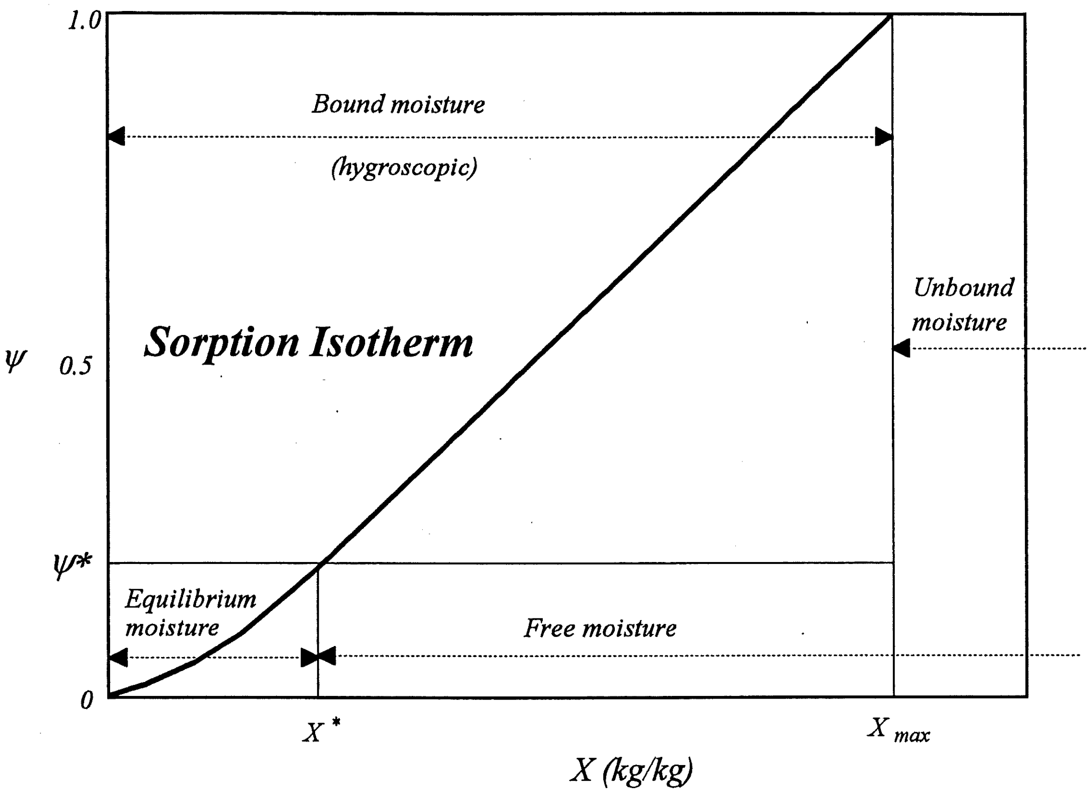


Figure 5.3 Illustration of various kinds of moisture for textile materials

Unbound moisture (capillary moisture) is that moisture contained by a wet material which exerts an equilibrium vapour pressure equal to that of a pure liquid ($\psi = 1.0$), and is held by surface tension in the inter-yarn and inter-fiber spaces. The moisture available in a material due to wet soaking is unbound moisture.

Free moisture is that moisture contained by a material in excess of the equilibrium moisture. Only free moisture can be evaporated.

For any given condition, the equilibrium moisture (X^*) cannot be reduced below a certain value. This depends upon temperature, relative humidity (ψ) and the nature of the material. Once the moisture content attains this value, any exposure to gas at the same relative humidity will not reduce the moisture further. The equilibrium moisture may usually be measured by experiment, but also calculated by the classical Brunauer-Emmett-Teller (BET) relationship (KEEY, 1993).

Usually, a textile material after dyeing by padding is in the state where the water content is above the bound water content. A textile fabric is a capillary porous material. Moisture in a porous material is held within the voids of the solid matrix. Plumb used the microscopic models to describe transport phenomena in capillary porous media (PLUMB et al, 1992). On drying, capillary-driven flows empty the large pores, often maintaining the exposed surface sufficiently wet for the drying rate to be controlled entirely by the moisture/vapour transport through the surrounding air.

5.3 Basic Principles of Heat and Mass Transfer

In drying and fixation processes, the transport phenomena include the transfer of heat and of mass which may be described in terms of potentials that determine the extent of change. Clearly the potential for heat transfer is the extent of temperature difference, and that for mass transfer is the difference in humidity.

A detailed description of drying phenomena in a porous material can be found using the following equations for the heat and moisture fluxes based on the mass and energy balances over the material in terms of Fourier's law of heat conduction and Fick's law of diffusion.

5.3.1 Fourier's law of heat conduction

Fourier's law gives the rate equation which may be used to compute the amount of heat energy being transferred per unit time. For a one-dimensional fabric sheet, having a temperature distribution $T(x)$, the rate equation is expressed as

$$J_Q = -k\frac{dT}{dx} \qquad \text{or} \qquad J_Q = -k\nabla T \tag{5-8}$$

The heat flux J_Q (W/m^2) is the heat transfer rate in the x direction per unit area perpendicular to the direction of transfer, and it is proportional to the temperature gradient, dT/dx, in this direction. The proportionality constant k is a transport property known as the thermal conductivity (W/m.K) and is a characteristic of the material. The thermal conductivity of dry cotton fabric and water are 0.06 W/m.K and 0.6 W/m.K, respectively (FRANK et al, 1990). The thermal conductivity of wet fabrics depends on temperature, moisture content and the structure of the material. Two calculation models for the conductivity of dry, porous materials were developed (KEEY, 1972). Normally, the thermal conductivity of wet fabrics may be measured by experiment (NAKA and KAMATA, 1977). In equation 5-8, the wet material was assumed to be homogeneous and k stands for the average thermal conductivity of the wet fabric within the range of temperature and moisture variations.

5.3.2 Heat convection transfer

In hot air drying processes, heat energy is transferred by convection into the wet material. The term "convection" is used to describe energy transfer between the surface of a material and a fluid moving over the surface. A material being dried commonly derives the heat needed for evaporating moisture from convection from an airstream moving over the material. The motion may be caused by external forces, when air is blown through the solid. In such cases, we describe the convection as forced. In other cases, the motion of the air is caused entirely by differences in density which are set up through the presence of temperature gradients, in which case heat transfer is called free convection. Only forced convection will be discussed for the cases of hot air drying and fixation process.

A hot, dry material loses heat, and a cold material gains heat, at a rate q_f that is proportional to the difference in temperature between the surface of the material T_f and the surrounding air T_a. The coefficient of proportionality is defined as the heat-transfer coefficient h_{af} in terms of Newton's law of cooling:

$$q_f = h_{af}(T_a - T_f) \tag{5-9}$$

The local heat flux may also be obtained by applying Fourier's law to the fluid at $x = \frac{L}{2}$. That is:

$$q_f = -k\left(\frac{\partial T}{\partial x}\right)_{x=L/2} \tag{5-10}$$

By combining equations 5-9 with 5-10, we then obtain:

$$h_{af} = \frac{-k(\partial T/\partial x)_{x=L/2}}{T_a - T_f} \tag{5-11}$$

Firstly, the velocity profile in the velocity boundary layer in the y direction may be obtained from the momentum balance and used to find the temperature profile. From equation 5-11, the convection heat transfer depends on the temperature profile in the thermal boundary layer which can be obtained from the energy balance of the boundary layer and depends on the velocity profile (BIRD et al, 1960). It is convenient to evaluate the heat transfer coefficient by convection in terms of its dimensionless counterpart, the Nusselt number, Nu_y, where

$$Nu_y = \frac{h_{af}y}{k} \tag{5-12}$$

where k is the thermal conductivity of air and h_{af} the heat-transfer coefficient between air and fabrics.

Substitution of equation 5-11 into equation 5-12

$$Nu_y = -\frac{y}{(T_a - T_f)}\left(\frac{\partial T}{\partial x}\right)_{x=L/2} \tag{5-13}$$

The normal temperature gradient at the surface of a flat sheet may be expressed by a differential equation (KEEY, 1972), in which the heat balance at any point in the boundary layer based on heat diffusion (equation 5-58) and dy/u replaces dt. u is the lengthwise velocity component and u_m is mean lengthwise velocity. The solution is

$$\frac{T-T_f}{T_a-T_f}=erf\left(x\sqrt{\frac{u_m}{4\alpha y}}\right) \tag{5-14}$$

Hence,

$$Nu_y=\frac{1}{\sqrt{\pi}}\sqrt{\frac{u_m y}{\alpha}}=\frac{1}{\sqrt{\pi}}\left[\frac{u_m y}{\nu}\right]^{\frac{1}{2}}\left[\frac{\nu}{\alpha}\right]^{\frac{1}{2}} \tag{5-15}$$

Where $\nu=\mu/\rho$. The local Nusselt number at a distance y from the leading edge depends upon the Reynolds number $Re_y=u_m y/\nu$ and the Prandtl number $\Pr=\nu/\alpha$. The Reynolds number is the ratio of the inertial and viscous forces and describes the influence of air motion on the heat transfer coefficient. The Prandtl number is the ratio of the momentum and thermal diffusivities. If the velocity profile is assumed to take the form of a cubic polynomial in y, then it can be shown that u_m is five-eights that of the total average u_G taken to be equal to that just outside the boundary layer. In terms of the Reynolds number $u_G y/\nu$, equation 5-15 becomes:

$$Nu_y=\sqrt{\left(\frac{5}{8\pi}\right)}\,Re_y^{1/2}(\Pr)^{1/2} \tag{5-16}$$

The average Nusselt number over the whole length L_f is:

$$Nu_{L_f}=\frac{1}{L_f}\int_0^{L_f} Nu_x\frac{L_f}{y}dy=2\sqrt{\frac{5}{8\pi}}\,Re_{L_f}^{1/2}(\Pr)^{1/2} \tag{5-17}$$

The Nusselt number is a dimensionless temperature gradient at the surface and depends on the flow state of the surrounding air and the temperature profile within the boundary layer. It is expressed as a function of a prescribed geometry, and the Reynolds Re_{L_f} and Prandtl numbers $\Pr$. That is:

$$Nu_{L_f}=f\left(y, Re_{L_f}, \Pr\right) \tag{5-18}$$

Hence:

$$h_{af} = \frac{kNu_{L_f}}{L_f} \qquad (5\text{-}19)$$

5.3.3 Radiation heat transfer

(1). Infrared radiation

Any hot material emits radiant energy and its transport does not require the presence of any matter and may be viewed as the propagation of electromagnetic waves. The properties of wavelength λ and frequency ν of an electromagnetic wave in free space are related by

$$\lambda = \frac{c}{\nu} \qquad (5\text{-}20)$$

The wavenumber $\bar{\nu}$ may be obtained by $\bar{\nu} = 1/\lambda$. The complete electromagnetic spectrum includes short wavelength gamma rays, X rays, and ultraviolet (UV) radiation of high energy, the long wavelength microwaves and radio waves, and the intermediate wavelengths which includes a portion of the UV and all of the visible and infrared (IR), shown in Figure 5.4. Infrared radiation is thermal radiation and is pertinent to heat transfer. Infrared radiation will be discussed in this chapter because of the infrared drying and fixation process we used.

Infrared radiation is a form of electromagnetic radiation located between the visible and microwave regions, i.e. between the wavelengths 0.76 and 1,000 μm, approximately. The typical wavelength region for industrial heating applications is in the 0.76 - 10 μm range that is usually divided into three bands identified by the wavelength of maximum emission: short infrared from 0.76 to 2 μm, medium infrared from 2 to 4 μm and long infrared from 4 to 10 μm. In our infrared drying and fixation processes, infrared emitters of short wavelength (T-3 tube) and medium wavelength (Quartz tube) were used.

An electromagnetic wave consists of mutually perpendicular electric and magnetic fields transverse to the direction of propagation of the wave. It transmits energy from its place of origin to a point of absorption and does this at a certain rate. It is convenient to discuss the radiation process by utilizing a photon or quantum point of view. The photon is the basic unit of radiative energy. The energy transmitted by the beam is stored in the photons. Each photon carries an amount of energy

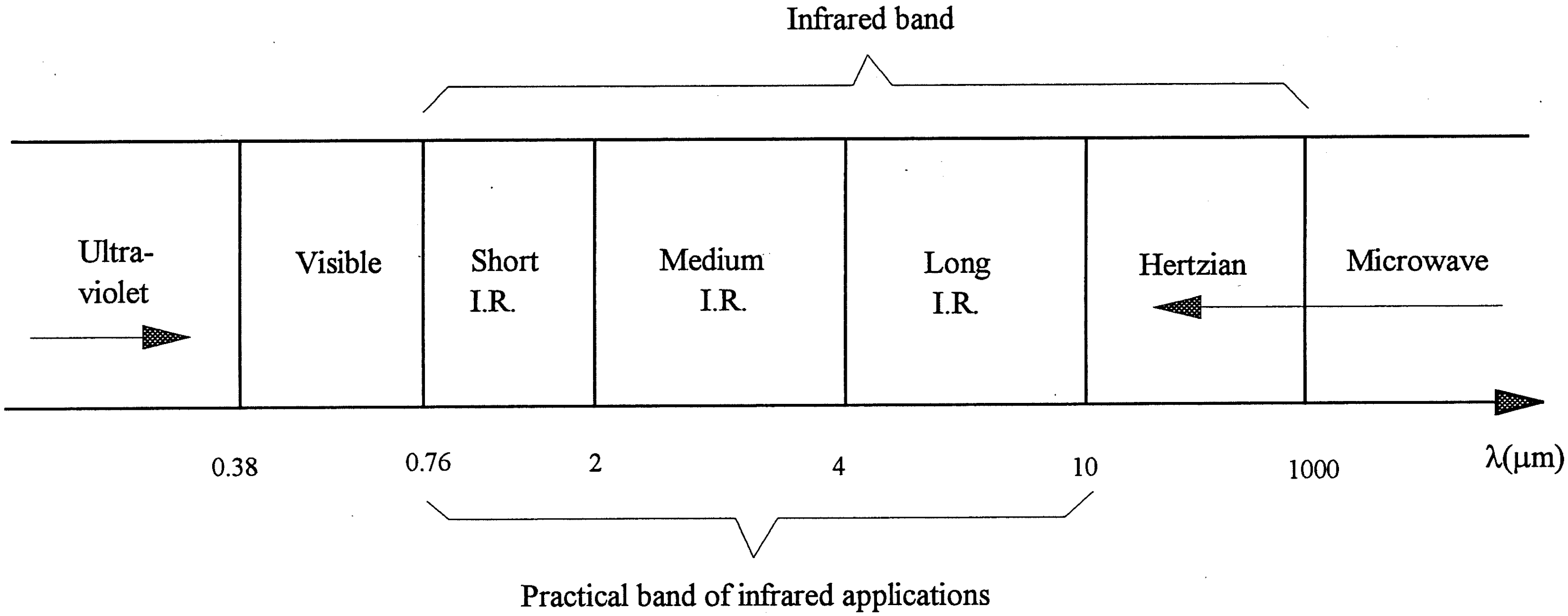


Figure 5.4 Infrared radiation spectral band

$$E = h\nu \quad (\mathrm{J}) \tag{5-21}$$

Here h is Planck's constant, which has a value of $6.6256 \times 10^{-34} (J \bullet s)$

(2). Absorption and emission of infrared radiation

Radiation energy (G_λ) falling on a surface may be absorbed (G_{abs}), reflected (G_{ref}), or transmitted (G_{tr}). The fractions of the incident energy that are distributed in these ways are called respectively: the absorptivity (α), the reflectivity (γ), and the transmissivity (τ). Clearly due to energy balance,

$$G_\lambda = G_{abs,\lambda} + G_{ref,\lambda} + G_{tr,\lambda} \tag{5-22}$$

and

$$\alpha + \gamma + \tau = 1 \tag{5-23}$$

Most solid materials are opaque to thermal radiation, and so $\tau = 0$. The radiation emitted from a solid originates within the solid so the solid can be considered an absorbing and emitting medium like a gas. Cotton fabric can absorb most infrared radiation and has an emissivity of 0.90 - 0.95. Dyed cotton fabric may be treated as an absorbing and emitting medium without scattering (SIEGEL and HOWELL, 1981). A substance that absorbs all the impinging radiation is called a black body. A real body may be grey, when it partially absorbs the radiation falling on it regardless of wavelength, or colored when the degree of absorption depends upon wavelength. In fact, radiative emission consists of the release of photons of energy, and absorption is the capture of photons. When a photon is emitted or absorbed, the energy of the emitting or absorbing particle is correspondingly decreased or increased. For a surface held at a given temperature, a black body is the best emitter of radiation and has an emissivity of 1.0.

Since the wavelength of infrared radiation we used is from 0.76 to 4 μm and has low photon energy (1.66×10^{-20} to 8.72×10^{-20}) compared to gamma rays, X rays, and ultraviolet (UV) radiation, the absorption of infrared radiation cannot break chemical bonds (energy which breaks chemical bonds should be more than 10^{-18} J). When a photon is absorbed or emitted by an atom or molecule, and there is no ionization or recombination of ions and electrons, the atom or molecule moves from one quantized energy state to another. However, the absorption energy ($10^{-23} \rightarrow 10^{-19}$ J) of infrared radiation will activate molecular vibrations and rotations and possibly accelerate the chemical reaction. For example, hydroxyl groups on the cellulose (secondary and primary alcohol, see Figure 1.2) have infrared absorption bands at about 3700 - 3300 cm^{-1} wavenumber (λ = 2.7 - 3.0 μm) that cause stretching vibrations. Also, water absorbs infrared radiation at about 3 μm and some moisture will be vaporized within the fabric. More detailed vibration and rotation energy transition models are described in the literature (SIEGEL and HOWELL, 1981 and STEWART, 1970). Absorption of infrared radiation in 0.76 - 4.0 μm wavelength range may excite the hydroxyl group of the cellulose, the reactive group of the reactive dye by increasing the thermal vibrations and rotation of the molecules. The reaction between cellulose and reactive dyes should therefore be easier and more uniform than that in a hot air fixation process.

(3). Infrared radiation transfer between the surfaces of material

The energy emitted by a surface in all directions at a given wavelength is a strong function of wavelength itself. The rate at which emission from a surface dA$_1$ passes through a surface dA$_n$ may be expressed in terms of the spectral intensity $I_{\lambda,e}$ of the emitted radiation. The directional nature of the radiation is shown in Figure 5.5 in which emission of radiation from a differential area dA$_1$ into a solid angle dω subtended by dA$_n$ at a point on dA$_1$.

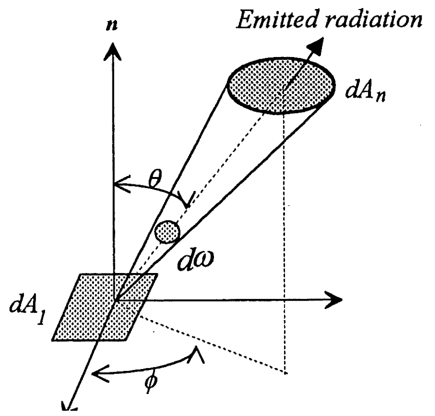


Figure 5.5 Directional nature of radiation

$I_{\lambda,e}$ may be defined as the rate at which radiant energy is emitted at the wavelength λ in the (θ,ϕ) direction, per unit area of the emitting surface normal to this direction, per unit solid angle about this direction, and per unit wavelength interval $d\lambda$ about λ. Therefore, the spectral intensity is then:

$$I_{\lambda,e}(\lambda,\theta,\phi) \equiv \frac{dE}{dA_1\cos\theta \cdot d\omega \cdot d\lambda} \tag{5-24}$$

or

$$E_\lambda(\lambda) = I_{\lambda,e}(\lambda,\theta,\phi)dA_1\cos\theta d\omega \tag{5-25}$$

or

$$E_\lambda(\lambda) = \int_0^{2\pi} \cdot \int_0^{\pi/2} I_{\lambda,e}(\lambda,\theta,\phi)\cos\theta\sin\theta d\theta d\phi = \pi I_{\lambda,e}(\lambda) \tag{5-26}$$

where E_λ is the emissive power at which radiation of wavelength λ leaves dA_1 and passes through dA_n. The total hemispherical emissive power E is the radiation heat flux at which radiation is emitted per unit area at all possible wavelengths and in all possible directions, may be obtained by:

$$E = \int_0^\infty E_\lambda(\lambda)d\lambda = \int_0^\infty \cdot \int_0^{2\pi} \cdot \int_0^{\pi/2} I_{\lambda,e}(\lambda,\theta,\phi)\cos\theta\sin\theta d\theta d\phi d\lambda = \pi I_e \tag{5-27}$$

where I_e is the total intensity of the emitted radiation.

According to the Planck distribution for a blackbody, the spectral emissive power may be obtained:

$$E_{\lambda,b}(\lambda,T) = \pi I_{\lambda,b}(\lambda,T) = \frac{C_1}{\lambda^5[\exp(C_2/\lambda T) - 1]} \tag{5-28}$$

where C_1 and C_2 are the first and second radiation constants. The total emissive energy of a blackbody E_b may be expressed as in terms of the Stefan-Boltzmann Law:

$$E_b = \int_0^\infty \frac{C_1}{\lambda^5[\exp(C_2/\lambda T) - 1]}d\lambda = \sigma T^4 \tag{5-29}$$

where σ is Stefan-Boltzmann constant $(5.670 \times 10^{-8} W/m^2K)$.

The emissivity $\varepsilon(T)$ of a real grey body is given by:

$$\varepsilon(T) = \frac{\int_0^\infty E_\lambda(\lambda, T) d\lambda}{\int_0^\infty E_{\lambda,b}(T) d\lambda} = \frac{E(T)}{E_b(T)} \tag{5-30}$$

The Stefan-Boltzmann law forms the basis of estimating the heat transfer between two radiating surfaces, for example, infrared emitter (r) and cotton fabric (f). The simplest situation occurs when both surfaces are black, are of identical area, and face each other in parallel positions separated by a non-absorbing gas. So the net heat transfer flux for unit area may be expressed by:

$$Q_{rf} = Q_r - Q_f = \sigma\left(T_r^4 - T_f^4\right) \tag{5-31}$$

Actually, the two interradiating surfaces are neither similar in area nor parallel, nor are they black. Hence, the equation has to be modified by:

$$Q_{rf} = \sigma F_\varepsilon F_{r\text{-}f}(T_r^4 - T_f^4) \tag{5-32}$$

where F_ε accounts for the emissivity of both surfaces and may be expressed by ε_r. $F_{r\text{-}f}$ is a shape or view factor which measures how much radiation the fabric surface can intercept from an infrared emitter, and depends on the geometries of the infrared emitter and cotton fabric surfaces and their relative disposition.

According to the same principles as for emitted radiation $I_{\lambda,e}$, incident radiation $I_{\lambda,i}$ may be related to the radiative flux or irradiation G_λ which may be expressed by:

$$G_\lambda(\lambda) = \frac{dG}{d\lambda} = \int_0^{2\pi} \cdot \int_0^{\pi/2} I_{\lambda,i}(\lambda, \theta, \phi) \cos\theta \sin\theta d\theta d\phi = \pi I_{\lambda,i}(\lambda) \tag{5-33}$$

The total irradiation G may be expressed by:

$$G = \int_0^\infty G_\lambda(\lambda) d\lambda = \int_0^\infty \cdot \int_0^{2\pi} \cdot \int_0^{\pi/2} I_{\lambda,i}(\lambda, \theta, \phi) \cos\theta \sin\theta d\theta d\phi = \pi I_i \tag{5-34}$$

The spectral and directional absorptivity $\alpha_{\lambda,\theta}(\lambda, \theta, \phi)$ may be defined as the fraction of the spectral intensity incident in the direction of θ and ϕ that is absorbed by the surface.

$$\alpha_{\lambda,\theta} \equiv \frac{I_{\lambda,i,abs}(\lambda, \theta, \phi)}{I_{\lambda,i}(\lambda, \theta, \phi)} \tag{5-35}$$

The total absorptivity α may be defined as the fraction of absorbed irradiation G_{abs} to the total irradiation (G) absorbed by a surface:

$$\alpha = \frac{G_{abs}}{G} = \frac{\int_0^\infty \alpha_\lambda(\lambda) G_\lambda(\lambda) d\lambda}{\int_0^\infty G_\lambda(\lambda) d\lambda} \tag{5-36}$$

If we consider a large, isothermal enclosure of surface temperature T_S, and such a surface forms a blackbody cavity, the irradiation experienced by any body in the cavity is diffuse and equal to the emission from a blackbody at T_S.

$$G_{abs} = \alpha G = \alpha E_b(T_S) \tag{5-37}$$

Kirchhoff established that the ratio of the total emissive power to the absorptivity α is constant for all materials in thermal equilibrium with their surroundings. If two surfaces, one being black, are held at the same temperature, the emissivity is equal to the absorptivity, that is $\alpha = \varepsilon(T)$.

(5). Infrared radiant heat flux within the absorbing and emitting materials

The incident intensity ($I_{\lambda,i}$) of infrared radiation, as it passes through a material, is dissipated by the phenomena of scattering and absorption. For fabric cotton, radiation scattering and transmission are assumed negligible. Hence, according to the Bouguer-Lambert hypothesis, the energy absorbed by fabric cotton can be calculated as below and shown in Figure 5.6 for a non-emitting and non-scattering medium:

$$dI_{\lambda,i}(x) = -\alpha_{\lambda} I_{\lambda,i}(x) dx \qquad (5\text{-}38)$$

or:

$$\int_{I_{\lambda,i}(0)}^{I_{\lambda,i}(x)} \frac{dI_{\lambda,i}(x)}{I_{\lambda,i}(x)} = -\alpha_{\lambda} \int_{0}^{x} dx \qquad (5\text{-}39)$$

$$I_{\lambda,i}(x) = I_{\lambda,i}(0) \exp(-\alpha_{\lambda} x) \qquad (5\text{-}40)$$

where $I_{\lambda,a}(x) = I_{\lambda,i}(x)$ because of no emission. Thus:

$$I_{\lambda,a}(x) = I_{\lambda,i}(x) = I_{\lambda,i}(0) \exp(-\alpha_{\lambda} x) \qquad (5\text{-}41)$$

where: α_{λ} is assumed to be independent of x.

$I_{\lambda,a}(x)$ is the absorbed intensity of radiation in the x direction

$I_{\lambda,i}(x)$ is the incident intensity of radiation in the x direction

$I_{\lambda,i}(0)$ is the intensity of radiation entering the layer

Since infrared radiation gives exponential penetration within the fabric, absorption of the radiation by the cotton takes place not only at the surface but also to a certain depth below the surface.

If the solid material (cotton fabric) is considered as an absorbing-emitting medium, the radiant heat flux q_r in the control volume dV within the medium may be expressed by:

$$\frac{dq_r}{dx} = \frac{dq_{ra}}{dx} - \frac{dq_{re}}{dx} \qquad (5\text{-}42)$$

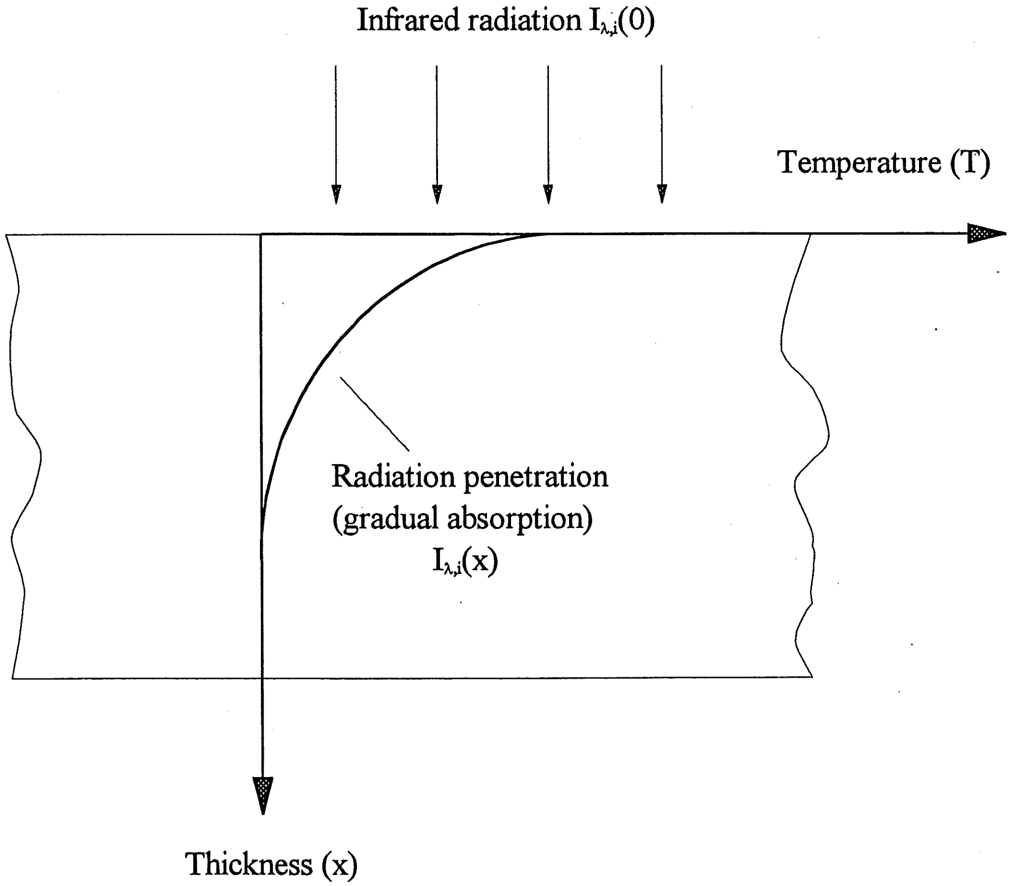


Figure 5.6 Penetration of infrared radiation

or
$$\nabla q_r = \nabla q_{ra} - \nabla q_{re} \tag{5-43}$$

where: q_r is the radiant heat flux within the medium

q_{ra} is the absorbed energy within the medium

q_{re} is the emitted energy within the medium

SIEGEL (SIEGEL and HOWELL, 1981) showed that the absorbed heat flux q_{ra} and emitted heat flux q_{re} in the control volume within the absorbing-emitting medium are expressed by:

$$\frac{dq_{ra}}{dx} = \alpha_\lambda A_f \int_0^\infty \cdot \int_0^{4\pi} I_{\lambda,a}(x) d\omega d\lambda = 4\pi\alpha_\lambda A_f \int_0^\infty I_{\lambda,a}(x) d\lambda \tag{5-44}$$

$$\frac{dq_{re}}{dx} = \alpha_\lambda A_f \int_0^\infty \cdot \int_0^{4\pi} I_{\lambda,b}(\lambda, T) d\omega d\lambda = 4\alpha_\lambda A_f \int_0^\infty E_{\lambda,b}(\lambda, T) d\lambda = 4\alpha_\lambda A_f \sigma T^4 \tag{5-45}$$

where A_f is the area of the cotton fabric.

Hence, the radiant heat flux vector within the medium may be expressed by:

$$\nabla q_r = 4\alpha_\lambda A_f \int_0^\infty [\pi I_{\lambda,a}(x) - \sigma T^4] d\lambda = 4\alpha_\lambda A_f \int_0^\infty [\pi I_{\lambda,i}(0) \exp(-\alpha_\lambda x) - \sigma T^4] d\lambda \tag{5-46}$$

The main challenge in corroborating radiation heat transfer within the absorbing-emitting medium is in the evaluation of the incident intensity $I_{\lambda,i}(0)$. It may be obtained from the Equation of Transfer (EOT), and a development model for EOT was made by BISWAS (BISWAS et al, 1997).

5.3.4 Fick's law of diffusion

Since the same physical mechanism is associated with heat and mass transfer by diffusion, the corresponding rate equations are of the same form for Fick's law which describes the rate equation which may be used to compute the amount of mass being transferred per unit time. For a one-dimensional fabric sheet and the transfer of moisture in a porous material (cotton fabric), having a concentration distribution C(x), the rate equation is expressed as:

$$J_M = -D\frac{dC}{dx} \quad \text{or} \quad J_M = -D\nabla C \tag{5-47}$$

Fick's first law of diffusion can be expressed in terms of the dry-basis moisture content by noting that $C = \rho_f X$, and having moisture distribution X(x)

$$J_M = -\rho_f D\frac{dX}{dx} \quad \text{or} \quad J_M = -\rho_f D\nabla X \tag{5-48}$$

Just as Fourier' law serves to define one important transport property, the thermal conductivity, Fick's law defines a second important transport property, namely, the diffusion coefficient or mass diffusivity, D. The quantity J_M is defined as the mass flux of moisture. It is the amount of moisture that is transferred per unit time and per unit area perpendicular to the direction of transfer, and it is proportional to the average mass density ρ_f within the range of temperature and to the moisture gradient X(x). The diffusion coefficient D depends on the moisture gradient, the structure and density of the cotton fabric, and the temperature. It increases very rapidly with temperature. Normally, it may be experimentally determined.

If the temperature gradient in the direction of mass diffusion is considered, the mass flux J_M becomes equation 5-49 (KEEY, 1972, CHEN, 1996, and HASATANI, 1996) in terms of thermodynamic forces:

$$J_M = -\rho_f D\nabla X - \rho_f D\delta\nabla T \tag{5-49}$$

Equation 5-49 is the starting point for most analyses of moisture migration. The coefficient δ is called the temperature-gradient coefficient $(°C)^{-1}$ and is a measure of the rate at which material is conveyed through the influence of the temperature gradient, and may be described by:

$$\delta = \frac{J_M \Delta x - D\rho_f \Delta X}{D\rho_f \Delta T} \tag{5-50}$$

where ΔT and ΔX are, respectively, the temperature and moisture-content differences over a slice of thickness Δx.

The mass diffusivity D for a binary system is a function of temperature, pressure, and composition, whereas the thermal conductivity k for a pure fluid is a function only of temperature and pressure. The data available on D for most binary mixtures are, quite limited in range and accuracy. Bird provides detailed discussions of available theoretical treatments and comparisons with experiment (BIRD et al, 1960).

5.4 Transport Equations In Drying Processes

5.4.1 Mass transfer equation

Moisture may exist in the liquid and vapour state hereafter designated by the subscripts l and v, respectively. A mass balance for transfer within each state expresses that the rate at which mass (moisture) enters a control volume minus the rate at which it leaves the control volume must equal the rate at which the mass is stored in the control volume.

$$\boxed{\begin{array}{c}\textit{Accumulation rate}\\ \textit{in control volume}\end{array}} = \boxed{\begin{array}{c}\textit{Rate of mass enter}\\ \textit{into control volume}\end{array}} - \boxed{\begin{array}{c}\textit{Rate of mass leave}\\ \textit{from control volume}\end{array}}$$

It is assumed that moisture is neither lost nor created. Hence, we can obtain

$$\frac{\partial(\rho_f X)}{\partial t} = -\nabla(J_l + J_v) \tag{5-51}$$

Where $X = X_l + X_v$ is the total moisture in the liquid X_l and vapour states X_v. Equation 5-49 may be used to evaluate the moisture flux J_l and J_v,

$$J_l = -\rho_f D_l \nabla X_l - \rho_f D_l \nabla T \tag{5-52}$$

$$J_v = -\rho_f D_v \nabla X_v - \rho_f D_v \nabla T \tag{5-53}$$

and the final expression for mass transport after some algebraic manipulations becomes

$$\frac{\partial X}{\partial t} = D\nabla^2 X + D\delta\nabla^2 T \tag{5-54}$$

where $D = D_l + D_v$

5.4.2 Heat diffusion equation

As for the mass transfer balance, the heat energy balance shows that the rate at which energy enters a control volume minus the rate at which it leaves must equal the rate at which the energy is stored in the control volume. There is no energy generation within the wet material.

$$\boxed{\begin{array}{c}\textit{Accumulation rate}\\ \textit{of energy}\\ \textit{in control volume}\end{array}} = \boxed{\begin{array}{c}\textit{Rate of energy enter}\\ \textit{into control volume}\end{array}} - \boxed{\begin{array}{c}\textit{Rate of energy leave}\\ \textit{from control volume}\end{array}}$$

The rate of energy entering the control volume includes the conduction heat rate and the infrared radiant heat flux, and rate of energy leaving the control volume includes the conduction heat rate, the energy of vaporization and the infrared radiant heat flux. Hence, the heat energy transport equation may be expressed (SIEGEL and HOWELL, 1981, BISWAS et al., 1997 and NAVARRI and KAMATA, 1992):

$$\overline{C}_p \rho_f \frac{\partial T}{\partial t} = -\nabla J_Q + \nabla q_r + \rho_f \Delta H_{lv} \frac{\partial X_l}{\partial t} \tag{5-55}$$

Therefore (from equation 5-8):

$$\frac{\partial T}{\partial t} = \nabla(\alpha \nabla T + q_r) + \frac{\Delta H_{lv}}{\overline{C}_p} \times \frac{\partial X_l}{\partial t} \tag{5-56}$$

where $\overline{C}_p$ is the mean heat capacity of the moist material and ΔH_{lv} is the enthalpy difference for a change between the condensed and vapour states, the coefficient $\alpha = k/\rho_f \overline{C}_p$ is called the thermal diffusivity by analogy with the mass diffusivity. X_l is the moisture in the liquid state, and q_r is the total infrared radiant heat flux and may be obtained from equation 5-46.

Substitution of equation 5-54 into 5-56 leads to:

$$\frac{\partial T}{\partial t} = \alpha_e \nabla^2 T + \varepsilon_l \left(\frac{D_{AB,l} \Delta H_{lv}}{\overline{C}_p}\right) \nabla^2 X + \nabla q_r \tag{5-57}$$

where $\alpha_e = \alpha + \alpha_l \delta \Delta H_{lv}$ and ε_l is the fraction of moisture moving in the liquid phase.

Equation 5-57 may be used for infrared drying and fixation processes. In hot air drying and fixation process, since there is no infrared absorption and emission, and no vaporization within the control volume, and the heat energy is transferred by forced convection into the surface of wet material and then by conduction through the wet material. Most vaporization of moisture occurs at the surface of the material. Thus, the terms relating to the internal vaporization in equation 5-57 are neglected and the heat diffusion equation becomes

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T \qquad (5\text{-}58)$$

The pair of transport equations 5-54 and 5-57 or 5-58 may be solved simultaneously according to different initial conditions and boundary layer conditions. More details for the initial conditions and the boundary layer in these transport equations will now be discussed.

5.4.3 Initial and boundary conditions for the heat diffusion equation

The rate of drying of a moist body depends upon the rate at which heat can be supplied. Sometimes, this rate is limited to prevent thermal degradation of the material, but often the rate is limited by the speed at which heat can be conducted through the material, especially in the later stages of drying. The speed of heat transfer within the wet material depends mainly on the boundary and initial conditions.

For a hot air fixation process, equation 5-58 will be used as the heat transfer equation, and the initial conditions can be expressed by

$$T(x,0) = T_0 \qquad (5\text{-}59)$$

where T_0 is initial temperature of wet fabric.

For a fabric sheet of symmetry in Figure 5.1, the temperature gradient at $x = 0$ is equal to zero, that is

$$\frac{dT(0,t)}{dt} = 0 \qquad (5\text{-}60)$$

whereas the boundary conditions at $x = \frac{L}{2}$ may be obtained from the energy balance at the surface of the material. The heat-energy flux at the surface is equal to the energy obtained by convection minus the energy for evaporation. Hence it can be expressed:

$$J_Q = Q_{af} - Q_{evap} \tag{5-61}$$

Therefore:

$$-k\frac{dT(\frac{L}{2},t)}{dt} = h_{af}(T_a - T(\frac{L}{2},t)) - \rho_f(\Delta H_{evap} + \Delta H_{des})\frac{dX(\frac{L}{2},t)}{dt} \tag{5-62}$$

The energy required for water evaporation includes the enthalpy of vaporization and the enthalpy required for water desorption from the hydrophilic fibers.. The drying rate $\rho dX(\frac{L}{2},t)/dt$ may also be obtained in terms of the variation of the air humidity (CÔTÉ, 1988). h_{af} is the heat transfer coefficient by convection from hot air to the fabric.

In infrared drying and fixation processes, the infrared radiation is not only absorbed on the surface of the wet material and transferred into the material by conduction, but also penetrates into the material and is then absorbed. Therefore, internal vaporization of moisture becomes possible. Equation 5-57 may be used as the heat diffusion equation. The conditions from equations 5-59 and 5-60 may also be used for the heat diffusion equation of infrared drying. However, the boundary condition at $x = \frac{L}{2}$ is different from that of hot air drying. It can be obtained in terms of the energy balance at the surface of the wet material. The heat-energy flux is equal to total energy from the infrared radiation absorbed at surface minus the energy by convection with air and energy for evaporation.

$$J_Q = Q_{rf} - Q_{fa} - Q_{evap} \tag{5-63}$$

therefore:

$$-k\frac{dT(\frac{L}{2},t)}{dt} = F_{f-r}\sigma\varepsilon_r\left(T_r^4 - T^4(\frac{L}{2},t)\right) - h_{fa}(T(\frac{L}{2},t) - T_a) - \rho_f(\Delta H_{evap} + \Delta H_{des})\frac{dX(\frac{L}{2},t)}{dt} \tag{5-64}$$

where σ is the Stephan-Boltzmann constant (W/K^{4}cm^2), ε_r is the emissivity of the infrared emitter, T_r is the temperature of the emitter, h_{fa} is the heat transfer coefficient by convection from fabric to air and the constant $F_{f\text{-}r}$ is the shape or view factor and, for the pilot scale infrared oven in the laboratory, is given by (CÔTÉ, 1988)

$$F_{f\text{-}r} = -1.86 \times 10^{-2} W_f^2 + 2.36 \times 10^{-3} W_f + 1.33 E_{rf}^2 - 0.70 E_{rf} + 0.11 \qquad (5\text{-}65)$$

with a linear correlation coefficient (R^2) of 0.9987. In this equation, W_f is the width of the fabric (m), E_{rf} is the distance between the emitter and fabric (m).

In reactive dye-fibre systems, dyeing and fixation are exothermic reaction processes (BIRD and BOSTON, 1975). Since the enthalpy changes for these are very small comparing with the convective and radiative energy transferred during thermal fixation, equations 5-62 and 5-64 do not take into account the enthalpy of dye absorption or of reaction with the cotton. No data are known for these parameters. Even the enthalpy of water desorption ΔH_{des} is also probably negligible. In addition, any influence of salt or dye in the absorbed solution on the various parameters such as ε_γ or ΔH_{evap} is neglected.

5.4.4 Initial and boundary conditions for mass transfer equation

For the mass transfer in hot air and infrared fixation processes, equation 5-54 may be used as the mass diffusion equation. Since equation 5-54 includes the influence of temperature gradient on moisture, equation 5-54 may be solved with equations 5-57 or 5-58. In the absence of a temperature gradient, equation 5-54 for moisture transfer becomes:

$$\frac{\partial X}{\partial t} = D\nabla^2 X \qquad (5\text{-}66)$$

Initially, it may be considered that the moisture is uniform and specified at some value X_0. Thus at $t = 0$, we have

$$X(x,0) = X_0 \qquad (5\text{-}67)$$

For a fabric sheet of symmetry in Figure 5.1, the moisture gradient at $x = 0$ is equal to zero, that is:

$$\frac{dX(0,t)}{dx} = 0 \qquad (5\text{-}68)$$

whereas the boundary conditions at $x = \frac{L}{2}$ may be obtained by the mass balance at the surface of the fabric sheet. In terms of Fick's law (equation 5-48).

$$J_M = M_{evap} \qquad (5\text{-}69)$$

Therefore,

$$-\rho_f D \frac{dX\left(\frac{L}{2}, t\right)}{dx} = h_m (Y_a - Y_f) \qquad (5\text{-}70)$$

where M_{evap} is the evaporation mass flux

h_m is the mass transfer coefficient

Y_f is the air humidity over the fabric

The boundary condition requires a value of the mass transfer coefficient h_m which could be obtained by

$$h_m = \frac{\rho_f D}{(Y_f - Y_a)} \times \frac{dX\left(\frac{L}{2}, t\right)}{dx} \qquad (5\text{-}71)$$

A dependent dimensionless parameter termed the Sherwood number (Sh) may be defined by:

$$Sh_y \equiv \frac{h_m y}{D} = \frac{\rho_f y}{(Y_f - Y_a)} \left(\frac{\partial X}{\partial x}\right)_{x=\frac{L}{2}} \qquad (5\text{-}72)$$

The average Sherwood number (KEEY, 1972) over the whole length L_f for a flat sheet is

$$Sh_L = \frac{1}{L_f} \int_0^{L_f} Sh_y \frac{L_f}{y} dy = 0.33 \frac{\ln(1 + B)}{B} Re^{0.72} Sc^{0.24} \qquad (5\text{-}73)$$

where B is the dimensionless driving force based on moisture

Re is the Reynolds number ($Re = u_m y/\nu$)

Sc is the Schmidt number ($Sc = \nu/D$), ratio of the momentum and mass diffusivities.

The Sherwood number is a dimensionless moisture concentration gradient at the surface and depends on the flow state of the surrounding air and the moisture profile within the boundary layer. It may be expressed as a function of a prescribed geometry, and the Reynolds and Schmidt numbers.

$$Sh_{L_f} = f(y, Re, Sc) \tag{5-74}$$

Thus

$$h_m = \frac{D Sh_{L_f}}{L_f} \tag{5-75}$$

5.5 Drying Rate And Dye Migration During Fixation

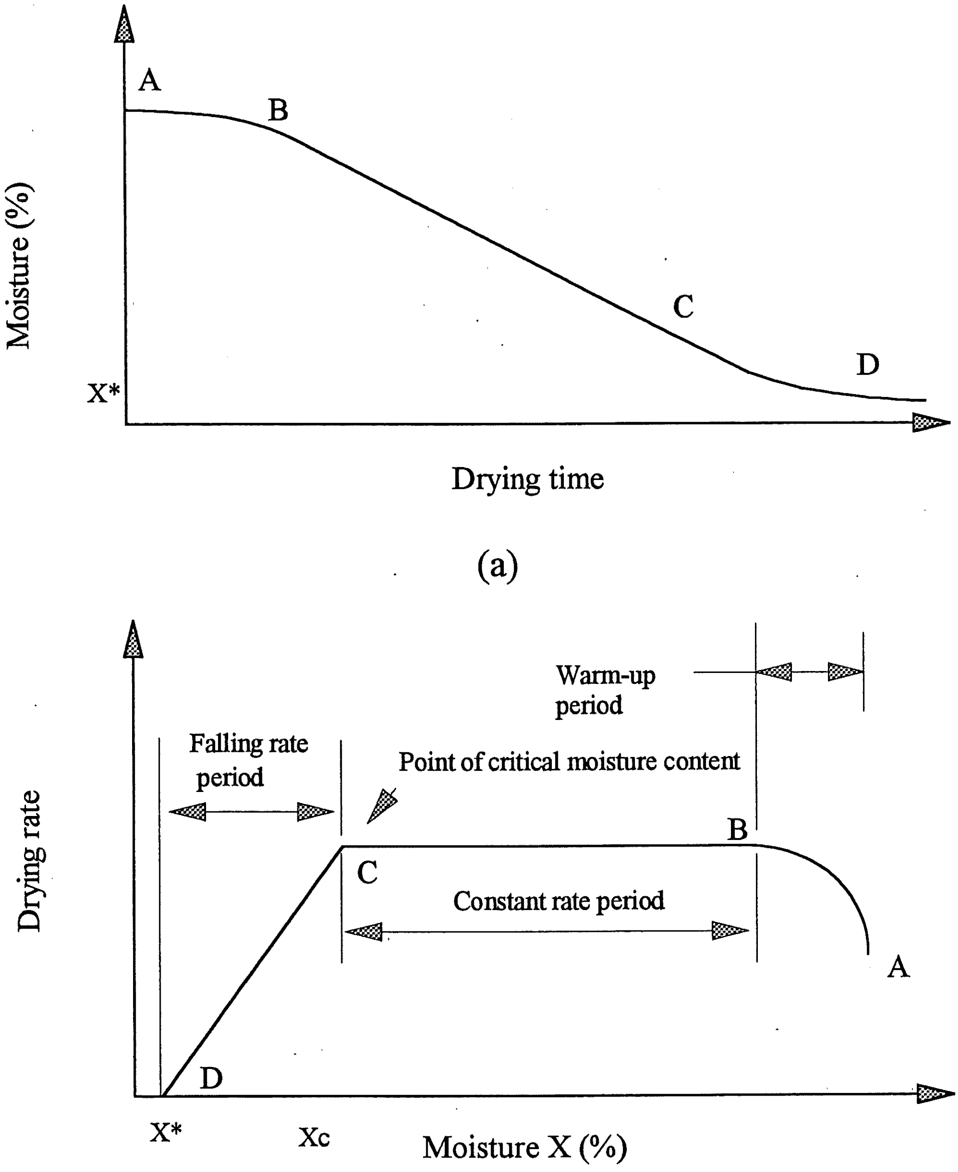
5.5.1 Typical drying curves and mechanism

Drying is the process of removing the water which is contained in the material by converting the liquid water to a vapor and removing this vapor. Evaporation of water requires the addition of thermal energy, nominally equal to the latent heat of vaporization for water (KEEY, 1993). The rate at which drying proceeds depends upon the rate at which thermal energy is transferred to the site of evaporation and the rate at which water is transferred within and from the material. It is normally desirable to achieve the maximum drying rate attainable without inducing material degradation from excessive temperatures within the material.

The typical drying curves are shown in Figure 5.7. Figure 5.7 (a) presents moisture as a function of drying time. Figure 6.3 agrees with this. Figure 5.7 (b) shows the drying rate curve ABCD. The portion AB of the curve represents an initial warm-up period which is an non-steady state period. Section BC represents the constant drying rate period. If the material surface is being heated, the moisture movement within the material must be rapid enough to maintain a saturated condition at the surface. The rate of evaporation balances the rate of heat transfer and the temperature of the water-saturated surface remains constant. The moisture content at the end of the constant-rate period (point C) is termed the critical moisture content X_c and the drying rate at this point is designated as N_c. The total amount of moisture in the material and the elapsed drying time at this critical moisture content are dependent upon the drying rate and the initial moisture content of the material, as well as upon the physical represents the falling rate period. During this period, the moisture flow to the surface of the material is no longer sufficiently rapid to maintain saturation at the surface. The surface becomes partly dry or unsaturated and the drying rate is governed by the rate of internal moisture and energy transport and controlled by diffusion. The influence of the external variables diminishes. When drying fibrous materials to low moisture contents, this period usually predominates in determining the overall drying time. Eventually, the moisture decreases until the equilibrium moisture (X^*) is reached. At this point, drying stops for the given conditions.

The most important mechanisms of moisture transport inside a porous, fibrous material are diffusion of vapor, capillary flow of liquid due to a total pressure gradient, and the evaporation-condensation sequence. There are several important energy transport mechanisms: energy conduction through the fiber structure and through the moisture in the pores, convection by the moving hot vapor and air, radiation transfer within the porous structure, and the evaporation-condensation sequence.

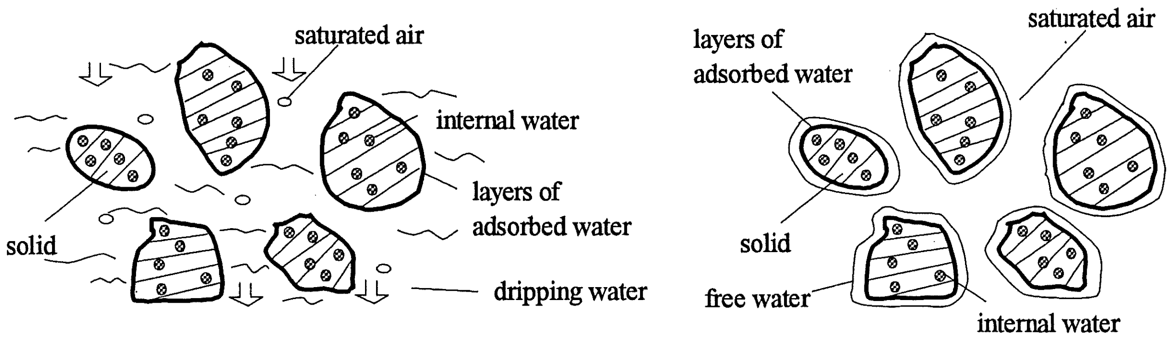
The moisture phases during drying processes are shown diagrammatically in Figure 5.8 (SCHNEIDER and HOSCHKE, 1992). When a textile material has a very high water content, water is transported downwards due to gravitation (phase A). Usually, a textile material after wetting and squeezing between two rollers is in the state shown by phase B where the water content is above the critical value or bound water content. After the initial warm-up period of drying, the surface water begins to evaporate. Since the capillary channels between fibers, connecting inner reservoirs to the surface, are full during the constant-rate drying period, the movement of water to the surface from the internal pores will maintain evaporation at a constant rate. When the water on the fiber and yarn surfaces has completely evaporated (phase C), the rate of drying decreases (falling rate period) until the moisture content reaches the equilibrium moisture (phase D). The water absorbed in the internal structure of the material is difficult to evaporate and transport to the surface.



(a)

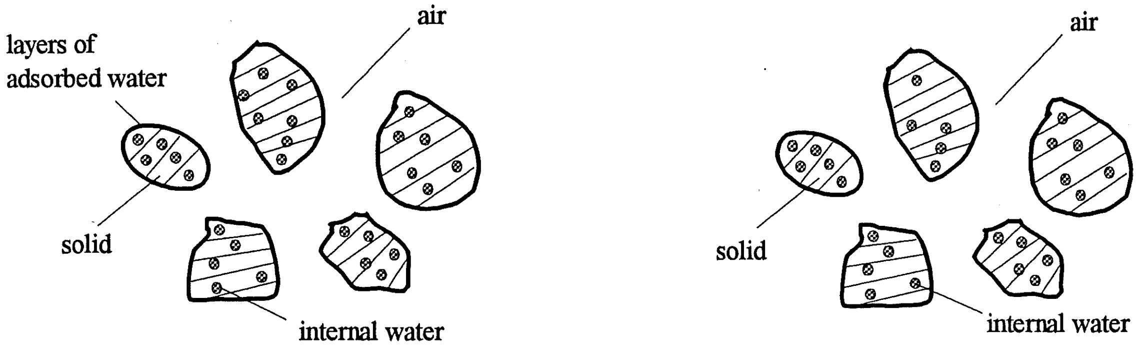
(b)

Figure 5.7 Typical drying curve (a) and drying rate curve (b)



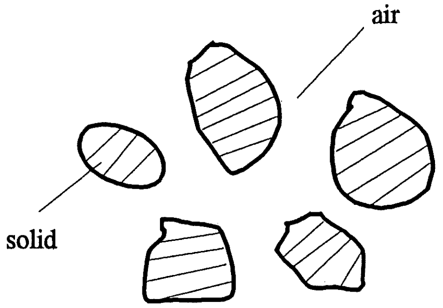
A) Very high moisture

B) Moisture above saturation



C) Moisture below saturation

D) Water is absorbed into structure of material in form of internal layers



E) Dry state

Figure 5.8 The various phases (moisture) diagrammatically

5.5.2 Drying rate

The drying rate N may be defined as the amount of moisture evaporated per unit area and time, and is usually obtained from the variation of the moisture content with time. It depends on whether drying occurs under constant rate or the falling rate conditions, and may be expressed by:

$$N = \frac{J_Q}{\Delta H_{evap}} \tag{5-76}$$

where ΔH_{evap} is the latent heat of vaporization.

The heat flux J_Q at $x = \frac{L}{2}$ which can be used for moisture evaporation may be obtained from equations 5-62 and 5-64, depending on whether hot air drying or infrared drying is involved, and may be expressed by:

$$J_Q = Q_{af} - Q_{cond} = h_{af}(T_a - T(\tfrac{L}{2}, t)) - \left(-k\frac{dX(\frac{L}{2}, t)}{dx}\right) \tag{5-77}$$

for hot air drying process, and by

$$J_Q = Q_{rf} - Q_{fa} - Q_{cond} = F_{f\text{-}r}\sigma\varepsilon_r\left(T_r^4 - T^4(\tfrac{L}{2}, t)\right) - h_{fa}(T(\tfrac{L}{2}, t) - T_a) - \left(-k\frac{dX(\frac{L}{2}, t)}{dt}\right) \tag{5-78}$$

for infrared drying process, where the temperature and moisture gradients, $T\left(\frac{L}{2}, t\right)$ and $X\left(\frac{L}{2}, t\right)$, may be obtained from the solutions of equations 5-54 and 5-57 or 5-58.

If the mass transfer coefficient h_m is known, then the drying rate N may also be expressed by:

$$N = h_m(Y_f - Y_a) \tag{5-79}$$

Since the drying rate may be expressed by:

$$N = -\rho_f Z_f \frac{\Delta X}{\Delta t} = -\rho_f Z_f \frac{dX}{dt} \qquad (g/cm^2 s) \tag{5-80}$$

the drying time can be calculated by:

$$t = \rho_f Z_f \int_{X_2}^{X_1} \frac{dX}{N} \tag{5-81}$$

where Z_f is the fabric thickness.

The constant drying rate may be expressed by N_c at $X = X_c$. The drying time to reach the critical moisture content may be obtained by:

$$t_c = \frac{M_f(X_1 - X_c)}{A_f N_c} \tag{5-81}$$

where X_1 is the initial moisture.

If the portion of the falling-rate period is treated as a straight line with slope m and hence,

$$N = m(X - X^*) \tag{5-82}$$

then

$$N_c = m(X_c - X^*) \tag{5-83}$$

or

$$m = \frac{N_c}{X_c - X^*} \tag{5-84}$$

Substituting equation 5-84 into 5-85, we can obtain the drying rate

$$N = \frac{N_c(X - X^*)}{X_c - X^*} \tag{5-85}$$

The drying time for the falling-rate period may be calculated by:

$$t = \rho_f Z_f \int_{X}^{X_c} \frac{dX}{N} = \frac{\rho_f Z_f (X_c - X^*)}{N_c} \int_{X}^{X_c} \frac{dX}{(X - X^*)} = \frac{\rho_f Z_f (X_c - X^*)}{N_c} \ln \frac{X_c - X^*}{X - X^*} \tag{5-86}$$

5.5.3 Dye migration during drying

Drying usually occurs at higher speed on the surface of a fabric than inside because, for example in hot air drying process, heat must be transferred from the surface of the material into the material and also the surrounding air is not saturated with water vapor. If there are capillary channels between fibers, that connect inner reservoirs to the surface and if the channels are full, migration occurs when water in the fabric's internal capillaries is drawn to the surfaces where rapid evaporation is occurring. This is a key process at moisture contents above the critical moisture content. The transported water will carry with it any chemicals, such as dyes that are in solution or fine dispersion, and these accumulate on the fiber surfaces during drying (BURY and RICHTER, 1984). The degree of dye migration can usually be described by the Kubelka-Munk K/S value (KHALIL, et al., 1981). Microscopic examination of the dye distribution in cross-sections of dyed fabric is also useful for confirming dye migration (see Chapter 6). Dye migration may be described by a model (MCDOWELL et al., 1966).

The textile material can be considered as a continuous or semi-continuous capillary network, with migration of water during drying being mainly through inter-yarn and inter-fiber capillaries. The capillary network will supply liquid to the yarn surface where evaporation is occurring. When the liquid is a solution (dye solution), the actual solute (dyes) transport involved in the liquid movement is referred to as 'solute migration' or 'dye migration' (ROWLAND, et al., 1984). The rate at which dye solution will be supplied to the surface of evaporation is governed by the rate of evaporation of water at that surface (ETTERS, 1990). The rate of evaporation is controlled by the rate of diffusion of water vapor through the boundary layer into the drying air-stream (BENDAK, et al., 1981), and is constant during the constant-rate period of drying as long as the capillary network can supply the surface of evaporation with sufficient liquid. The consequence is that most dye migration can be expected during the period of constant rate drying. When the network becomes insufficient in liquid, it breaks down in an irregular manner, leaving groups of flooded capillaries among large areas of empty capillaries, and a new surface of evaporation is formed beneath the level of the broken-down capillary network. The diffusion of the water vapor causes a fall in the overall evaporation rate (falling-rate period). During this period, the migration of solute will decrease rapidly (BOER, 1980).

Since the capillary channels between fibers, connecting inner reservoirs to the surface, are full during the constant-rate drying period, the movement of water to the surface from the internal pores will maintain evaporation at a constant rate. The migration rate will be constant during the constant rate period of drying. Initial migration of the dye solution to the yarn surfaces, and concentration of this solution by evaporation, will establish a concentration gradient. Once drying enters the falling rate period, migration will also diminish. Hence, the dye migration only in the constant rate period will be discussed.

McDowell developed a dye migration model (MCDOWELL et al, 1966) for the drying processes. The factors to be considered for this model are:

(a) evaporation of moisture at a fixed surface
(b) migration of dyes to the fixed surface
(c) back-diffusion of dyes from the fixed surface
(d) diminution of total solution volume

In this model, the concentration gradient of the dye is caused by evaporation from the surface. It is assumed that this diffusion process will obey Fick's second law, which implies that the concentration of dye $c(x, t)$ must satisfy the equation:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{5-87}$$

The dye migration may be described based on the depth of dye within the fabric, as function of time. It was expressed by:

$$l(t) = l_0 - \int_0^t \frac{N(t)}{A_f \rho_f} dt \tag{5-88}$$

where $l(t)$ is depth of the dye from surface to mid-sheet.
l_0 is the initial depth of dye
$N(t)$ is the drying rate

From equation 5-88, when there is a high drying rate $N(t)$, there results a low depth of dye. Most dye will have migrated to near the surface of the fabric.

Evaporation of the water occurs almost exclusively at the yarn surfaces (MILES, 1985) and dyes will migrate to the surface of evaporation with movement of water from internal pores to the surface. For the infrared drying process, since infrared radiation can penetrate to the inside of the yarns and then be absorbed by cotton fabric, there will be a more uniform temperature profile within the fabric. The evaporation of water will occur throughout the material rather than just at the yarn surfaces. Therefore, the dye migration to the surface will be much reduced (MILES, 1985). Results on the mechanisms of heat and mass transfer in textile webs being dried with infrared radiation have been published (DHIB et al., 1994) but there are no data for thick webs such as geotextiles. Studies have been conducted for paper webs (KUANG et al., 1994 and LAMPINEN et al., 1991) and for combined convective and infrared drying of capillary porous materials (PARROUFFE, 1992a and PARROUFFE et al., 1992b). Radiative drying, however, is known to suppress migration of water (BROADBENT, 1990c). Suppression of dye migration should depend upon the wavelength of infrared radiation. Since short wavelength of infrared radiation can penetrate more easily into the materials than medium wavelength, it gives more uniform heating within the fabric. A detailed study of this phenomenon is highly desirable.

5.6 Analysis And Discussion Of Effect Of Drying Process On Fixation Yield

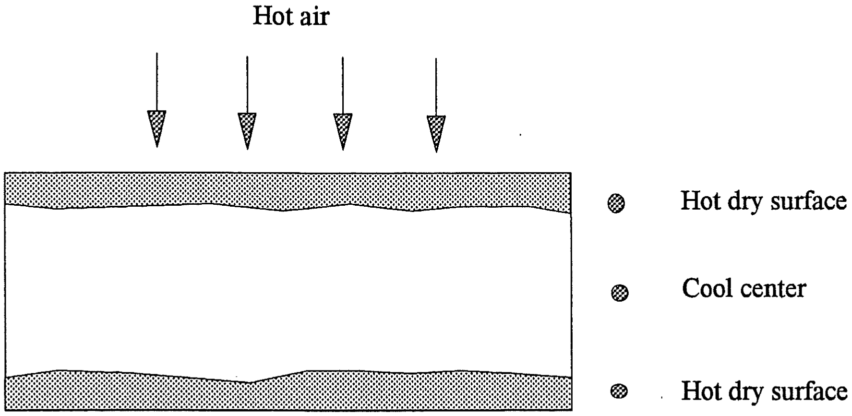
Infrared radiation can penetrate into the fabric to a certain depth from the surface and may be absorbed by the material to be heated. The absorbed intensity of incident radiation can be obtained by Equation 5-41 and the absorbed energy of infrared radiation may be expressed by equation 5-44. In general, penetration increases as the radiation wavelength decreases and short-wave infrared radiation is usually the most penetrating. The total radiant energy flux within the absorbing-emitting material can be obtained by equation 5-46. Comparing the heat diffusion equations for infrared drying (equation 5-57) and hot air drying (equation 5-58), infrared radiation drying should give more uniform temperature distribution within the fabric.

The conversion of absorbed electromagnetic energy into thermal energy occurs throughout the material, producing internal as well as surface heating, and should result in moisture evaporation not only on the surface of the fabric as in hot air drying, but also within the fabric. Thus, the evaporation of water during infrared heating may occur throughout the material (MILES, 1985). Because of the high radiation power density, the drying rate may be much higher than for convection heating (CÔTÉ et al., 1990).

Radiative heating therefore gives a more uniform moisture profile within the fabric which should reduce dye migration during the early stages of drying. Infrared drying and fixation should give a more uniform distribution of dye within the fabric. The uniform distribution of dyes within the fabric for infrared fixation process has been illustrated using measurements of the Kubelka-Munk K/S value and examination of dyed fabric cross-sections (Figures 6.8 to 6.11, and Figures 6.12 and 6.15). For hot air convective drying, water evaporation occurs mainly at the yarn surfaces. Any reactive dye which has not reacted with the cotton fiber will be free to migrate to the surface of evaporation during the constant rate period of drying. This results in non-uniform dye distribution within the fabric. The actual concentration of the dye solution undergoing migration will of course depend on the substantivity of the dye for the cotton fibres. For highly substantive dyes, the magnitude of the change in dye distribution arising from migration will be much less. A comparison of convective hot air and infrared drying behavior is described in Figure 5.9.

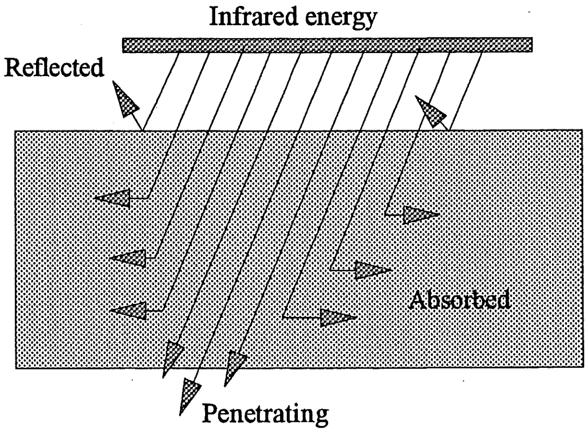
For infrared heating, the internal temperature and moisture profiles are quite different from those for convective heating. Since the wet material is heated more uniformly throughout, evaporation occurs fairly uniformly throughout the material. If the surface is cooled by heat loss to the surrounding atmosphere, inner portions of the sample may dry more rapidly than the surface.

In infrared fixation processes, less migration of dye may improve the fixation yield because the dye distribution is more uniform and could react with cellulose more uniformly. In hot air fixation processes, high dye migration results in non-uniform dye distribution within the fabric and most dye will be accumulated on the yarn surface, and some dye cannot then react with the cellulose and will be washed out. This gives a low fixation yield but a higher color yield.



- Drying depends on outside heat convection
- Surface dye concentration high
- Center dye concentration low
- Uneven moisture distribution within the material
- Uneven temperature distribution within the material

(a) Enlarged view of fabric segment for hot air drying



- Uniform moisture distribution
- Uniform temperature distribution
- Uniform dye distribution

(b) Enlarged view of fabric segment for infrared drying

Figure 5.9 Comparison of convection and infrared drying behavior (SHARMA, 1986)

6. COMPARISON OF INFRARED, HOT AIR AND COLD FIXATION OF REACTIVE DYES

6.1 Introduction

In chapters 3 and 4, fixation conditions of single reactive dyes on cotton were studied. The most important factors influencing the fixation yields were the pH value of the dyeing solution and, for the less reactive dyes, the emitter power and the residence time required in the infrared oven to bring the cotton fabric to a final temperature of about 140°C.

The work described in this section concerns comparison of the fixation yields of several different reactive dyes on cotton achieved by either infrared heating, by hot air heating, or by storing at room temperature (cold pad-batch). For each of these fixation processes, the same dyeing solution was used. The objective was to compare the high fixation yields obtained by infrared heating with those obtained by the alternative fixation methods and to evaluate why the infrared process is so efficient. Considerable migration of water and dye occurs from the yarn interior to the surface during the early stages of drying in hot air and results in high color yield. The color yield which is the depth of color perceived, can be assessed from the slope of the graphs of K/S versus fixed dye, evaluated by reflection spectrophotometry. The color yield is usually greater the higher the proportion of the total dye deposited at the yarn surfaces as a consequence of migration during drying. Dyeings obtained by the cold pad-batch method, in which fixation occurs at room temperature without any drying, served as color yield standards corresponding to zero migration. Any increase in color yield (K/S per amount of fixed dye) above that obtained in the cold pad-batch process should be related to the degree of migration of dye to the yarn surfaces during the initial phase of drying in the infrared and hot air fixation processes. Microscopic examinations of cotton fibre and yarn cross sections were also carried out in an attempt to establish the distribution of fixed dye inside the cotton fibre and yarn, and to evaluate the uniformity of dyeing for different dyeing and fixation processes.

6.2 Experimental

6.2.1 Materials

A 100% cotton woven fabric (164 g/m^2) that had been scoured and bleached was used for all the dyeings. Four reactive dyes with different reactivities were selected for this study. They were: Remazol Black B, Remazol Blue R, Drimarene Red X-6BN and Procion Blue H-ERD. Details of these are given in Table 2.1 in Chapter 2.

6.2.2 Equipment

The equipment used for infrared fixation consisted of a pad unit and an electric infrared oven, shown in Figure 2-1. Two different types of infrared sources were used: quartz tubes which give medium-wave and T-3 tubes which give short-wave radiation. These are described in Section 2.3.

The experimental equipment for the hot air fixation process consisted of a pad bath and a laboratory curing oven (Benz AG, Zurich, Model LTF 97085, 9.0 kW), as shown in Figure 6.1. These were located in the laboratory of C.S. Brooks Canada Inc., Magog, Québec. The wet fabric sample, cut after padding with the alkaline dye solution, was mounted on the pin frame that was fixed onto the guides leading into the curing oven. On activating the mechanism, the pin frame and fabric automatically moved into the hot curing oven for a pre-set time, where upon it automatically slid out again. In the oven, hot air from the air jets, situated 5 cm above and below the pin frame, impinged on both faces of the fabric at a linear speed of 2.0 m/s, as measured with a vane aneometer. The curing oven had a variety of instruments and meters for measurement of the air temperature, the air flow rate and heating time. A hand-held infrared pyrometer, with the Raynger II Data System (on loan from LTEE, Hydro-Quebec), was mounted at the exit of the oven, and used to measure the temperature of the fabric surface as it was returned after heating. The pyrometer optics limit the infrared wavelengths reaching the detector thus preventing errors caused by carbon dioxide, water vapor, sunlight, and material color. The response of the pyrometer is shown in Figure 6.2. The maximum reading obtained was as taken as the final fabric temperature. Figure 6.2 shows that the measuring error would be about 6°C at around 165°C when the curve was extrapolated to t=0.

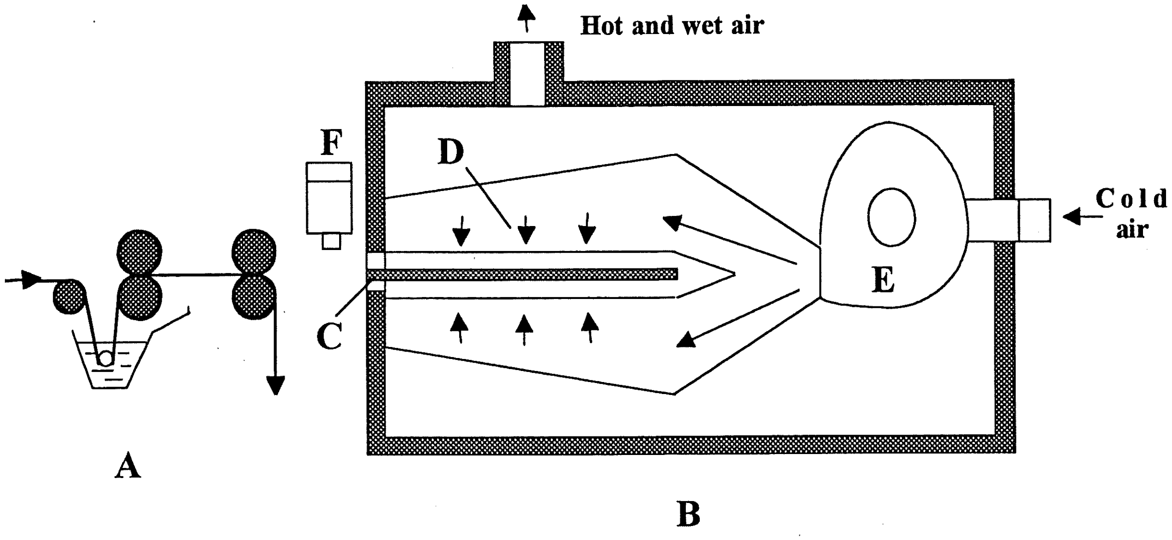


Figure 6.1 Scheme of hot air fixation unit

A. Pad bath	D.Hot air jet
B. Hot air oven	E. Supply fan with heater
C. Pin frame	F. Infrared pyrometer

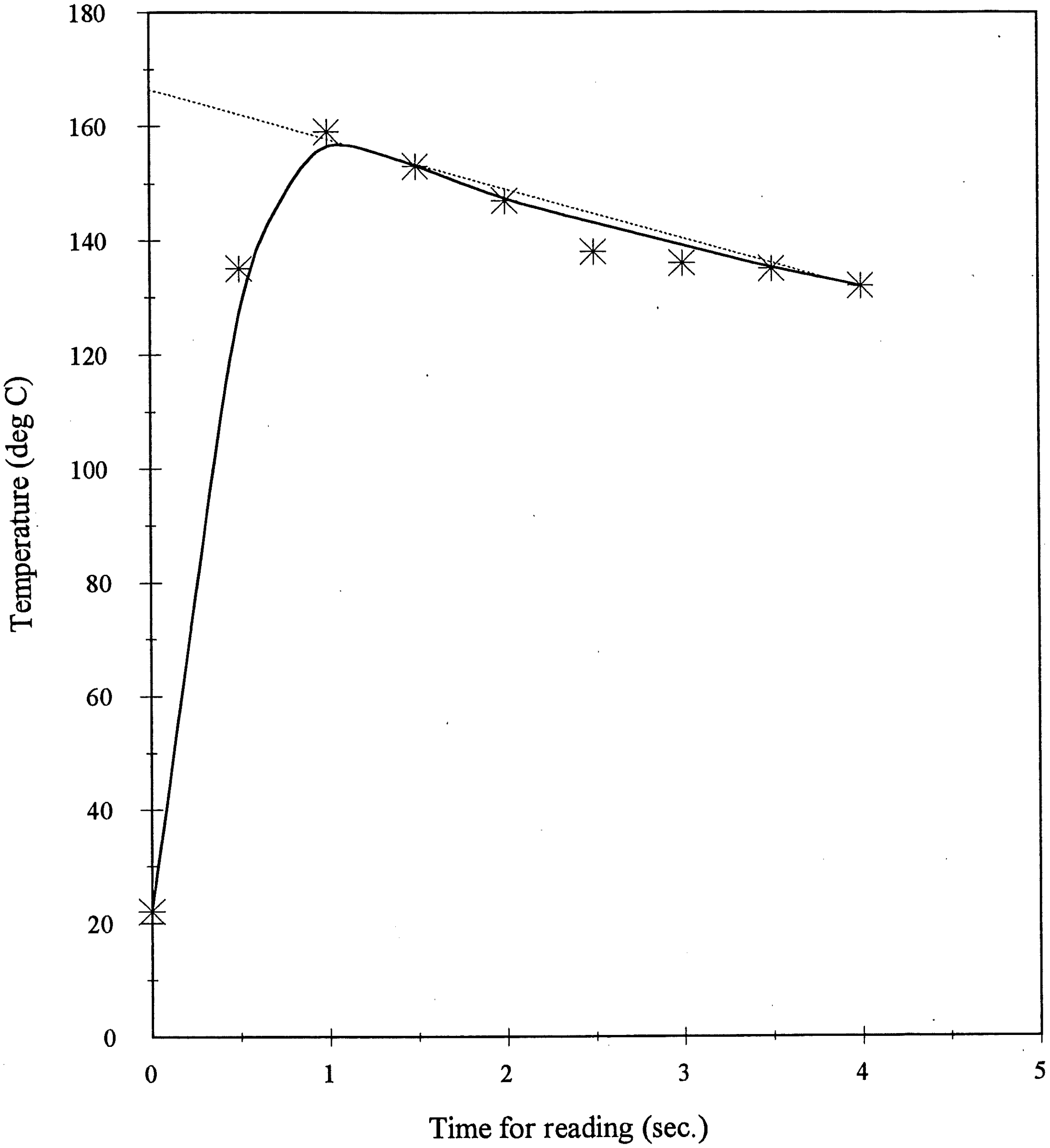


Figure 6.2 Temperature vs time for pyrometer readings

6.2.3 Dyeing and fixation procedures

The concentration of dye in the padding solution was always 20 g/L. The solution also contained NaCl (25 g/L) and NaOH (5 g/L). The dyeing and analytical procedures are fully described in Chapter 2.

In the infrared fixation process, a sample of padded fabric was mounted on a pin frame, that was then placed in the hole on the mesh conveyer, and passed through the infrared oven at various speeds using a total emitter power of 13.06 kW. Then it was quickly moved out from the infrared oven and held stationary for measurement of the fabric outlet temperature using the infrared pyrometer. Again, the maximum reading of the pyrometer was taken as the final fabric temperature.

For the hot air fixation process, a sample of padded fabric was mounted on the pin frame and moved into the Benz curing oven for different residence times. The oven was operated with air temperatures of 172 or 214°C. The fabric surface temperature after fixation was measured by the LTEE infrared pyrometer.

For dyeing trials with pre-drying, padded samples were heated at 75°C for 30 seconds in the Benz curing oven, then placed in sealed plastic bags. The water content of the samples after predrying was reduced to about 34%. When the air temperature of the Benz oven reached 172°C after about 5 minutes, the preheated samples were then heated for different residence times in the oven.

For cold batch fixation, a fabric sample padded with alkaline dye solution was sealed in a plastic bag and stored for 24 hours at room temperature.

Chapter 2 described the washing procedure and analysis method of fabric samples in detail.

6.2.4 Determination of the amount of fixed dye

Kubelka-Munk K/S values at the wavelength of minimum reflectance were used to evaluate the color surface strength of the dyed fabric and were measured using the spectrophotometer (Diano Match Scan II). This was described in Chapter 2. The amount of fixed dye (W_f) retained by the cotton fabric was calculated from the amount of dye initially present and the fixation yield determined according to procedures in Chapter 2 (equation 2-14). The color yield is the slope of the graph of K/S as a function of W_f. (g dye/100 g fabric).

$$W_f = (D_i + D^*) - D_u = (D_i + D^*) \times F_2 \qquad (6\text{-}1)$$

6.2.5 Optical microscopy for cross-section of dyed fibre

The objective of optical microscopy is the examination and evaluation of the degree of dye migration within the cotton fibre and yarn during the drying and fixation process. Samples of fabric dyed with either Drimarene Red X-6BN and Remazol Brilliant Blue R and fixed either by heating in hot air at 172°C, or by infrared heating with quartz tube sources, were examined in this way.

This was one of the most important aspects of the experimental work. The dyed cotton fabrics were embedded in a mold using UV polymerization or curing of methylacrylate monomers or oligomer, and were used to prepare samples for cutting cross-sections (BOYLSTON et al., 1995). A methyl-butyl methylacrylate monomer (60 g) and butyl methylacrylate monomer (40 g) to which was added a 1:1 (w/w) mixture of benzoyl peroxide (1g) catalyst and dibutyl phthalate stabilizer (1 g). This was heated in a water bath until the temperature of the solution slightly exceeded 65°C. The MBM stock solution was then cooled in an ice bath and stored in a refrigerator. The viscosity of the liquid at 4°C was similar to thick syrup. This solution is stable for about one year when kept refrigerated. The pre-prepared polymer solution was provided by M. Farid Motamedian.

The catalyst stock solution consisted of a 1:1 (w/w) mixture of benzoyl peroxide catalyst (1g) and dibutyl phthalate stabilizer (1 g) in methyl methylacrylate monomer (18 g). The catalyst stock solution was stored under refrigeration.

For embedding, catalyst sock solution (1 mL) and pre-polymerized MBM stock solution (5 mL) were combined and stirred. Pieces of dyed fabric were placed into this solution under vacuum, to remove air, and exposed 30 cm from UV radiation sources (350 nm) for 24 hours at -4°C, and then other 24 hours at +4°C. Cross-sections of the embedded fabric, 5 µm thick, were cut using a Richert-Jung Ultramicrotome, were placed on pre-heated microscope slides and covered with cover slips. Photomicrographs were taken at magnifications of x10 using a and covered with cover slips. Photomicrographs were taken at magnifications of x10 using a Carl Zeiss optical microscope and a camera loaded with Kodak Gold 100 ASA Color film.

6.3 Results and discussion

6.3.1 Fabric surface temperature and moisture profile

Measurements of the fabric water content (moisture) and of its surface temperature were obtained by drying samples impregnated with alkaline dye solution for various times in either the infrared or the hot air curing oven. The results are shown in Figure 6.3. The temperature and moisture profiles for infrared heating using both Quartz tubes or T-3 tubes were almost identical. The total emitter power for the T-3 tubes was 17.10 kW while that for the Quartz tubes was 13.06 kW. Hot air drying in the curing oven at an air temperature of 172°C was slower than the infrared processes but slightly faster than these when the air temperature was increased to 214°C. Hence, hot air drying at an air temperature of 172°C had a longer constant drying rate period and thus a longer migration time. All the drying processes showed about the same rate of drying and a stable drying temperature of around 50°C at water contents above about 20%. Once the water content fell below this level, the fabric temperature began to increase, the drying rate began to decrease and migration should come to an end. In all these trials, there was not much difference between the cotton water contents and surface temperatures until after completion of constant-rate period.

6.3.2 Influence of heating method on fixation yield

Based on chapter 5, it was anticipated that the different drying methods would result in different degrees of migration. These trials show the influence of the drying and heating method on the dye fixation yields for the four reactive dyes studied. The fixation yields as a function of heating time are illustrated in Figures 6.4, 6.5, 6.6 and 6.7 for the different infrared and hot air fixation processes. The results can be summarized as follows:

Towards the end of the heating period, the infrared fixation yields have either reached a high maximum value (Black B) or are still increasing sharply (Red X-6BN) as the fabric temperature increases. The fixation profiles for quartz tubes and T-3 tubes are very similar, although the T-3 tubes tended to give somewhat higher fixation in the early stages of heating.

This may be a consequence of the higher power density and more penetration within the yarns and fibers because of the short wavelength of the T-3 tube, so it results in the better suppression of migration during the early stages of drying. On the other hand, more absorption of infrared radiation may result in exciting vibrations of the reactive group and improve the possibility of reaction between cellulose and the reactive dye (detail in chapter 5). The fixation-temperature profiles for hot air heating were all roughly the same shape. Initial fixation was slow, increased sharply once drying was complete, at the end of constant-rate period. The maximum fixation yield, which did not increase more on further heating beyond 40 s, was from 10 to 25% lower than that obtained using infrared heating, apart from the more reactive Black B. This may be a consequence of different dye migration because of different temperature distributions within the yarns and fibers.

The shape of the fixation profile is influenced by the reactivity of the dye towards cotton. For the very reactive Black B (Figure 6.4), infrared fixation is complete at a fabric temperature around 50°C, even before drying is 50% complete. The hot air fixation process eventually gives almost the same fixation yield as infrared fixation, if the heating is continued for long enough. Thus, the high reactivity of this dye at low temperatures produces high fixation. The most striking feature of Figure 6.4 is the large difference in the fixation yields of the infrared and hot air process after about 1-15 s of heating. One explanation might be the effect of the infrared radiation in suppressing migration of the dye during the initial phase of drying. Figure 6.8 for a dyeing heated by hot air at 172°C shows a sharp increase in color yield in the early stages of the process which is indicative of extensive dye migration. The enhanced infrared fixation yields at short times are also likely a consequence of the more efficient penetration of energy into the yarns and fibers which is possible during radiative drying.

For the dye of medium reactivity, Blue R (Figure 6.5), the infrared fixation yield increased steadily with residence time but again there was a marked difference in the degree of fixation after heating for 10-20 s, the hot air processes being much less efficient possibly for the same reasons as above.

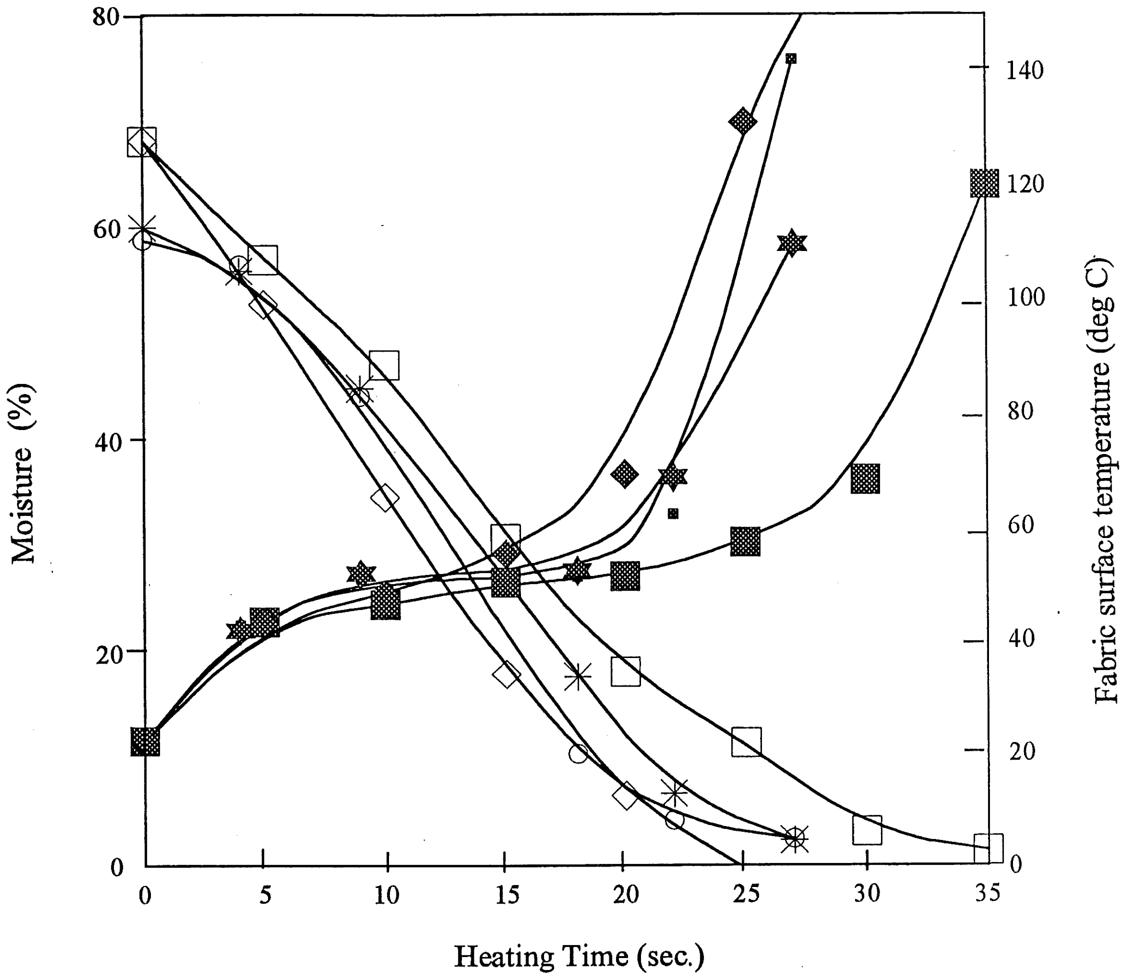


Figure 6.3 Fabric moisture and surface temperature profile

IR by Quartz tube	IR by T-3 tube	Hot air at 172 °C	Hot air at 214 °C
Moisture	Moisture	Moisture	Moisture
—✳—	—○—	—□—	—◇—
IR by Quartz tube	IR by T-3 tube	Hot air at 172 °C	Hot air at 214 °C
Temperature	Temperature	Temperature	Temperature
—■—	—✡—	—■—	—◆—

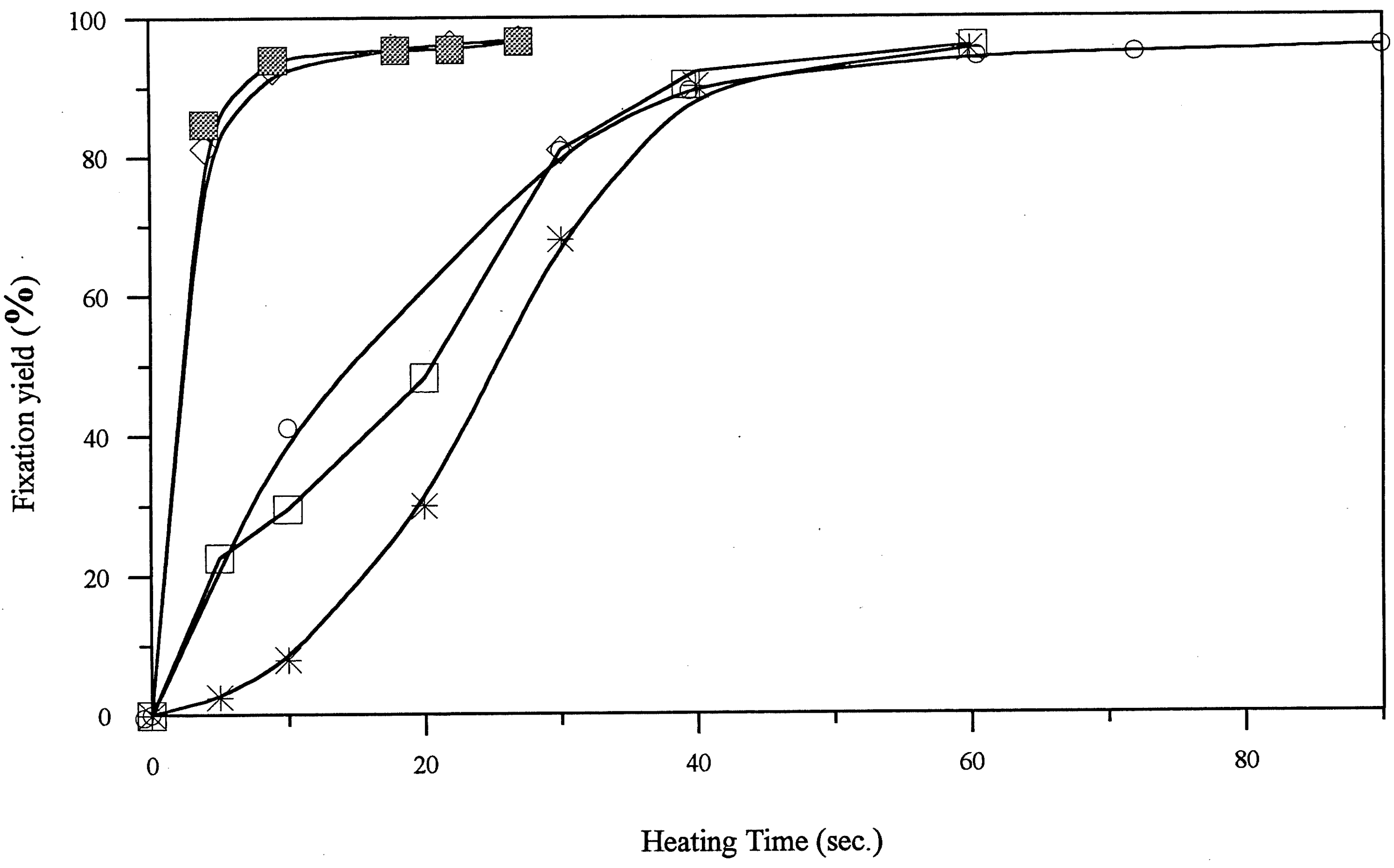


Figure 6.4 Fixation yield vs heating time for Black B

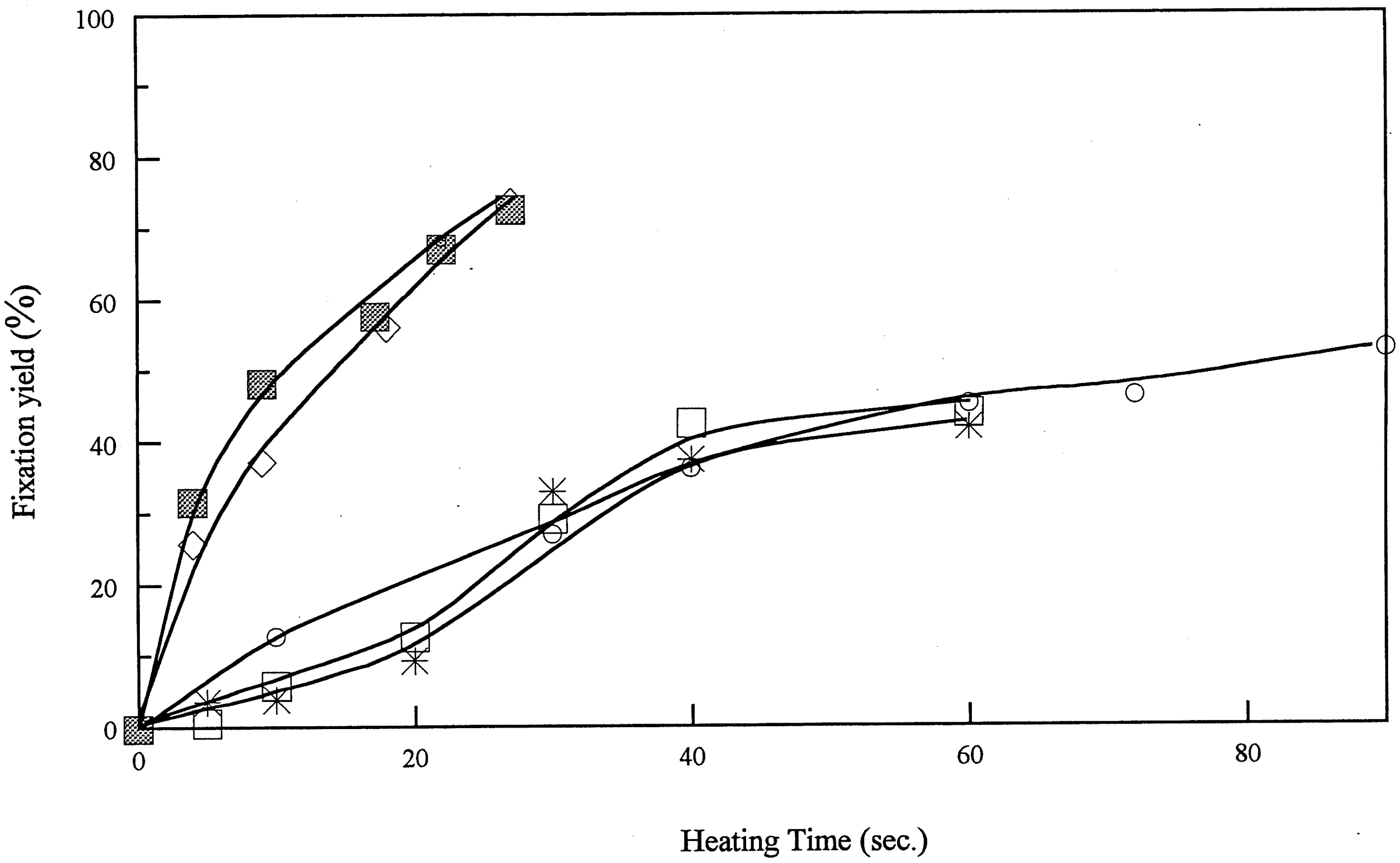


Figure 6.5 Fixation yield vs heating time for Blue R

Hot air at 172°C ✳

Hot air after pre-drying ○

Hot air at 214°C □

IR by Quartz tube ◇

IR by T-3 tube ▨

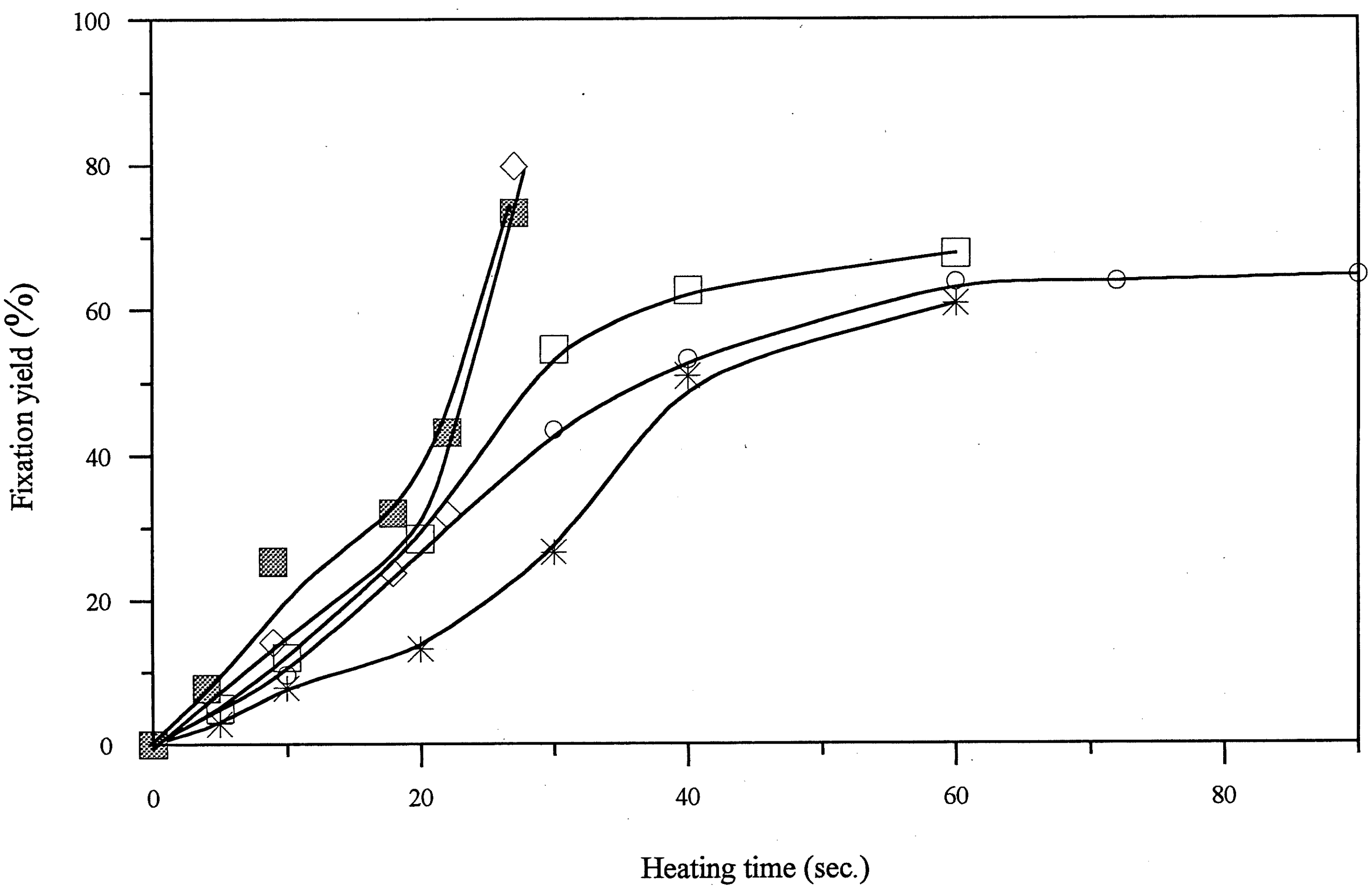


Figure 6.6 Fixation yield vs heating time for Red X-6BN

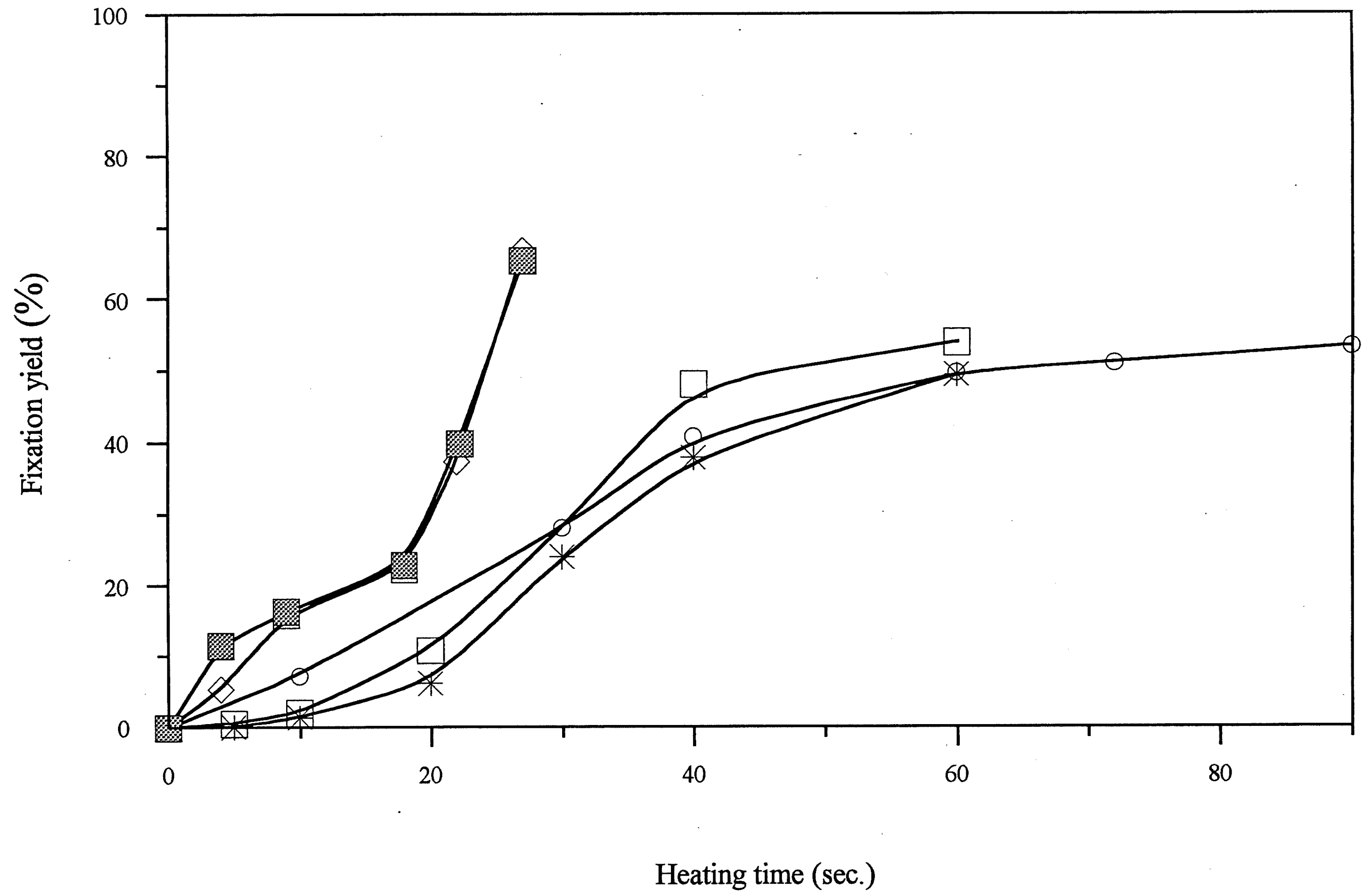


Figure 6.7 Fixation yield vs heating time for H-ERD

The fixation-temperature profiles for the dyes of low reactivity, Red X-6BN and Blue H-ERD (Figures 6.6 and 6.7), were similar but had a quite different shape from those for the high and medium reactivity dyes.

The Red X-6BN and Blue H-ERD did not react rapidly with the cotton at 50°C during the initial stages of drying because of their low reactivity. The fixation did not begin to increase significantly until the fabric temperature began to rise sharply on completion of drying (falling-rate period of drying).

In the early stages of this work, it was thought that perhaps the higher fixation yields obtained by heating with infrared radiation might be a consequence of the high power densities on the fabric surface that are possible with this method of heating. It was felt that this would give rapid drying at a relatively low temperature around 50°C and that this would minimize hydrolysis of the reactive groups of the dyes. This hypothesis was abandoned because of the similar temperature-humidity profiles for the two heating methods. The hot air curing oven with jet impingement of hot air on the fabric surface, proved to be equally efficient in drying the wet cotton. In fact, the temporal variations in fabric water content and surface temperature for the two infrared and two hot air processes used were slight (see Figure 6.3). This, however, does not exclude differences based on the extent to which the two methods of heating influence the initial temperatures within the fibers. The fixation profiles for the two modes of heating were quite different, the yield for fixation in hot air often considerably lagging behind that for infrared fixation. This was particularly true for the more reactive Black B and Blue R. The effect was less pronounced for the Red X-6BN and Blue H-ERD.

Hot air fixation at a temperature of 214°C, was more rapid than at 172°C and gave slightly higher fixation yields, although the fixation profiles at both temperatures were similar. It was anticipated that the use of hot air at 214°C would result in more rapid drying, a shorter constant rate drying period and less migration.

Pre-drying the impregnated sample in the curing oven for 30 s at an air temperature of 75°C did not produce particularly significant effects on the hot air fixation yields because the water content was still quite high about 35%. The effect of pre-drying on the fixation yield for Black B was quite pronounced but this is likely the effect of temperature on the high reactivity of this dye. In other cases, the effects were minimal.

In these trials, using the same dye solution containing 5 g/L of NaOH, the heating profiles were very similar and the much lower fixation yields for heating in hot air are significant. The high yields that were possible for infrared fixation are quite remarkable, particularly for the dyes of low to medium reactivity. With good temperature control, and the possibility of holding the temperature at 140-150°C, fixation yields above 90% should be achievable without thermal damage to the cotton.

6.3.3 Influence of heating method on the color yield of the dyeing

For all of the dyeings obtained at different residence times in the infrared or the curing oven, the depth of the surface color was evaluated by measurement of the Kubelka-Munk K/S value at the wavelength of minimum reflectance. The K/S values corresponding to different fixation times were plotted against the amount of dye fixed on the cotton (equation 6.1) as shown in Figures 6.8 to 6.11. The color yield of a dyeing is the depth of color obtained from a given amount of dye and can be assessed from the slope of the graphs of K/S versus fixed dye. The results are summarized as follows:

In fixation using the cold pad-batch method, fixation occurs at constant water content and temperature without any heating or drying. Under these conditions, it is assumed that there is no migration of water or dye to the yarn surfaces. This method gave the lowest color yield with K/S a linear function of fixed dye in the cotton. Cold batch fixation produces dyeings with more uniform dye distribution and fixation within the yarns and fibers.

Apart from one point for the Red X-6BN, the color yields for dyeing obtained by infrared heating using the short-wave T-3 tubes were very close to that obtained by the cold pad-batch method. The shorter wavelengths from a T-3 emitter can penetrate into the wet cotton the results clearly show the almost total suppression of dye migration. For most textile materials including cotton, the fabrics strongly absorb the radiation of wavelength longer than 2 microns. Infrared radiation that is not reflected or absorbed can penetrate into the fabric to a depth which depends on the wavelength and the fabric properties. Generally, the shorter the wavelength, the greater the penetration. As the infrared penetrates the fabric (ORFEUIL, 1986), infrared heating would give a more uniform temperature profile within the fabric than hot air heating which was discussed in Chapter 5. Therefore, water evaporation in infrared

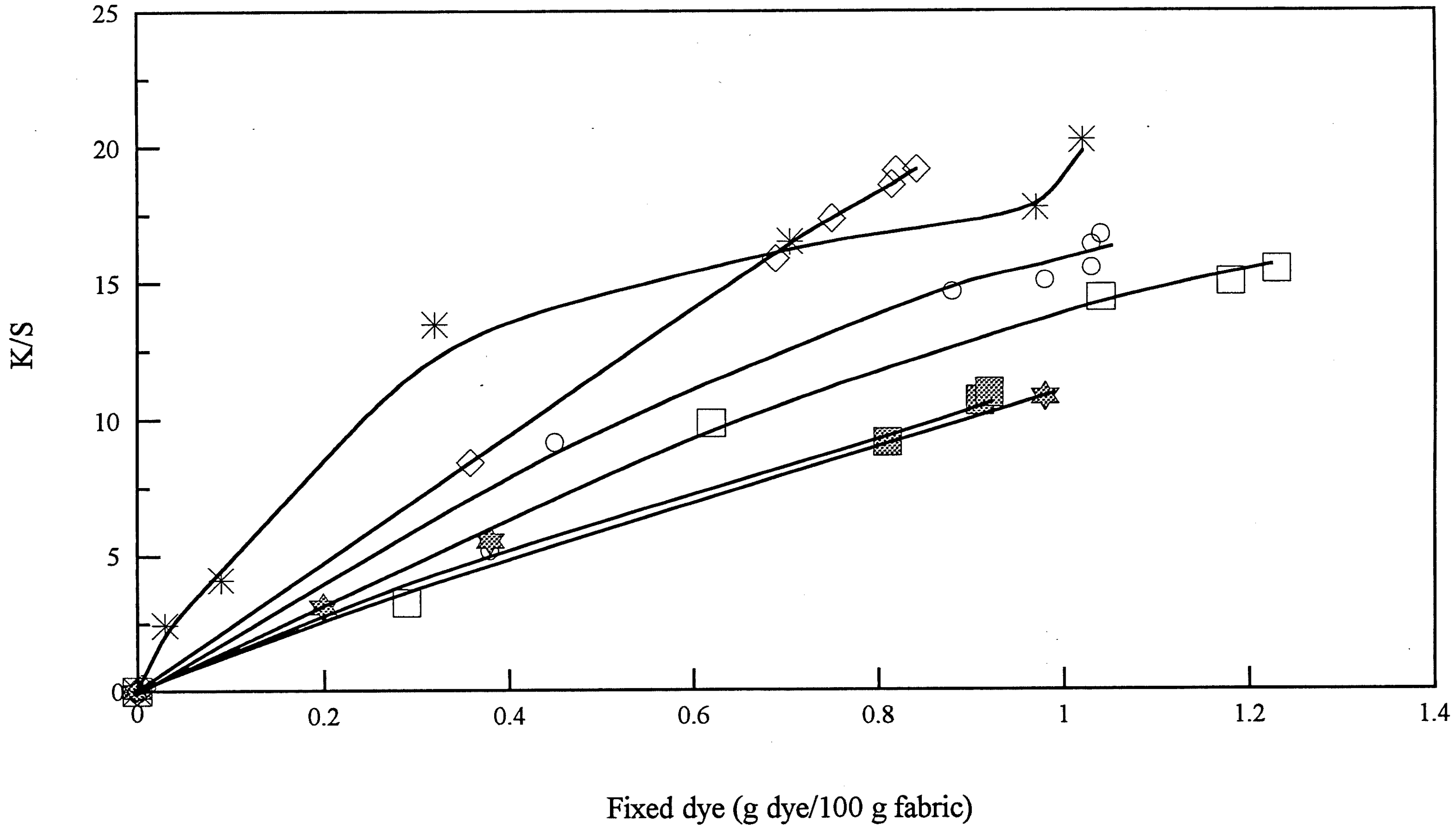


Figure 6.8 K/S value vs fixed dye for Black B

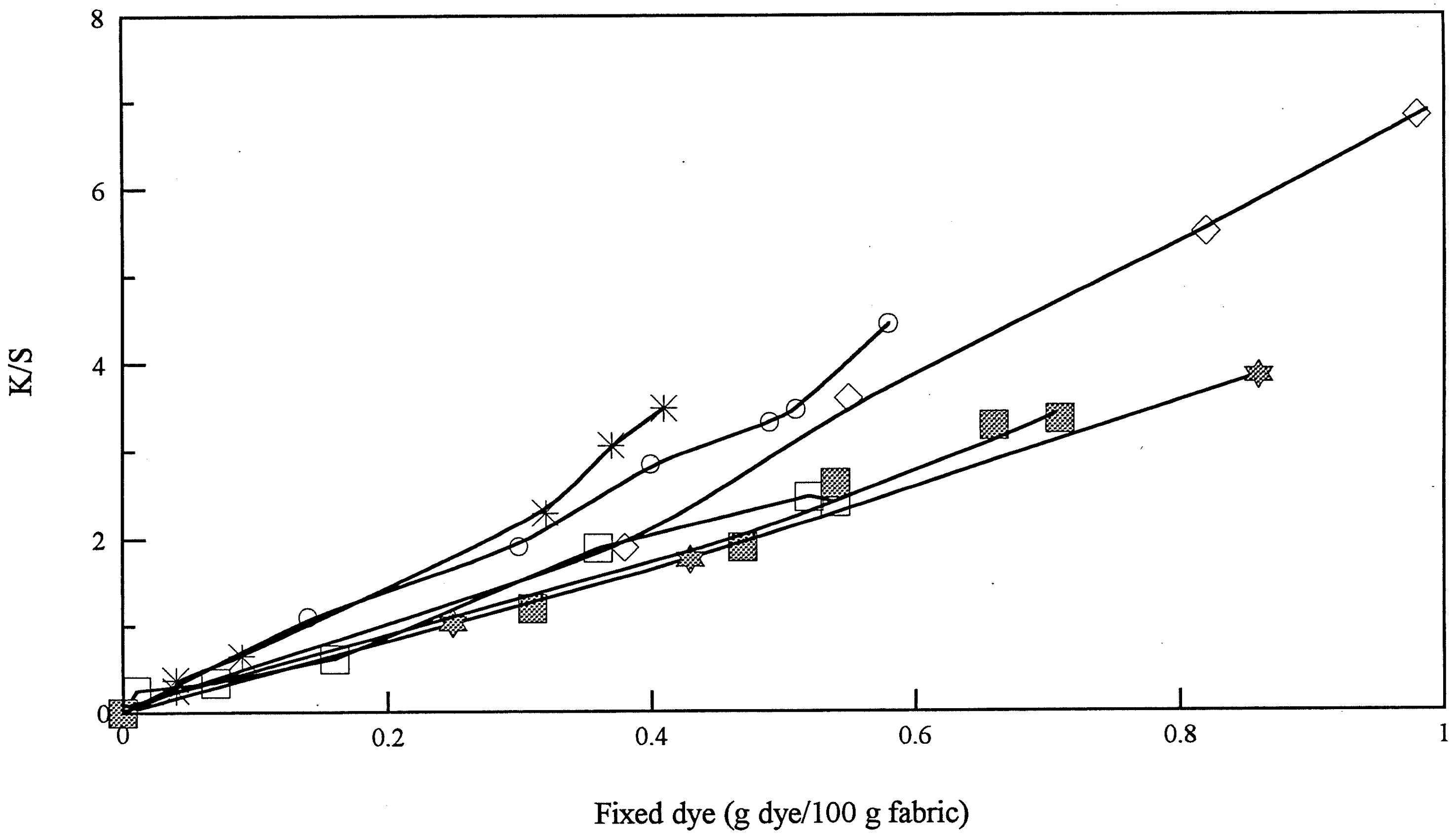


Figure 6.9 K/S value vs fixed dye for Remazol Blue R

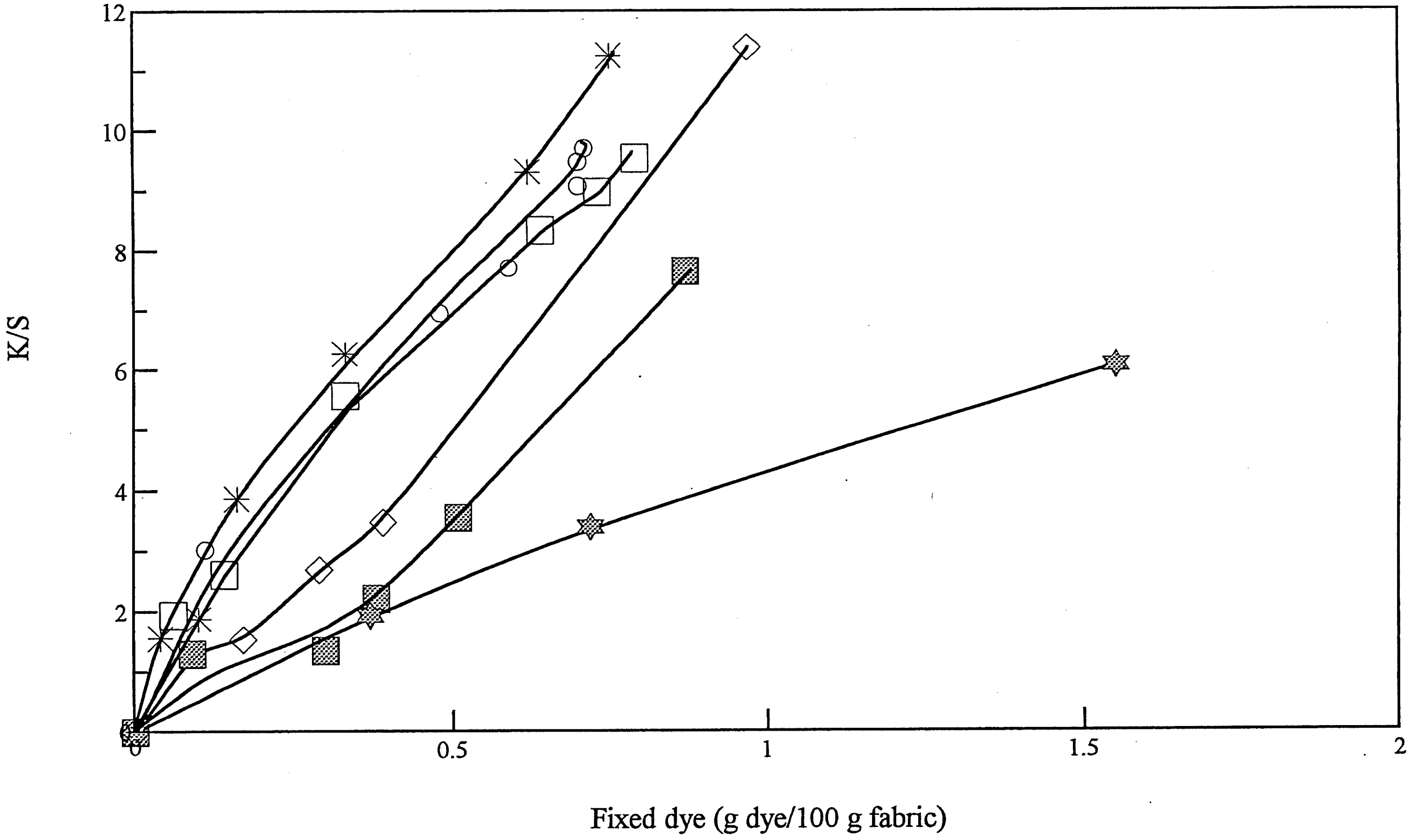


Figure 6.10 K/S value vs fixed dye for Red X-6BN

Hot air at 172 °C ✳

Hot air after pre-drying ○

Hot air at 214 °C □

IR by Quartz tube ◇

IR by T-3 tube ▨

Cold batch ✡

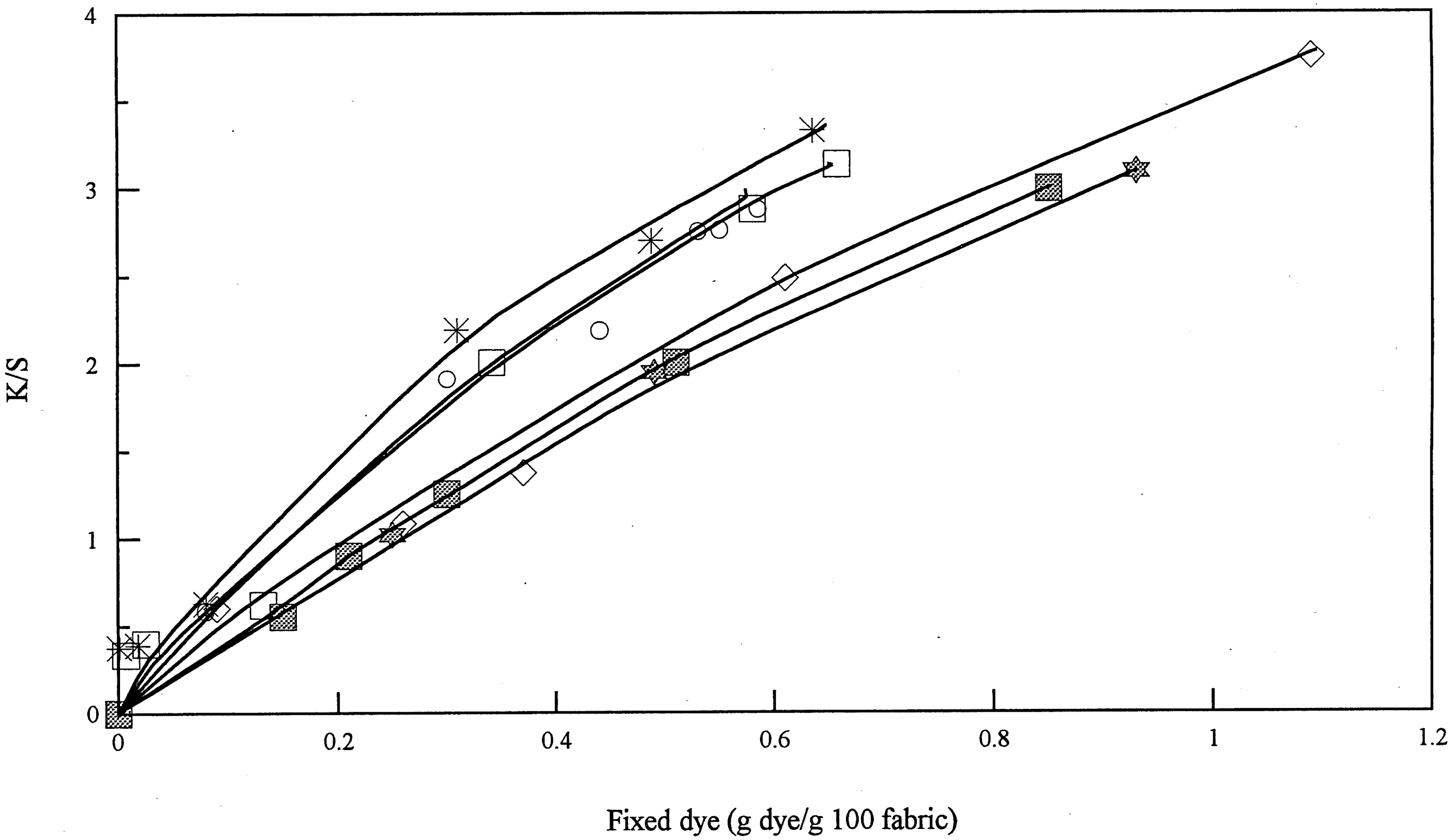


Figure 6.11. K/S value vs fixed dye for Blue H-ERD

drying could occur not only on the fabric surface but also within the fabric. This may be a major reason for the suppression of migration of water from the yarn interiors to their surface. The results show, that infrared heating, particularly with T-3 tubes, gave low dye migration during the thermofixation dyeing process.

Fixation in hot air at 172°C always had the highest color yield apart from the Black B at the end of the heating period. The color yield for dyeing obtained by heating in air at 214°C was generally lower than at 172°C indicating a lower degree of migration for the higher heating temperature.

The color yields for dyeing obtained using infrared heating with medium-wave quartz tubes were usually less than for fixation in hot air at 172°C and less than for hot air fixation at 214°C for the less reactive Blue H-ERD and Red X-6BN.

Pre-drying followed by hot air fixation at 172°C did decrease the color yields somewhat compared to dyeing heated at the same temperature but not pre-dried. This shows that the pre-drying conditions were not appropriate, possibly because the pre-drying was carried out in the hot air curing oven. Although the air temperature was quite low, and the drying time short, the water content was relatively high, around 35%, after predrying. Unfortunately, it was not possible to pre-dry padded fabrics using infrared drying at the location of the curing oven.

6.3.4 Examination of cross section of dyed fabric by optical microscopy

Cross sections of cotton fabric from dyeings with Drimarene Red X-6BN and Remazol Blue R were examined by optical microscopy. The dyeings were obtained by hot air fixation at 172°C and infrared fixation processes using quartz tubes. The photomicrographs of cross-sections of dyed fabric are in Figures 6.12, 6.13, 6.14 and 6.15, which show hot air and infrared fixation with Blue R, and hot air and infrared fixation with Red X-6BN, respectively.

Figure 6.12 for Blue R shows that most reactive dyes have migrated from the interior to the surface of the fabric or yarn, and some were fixed on the surface of the fabric or yarn. Since there is a temperature difference between the interior and surface of the fabric, hot air drying always gives higher dye migration because water moves from the interior to the surface. Not all the reactive dye migrating from the yarn interior to the surface may react with cotton and thus will be washed out after dyeing. Thus, the fixation yield would be reduced for hot air fixation processes. Figure 6.14 for Red X-6BN also shows that the hot air fixation process gives higher dye migration. Red X-6BN and Blue R of low or medium reactivity also have low substantivity. The term substantivity is often used as a qualitative description of the affinity of a dye for a particular fibre, which is the difference between the chemical potential of the dye in its standard state in the fibre and the corresponding chemical potential in the dyebath (BIRD and BOSTON, 1975). The substantivity is defined as the attraction between a substrate and a dye under the precise conditions of test. Since Red X-6BN and Blue R have low reactivity and substantivity, most of their reaction with the cotton fibre occurs in the falling drying rate period when the reactive dye has already migrated to the surface of the fabric or yarn. Dye that reaches the yarn surface is less likely to react with the cotton and will be washed out. The hot air fixation process would thus have a lower fixation yield. Since infrared fixation gives a more uniform temperature profile within the fabric and suppresses dye migration, as shown in Figures 6.13 and 6.15 it can give a higher fixation yield but a lower color yield for the same amount of fixed dye.

Although the relationships between dye migration and fixation yield can not be correlated theoretically or in mathematical model, the photomicrographs show that hot air fixation process with both reactive dyes results in high migration of the dye, whereas infrared fixation for both reactive dyes presents more uniform dye distribution within the dyed fabrics because of less dye migration. From analysis of Chapter 5, hot air drying process would cause a temperature difference between the surface and interior of the fabric, and results higher dye migration when water move from interior to surface of fabric or yarn (evaporation process). On the other hand, since infrared radiation can penetrate into the fabric or yarn and cause more uniform temperature distribution or less temperature difference between surface and interior of the fabric, less dye migration for infrared fixation process could be obtained. In the Chapter 6, the experimental results (Figures 6.8 to 6.11) also demonstrate that hot air heating and fixation process caused higher color yield (higher dye migration) for the same fixed dyes, whereas infrared fixation process gave less color yield which even close to that in cold batch fixation. Hence, the photomicrographs of cross-section of dyed fabric show agreement with the results in Chapter 6. Experimentally, they could be used to confirm the dye migration could be a main reason why hot air fixation give low fixation yield whereas infrared fixation give a high.

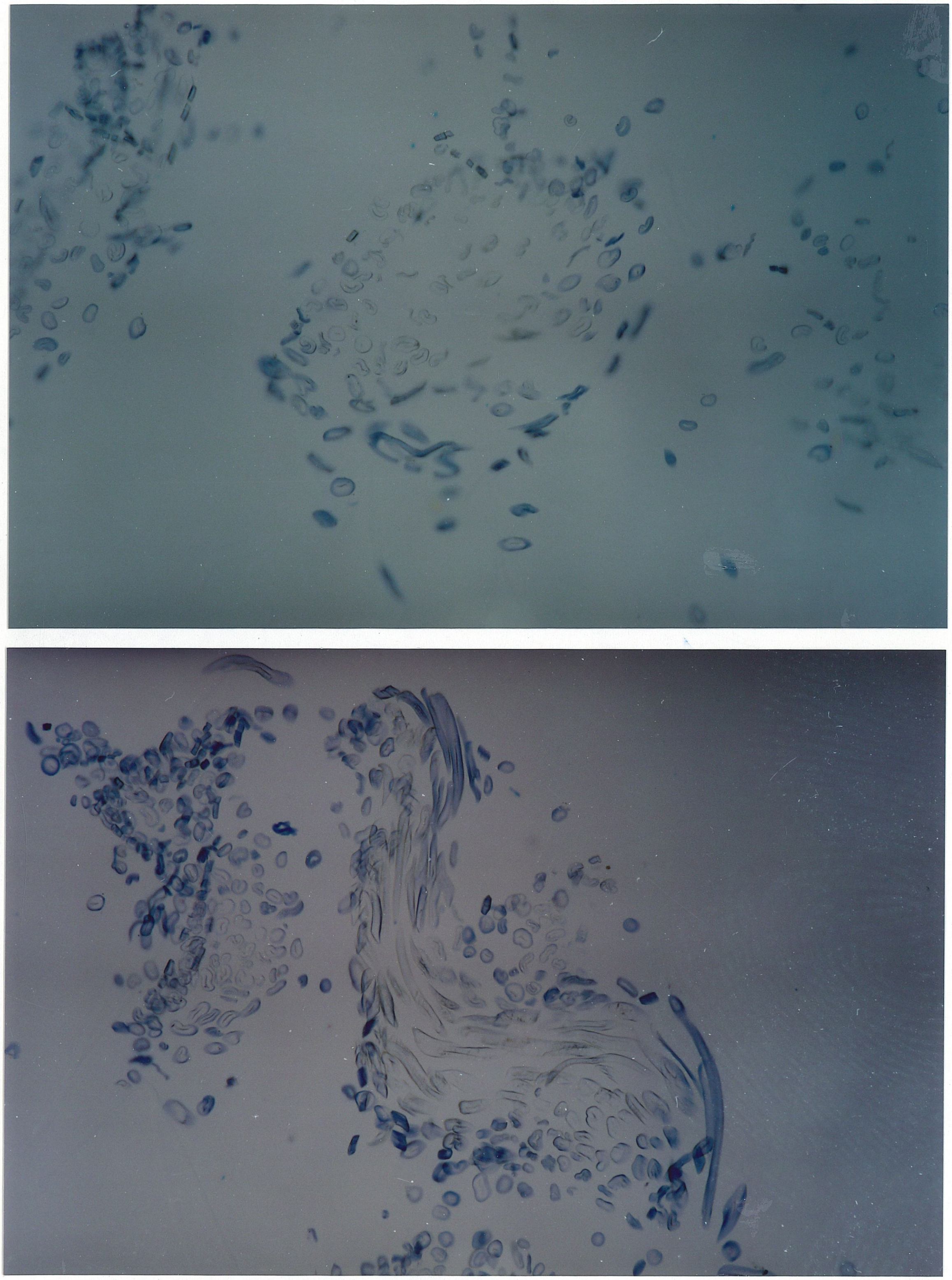


Figure 6.12 Cross section of dyed cotton fabric by optical microscope for Remazol Blue R in hot air fixation at 172°C

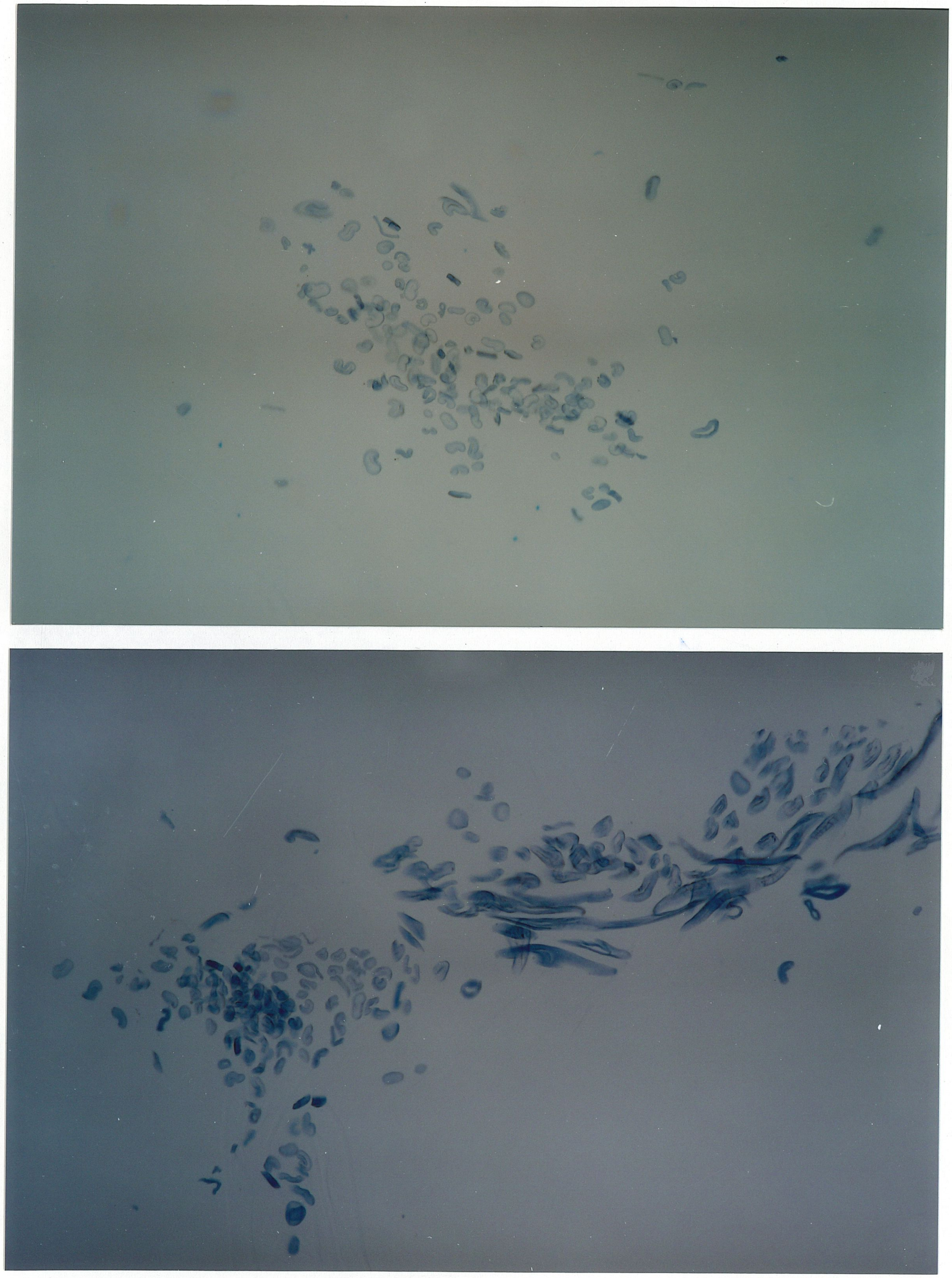


Figure 6.13 Cross section of dyed cotton fabric by optical microscope for Remazol Blue R in infrared fixation by Quartz at 13 kW

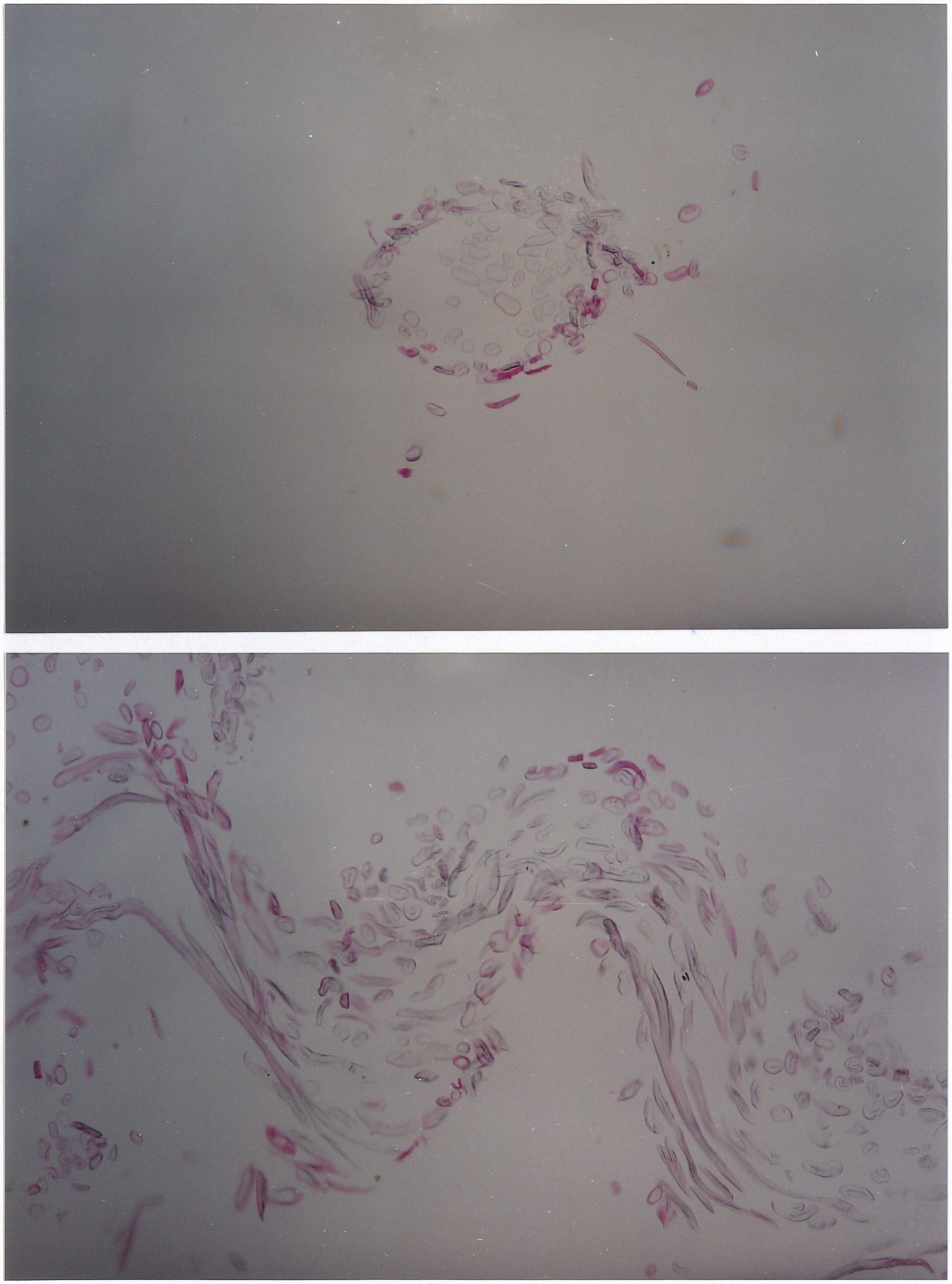


Figure 6.14 Cross section of dyed cotton fabric by optical microscope for Drimarene Red X-6BN in hot air fixation at 172°C

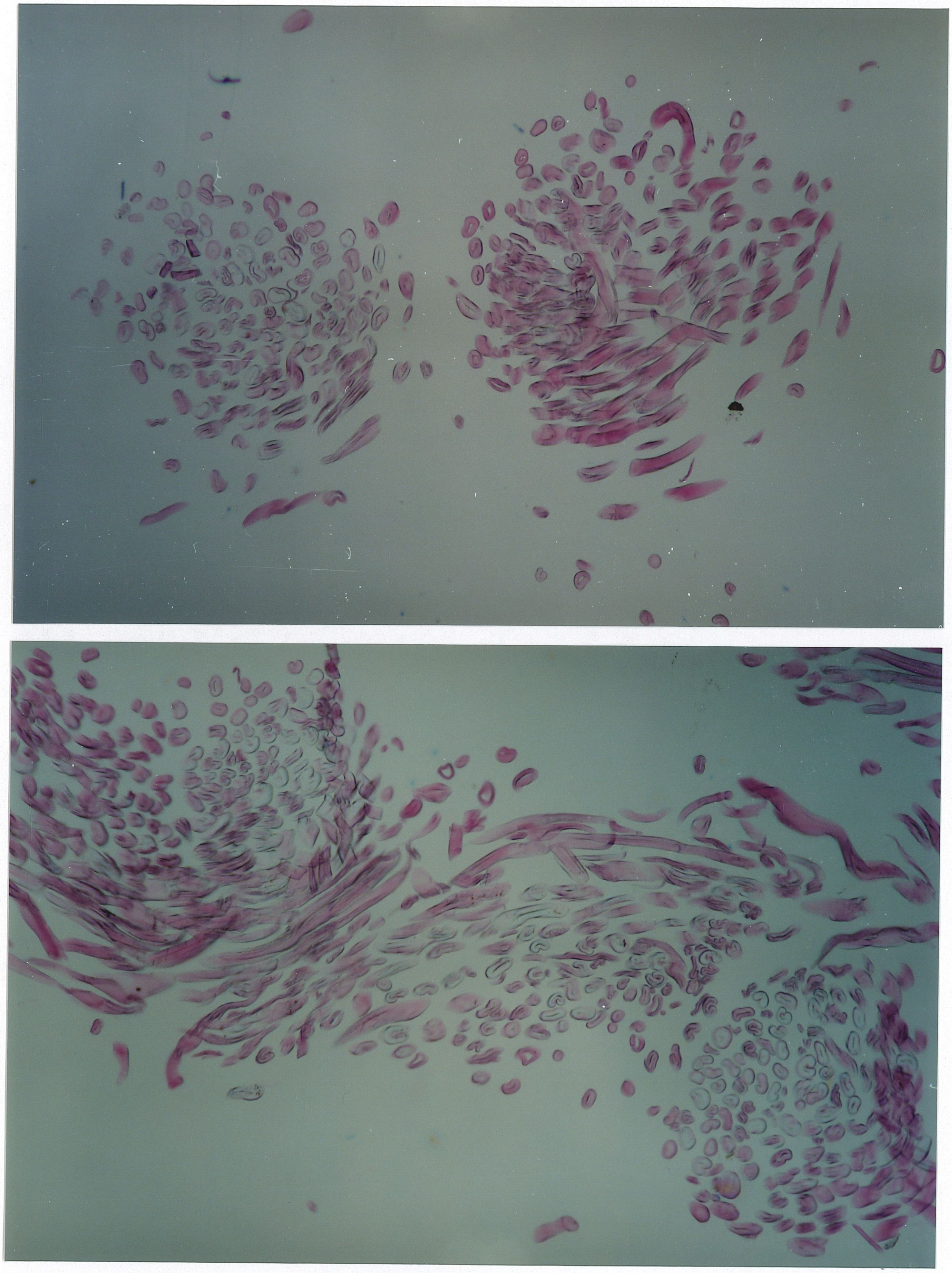


Figure 6.15 Cross section of dyed cotton fabric by optical microscope for Drimarene Red X-6BN in infrared fixation by Quartz at 13 kW

6.4 Conclusions

The results showed considerable differences in both the dye fixation yields and the fabric color strengths for dyeings obtained using either infrared heating or hot air as the means of inducing fixation. The infrared processes gave high fixation yields and relatively low color strengths or color yield whereas for the hot air processes, the fixation yields were lower and the color strengths higher.

Clearly, infrared radiation is capable of inducing high levels of fixation of reactive dyes on cotton and also of suppressing migration of the still unfixed dye in the early stages of drying. It is tempting to conclude that the suppression of the dye migration is the reason for the higher fixation yields. One could argue that migration of the unfixed dye to the yarn surfaces, once drying is underway, prevents its diffusion into the fibers within the yarn bundle. Dye on the yarn surface is much less able to react with the cellulose and thus will eventually be washed off the fiber surfaces. The examination of cross-sections of the cotton fabric from dyeings by optical microscopy experimentally provide linking these two separate phenomena - high fixation and low migration. The photomicrographs shows that infrared fixation may provide more uniform dyeing within the cotton fabrics with much less migration of dyes, whereas the hot air fixation gave higher migration of dyes and color yield. Recent work (BROADBENT and SANDIE, 1996) has indicated that such a relationship might exist and high levels of fixation ought to be possible for any dyeing method in which migration is suppressed, for example by predrying or vacuum extraction, and fixation is induced by any form of heat transfer. Two processes which merit further examination and which might provide information to support the suggestion of a link between migration suppression and high fixation are:

1. Pad - infrared pre-dry - bake in hot air
2. Pad - vacuum extract - (pre-dry) - bake in hot air

Another possibility remains. The high levels of fixation that have been found for infrared heating may arise from vibrational activation of the dye molecules. This would involve absorption of the wavelengths of infrared radiation responsible for exciting the vibrations of the bonds of the specific reactive group of the dye. With a high level of vibrational energy, the dye may react more rapidly with the cellulosate ions in the cotton.

7. CONTINUOUS DYEING AND INFRARED FIXATION PROCESS

7.1 Objectives

In the previous section, all the infrared dyeing and fixation processes were carried out using small samples which were passed through the infrared oven. The objective of the last phase of the work was to demonstrate that this new dyeing process using infrared fixation could be run on a continuous basis and give the high fixation yields previously found with good color consistency over a period of time.

7.2 Experimental

7.2.1 Materials

Bleached woven cotton fabric with a superficial weight of 132 g/m^2 was cut into strips 25 cm wide which were sewn together and wound up to form a large roll of fabric. The reactive dye used was Drimarene Red X-6BN. All other chemicals, salt and alkali were reagent grade.

7.2.2 Equipment

The equipment consisted of a pad bath, a chemical metering pump, the electric infrared oven and an electrically driven take-up roller with a potentiometer speed controller. The set up is illustrated in Figure 7.1. The volume of pad bath was 1 L and the level of dye solution in it was maintained constant by continuous addition of fresh alkaline dye solution using a chemical metering pump (Model DM2-1, MWP 125 psig, Clark-Cooper Corp., Cinnaminson, New Jersey). The fabric was padded at a speed of 2.0 m/min and had a water content of 80%. Because of the difficulty of balancing the fabric speed during padding and the rate of passage through the infrared oven to the driven wind-up roller, a floating roller was set up between the pad bath and the infrared. Initially, the fabric speed through the pad bath was set slightly higher than that for the take-up roller at the exit to the infrared oven and then subsequently adjusted as required to maintain the floating roller at constant height. The rate of passage of the fabric through the oven was maintained at 2.0 m/min.

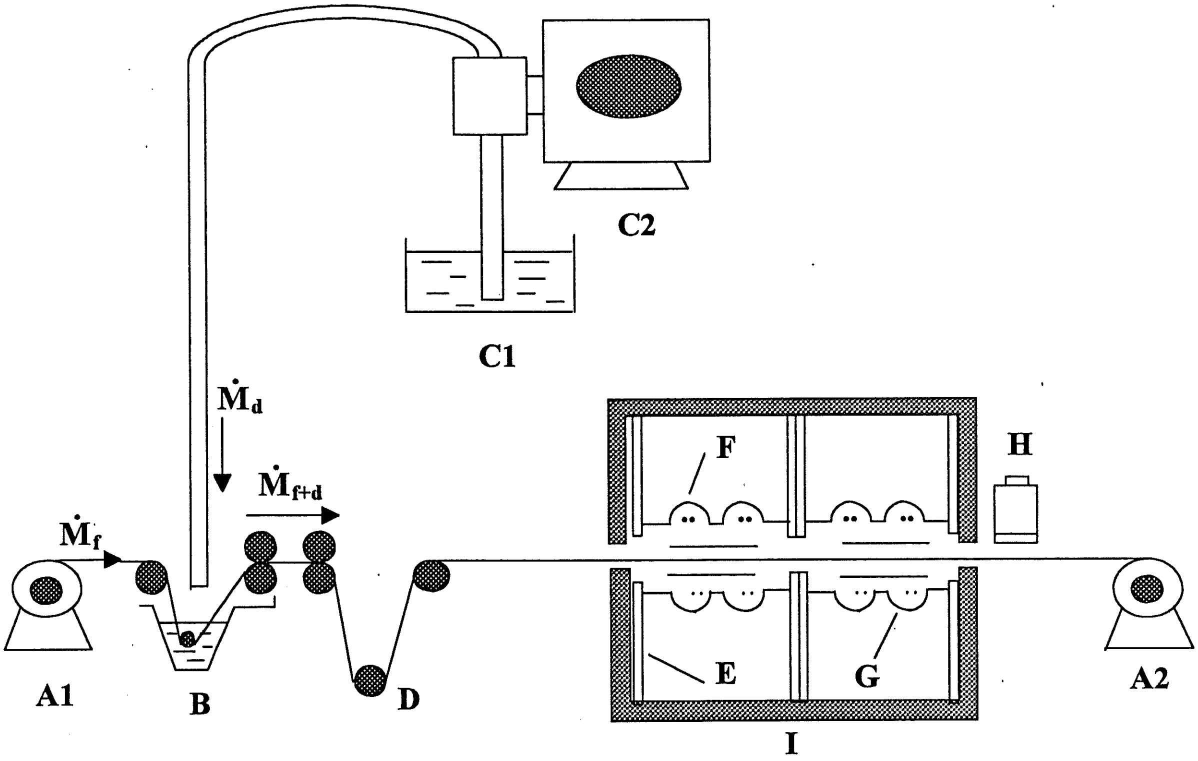


Figure 7.1 Scheme of continuous dyeing and fixation unit

A1. Free roller with no speed controller

A2. Roller with speed controller

B. Pad bath

C1. Reservoir of dye solution

C2. Chemical metering pump

D. Floating roller

I. Infrared oven

E. Air ducts

F. Tubular sources

G. Reflectors

H. Infrared pyrometer

Quartz tube sources, which gave a medium-wave infrared emission, were used in the continuous dyeing trials. Each module were operated under the same conditions. The emitter racks were situated at a distance of 5.5 cm from the fabric. The air supply and exhaust fans were set at the maximum level. The infrared pyrometer, situated at the exit of the infrared oven, was used to measure the fabric temperature as it left the oven.

7.2.3 Procedures

Two different dye solutions were used. One contained 20 g/L dye, 25 g/L salt and 5 g/L NaOH and the other 20 g/L dye, 100 g/L urea and 5 g/L NaOH, respectively. The NaOH was combined with the dye solution just prior to metering into the pad bath. A simple mass balance required that fresh dye solution be added to the pad bath at a constant rate to maintain a constant volume of dye solution (see Figure 7.1).

Dye solution rate into pad bath + Fabric rate into pad bath = Total rate out pad bath

$$\dot{M}_{d,in} + \dot{M}_{f,in} = \dot{M}_{d+f,out} = \dot{M}_{f,in}\,(1 + M_f) \qquad (7\text{-}1)$$

Hence:

$$\dot{M}_{d,in} = \dot{M}_{f,in} \times M_f = S_f \times W_f \times \rho_f \times M_f \qquad (7\text{-}2)$$

Where: $\dot{M}_{d,in}$ - the rate of dye solution into pad bath (g/min)

$\dot{M}_{f,in}$ - the rate of fabric into pad bath (g/min)

$M_{f+d,out}$ - total rate of dyed fabric out pad bath (g/min)

S_f - fabric speed pass pad bath (m/min)

W_f- width of fabric (m)

ρ_f - density of fabric (g/m^2)

M_f - fractional wet pick-up

According to equation 7-2, therefore, the pumping rate of dye solution from the reservoir into the pad bath should be 52.8 g/min or ml/min for a fabric with a speed of 2.0 m/min, 0.25 m wide, having a density of 132 g/m^2 and an 80% wet pick-up. A total volume of 2.65 liters of dye/alkali solution was needed for each experiment. The volume of the dye reservoir (C1 in Figure 7.1) was 4.0 liters. However, in order to reduce the effect of the alkali on dye hydrolysis, the reservoir was filled with freshly prepared alkaline dye solution every 10 min.

The infrared oven was operated with the emitters in each of the four modules at 380 V and about 7.9 A (12.0 kW) for the dyeing solution without added urea, and at 450 V and 9.22 A (16.6 kW) for that with added urea. Samples were cut after padding every 20 or 25 meters (10-12 min) to determine water and dye content of the fabric before heating. Samples after fixation were cut every 10 meters (5 min) for determining amount of fixed dye in the fabric. The infrared oven was operated for 30 min prior to actually cutting samples to ensure a steady state condition. The fabric outlet temperature was measured using the infrared pyrometer and fluctuated in the range of 130 - 135°C without urea and 160 - 167°C with added urea. These conditions avoided any adverse thermal effects on the cotton fabric.

7.3 Analysis method for the continuous dyeing process

In this study, the parameters that were measured were the dye fixation yield, the fabric surface temperature, the Kubelka-Munk K/S value at the wavelength of minimum reflectance and the color variation along the length of fabric being continuously dyed using the infrared fixation process. The measurement and calculation of the fixation yield was described in Chapter 2. The fabric surface temperature was measured using the infrared pyrometer (Chapter 2). The Kubelka-Munk K/S value gives a direct measure of the surface color strength and was measured using the reflectance spectrophotometer. Normally, the higher the fixation yield, the higher the K/S value, assuming no influence of dye solution migration during drying. However, color consistency along the length of dyed material is one of the most important quality control factors in continuous dyeing in the textile industry. A color difference (ΔE) may be described using the CIELAB color space (BILLMEYER. and SALTZMAN, 1981) and determined from tristimulus values measured using reflectance spectrophotometry. All K/S or CIELAB values were obtained on samples that had been washed to remove unfixed dye. The color difference value (ΔE) relative to the average color coordinates of all the samples was used to describe the color variations during the continuous dyeing and fixation process. Therefore, it is necessary to describe the CIELAB color space.

7.4 The CIELAB system

The Commission internationale de l'éclairage or International Commission on Illumination (CIE, 1978) has been responsible for almost all of the various systems of color measurement. In any of these systems, the objective is to determine the values of three parameters which completely define the color. If two colors have identical numerical descriptions, then the colors should appear to be identical for an average observer. The CIELAB system is extremely popular in the textile industry and defined by the mutually perpendicular axes for the three determined variables L^*, a^* and b^*. This color space, however, is not completely uniform, i.e., equal distances between the locations of color points in the color space do not exactly translate into equal visual color differences. In general, however, this non-uniformity does not hinder the wide use of this colour space for establishing industrial color tolerances.

The CIELAB color space is shown in Figure 7.2. The three parameters have the following characteristics: L^* is the lightness of the color and varies from about 100 to 0. A light color sample will have a high L^* value and a dark sample a low one. The parameters a^* and b^* are based on the opponent color vision theory: a^* is a measure of the red-green character and b^* a measure of the yellow-blue character of a color. Values of a^* range from 70 (saturated red) to -60 (saturated green), while b^* varies from 90 (saturated yellow) to -60 (saturated blue). The L^* axis with $a^* = b^* = 0$ is a line of grays running from white ($L^* = 100$) to black ($L^* = 0$). Figure 7.2 also shows points for standard and sample (std and spl) for a bright orange.

L^*, a^* and b^* are calculated from the X, Y and Z tristimulus values of the color sample and of the illuminant. The latter are calculated from the reflectance data (R) of the sample, the spectral power distribution (P) of the illuminant, and the color matching functions of the appropriate standard observer $(\bar{x}, \bar{y}, \bar{z})$. The X, Y, and Z values can be described by:

$$X = k\int PR\bar{x}d\lambda \tag{7-3}$$

$$Y = k\int PR\bar{y}d\lambda \tag{7-4}$$

$$Z = k\int PR\bar{z}d\lambda \tag{7-5}$$

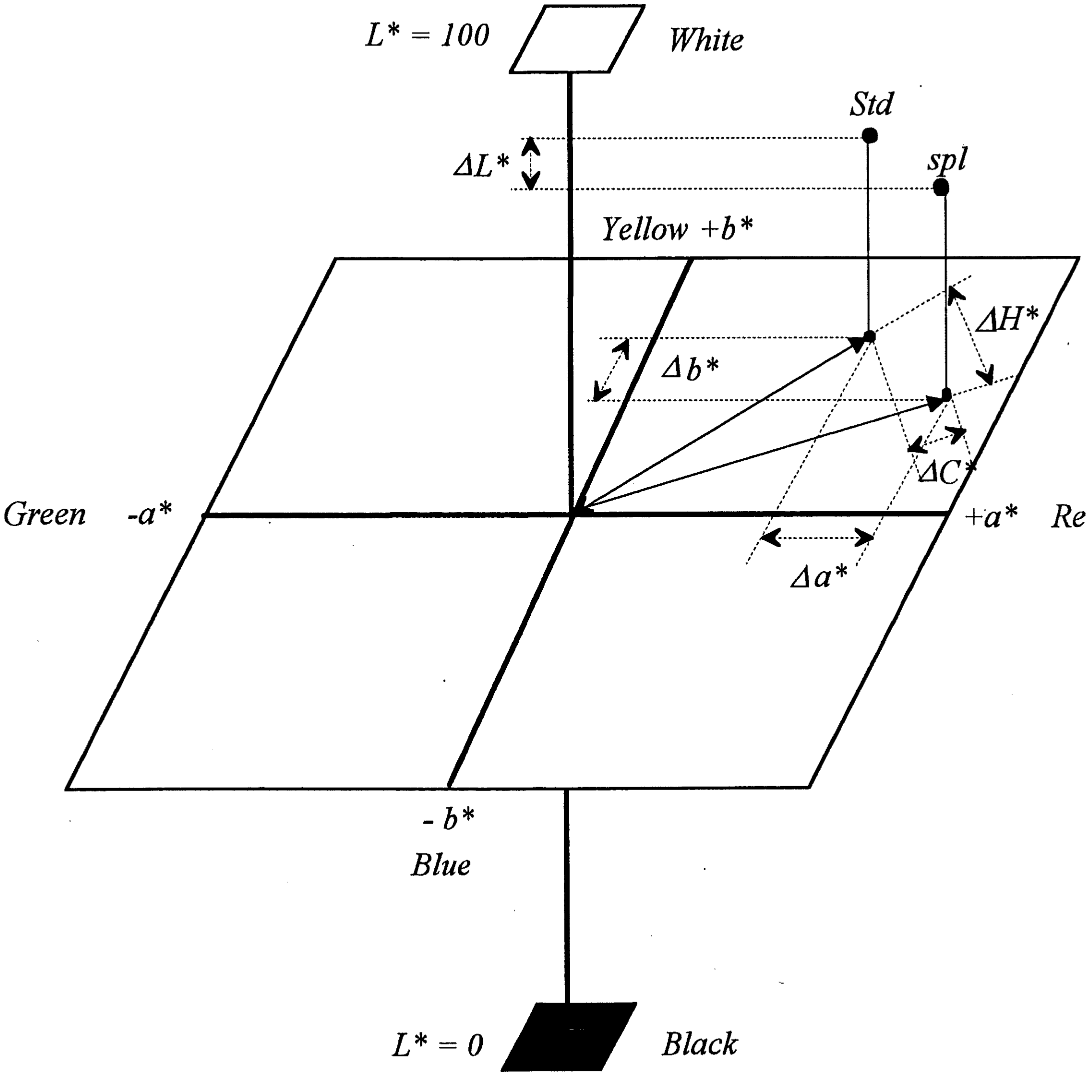


Figure 7.2 The CIELAB color space

Total color difference between standard (std) and sample (spl) and its components ΔL*, ΔC*, and ΔH* where:

$$k = \frac{100}{\int P\bar{y}d\lambda} \tag{7-6}$$

and $\bar{x}, \bar{y}, \bar{z}$, P and R all are functions of the wavelength λ from 380 to 780 μm.

CIELAB coordinates are given by:

$$L^* = 116(Y/Y_n)^{1/3} - 16 \tag{7-7}$$

$$a^* = 500\left[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}\right] \tag{7-8}$$

$$b^* = 200\left[(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}\right] \tag{7-9}$$

Where X_n, Y_n and Z_n are the tristimulus values of the illuminant and are calculated using equations 7.3 to 7.5 with R = 1.00. For very dark colors, with values of X/X_n, Y/Y_n or Z/Z_n less than 0.008856, these equations must be modified (CIE, 1978) by the following:

$$L^* = 116f(Y/Y_n) - 16 \tag{7-10}$$

$$a^* = 500[f(X/X_n) - f(Y/Y_n)] \tag{7-11}$$

$$b^* = 200[f(Y/Y_n) - f(Z/Z_n)] \tag{7-12}$$

where:

$$f(X/X_n) = 7.787(X/X_n) + 16/116 \tag{7-13}$$

$$f(Y/Y_n) = 7.787(Y/Y_n) + 16/116 \tag{7-14}$$

$$f(Z/Z_n) = 7.787(Z/Z_n) + 16/116 \tag{7-15}$$

The total color difference (ΔE) may be defined by the following:

$$\Delta E = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{\frac{1}{2}} \tag{7-16}$$

or:

$$\Delta E = \left[(\Delta L^*)^2 + (\Delta H^*)^2 + (\Delta C^*)^2\right]^{\frac{1}{2}} \tag{7-17}$$

Other measures of color difference include

ΔL^* - Lightness/darkness difference
Δa^* - Red/green color difference
Δb^* - Yellow/blue color difference
ΔC^* - Difference in chroma or saturation of a color
ΔH^* - Difference due to hue only
ΔE - Total color difference (Includes hue, chroma and lightness)

In terms of the two points for a standard and sample color (std and spl) in the CIELAB color space (shown in Figure 7.2), the relationships between L*, a* and b* and L*, H* and C* can be obtained using the law of Pythagoras:

$$C^* = (a^{*2} + b^{*2})^{\frac{1}{2}} \tag{7-18}$$

$$\Delta C^* = C^*_{spl} - C^*_{std} \tag{7-19}$$

$$\Delta L^* = L^*_{spl} - L^*_{std} \tag{7-20}$$

$$\Delta a^* = a^*_{spl} - a^*_{std} \tag{7-21}$$

$$\Delta b^* = b^*_{spl} - b^*_{std} \tag{7-22}$$

$$h^* = ARCTAN(b^*/a^*) \tag{7-23}$$

$$\Delta H^* = [(\Delta E)^2 - (\Delta L^*)^2 - (\Delta C^*)^2]^{\frac{1}{2}} \tag{7-24}$$

Where: std = standard color
spl = sample color

In order to examine the color consistency for all samples during the continuous dyeing process, the standard for comparison purposes was taken as that having the average values of L^*, a^* and b^* over the entire sampling period. Therefore, ΔL^*, Δa^*, Δb^*, ΔC^* and ΔH^* can be calculated and ΔE gives the CIELAB color difference relative to the average color. In general, despite the non-uniformity of the CIELAB color space, if the ΔE value is less than about 1.0, an average human observer will have difficultly perceiving any significant color difference between the standard and sample. The sample color would therefore be an acceptable match of the standard.

7.5 Results and discussion

7.5.1 Variation of fixation yield and fabric temperature

The results of this experiment, illustrated in Figures 7.3 to 7.4, show that the continuous dyeing and fixation process using infrared heating can give a high fixation yield of the reactive dye on cotton. For Red X-6BN, the fixation yield was 75-81% without urea present in the dyeing solution. If urea was added to the dye solution, the fixation yield improved to around 90%. These yields were close to the values found previously for the respective dyeing conditions. With urea present in the dye solution, the dried fabric could be heated to a higher temperature (170°C) without burning so that a high fixation yield was possible. The addition of salt has no significant effect on the fixation yield. The experiments in chapters 3 and 4 confirmed these results. Although there is no salt in the dye solution in experiment reported in Figure 7.4, the fixation yield still can reach around 90%.

7.5.2 Variation of color yield and color difference

Figures 7.5 to 7.8 show the variations of K/S and the color differences during the continuous dyeing and infrared fixation process. The observed variations are well within acceptable color tolerances showing that the process was stable. Tables 7.1 and 7.2 show CIELAB values during the continuous infrared dyeing and fixation processes. When all experimental conditions were set up, the key factor influencing the fixation yield, K/S value and color difference is the fabric speed through the pad bath and infrared oven. A slight variation of fabric speed through the infrared oven could cause a significant change of the final fabric temperature and moisture resulting in variations of the fixation yield and color difference.

Although the trials described here were essentially under manual control, the small variations of fabric temperature and fixation yield, which tended to parallel each other, did not result in visible color variations along the length of dyed material. The suggested best method for controlling the temperature of the fabric would be a computer control system in which the voltage supplied to the infrared sources could be adjusted automatically according to variation of fabric temperature and moisture.

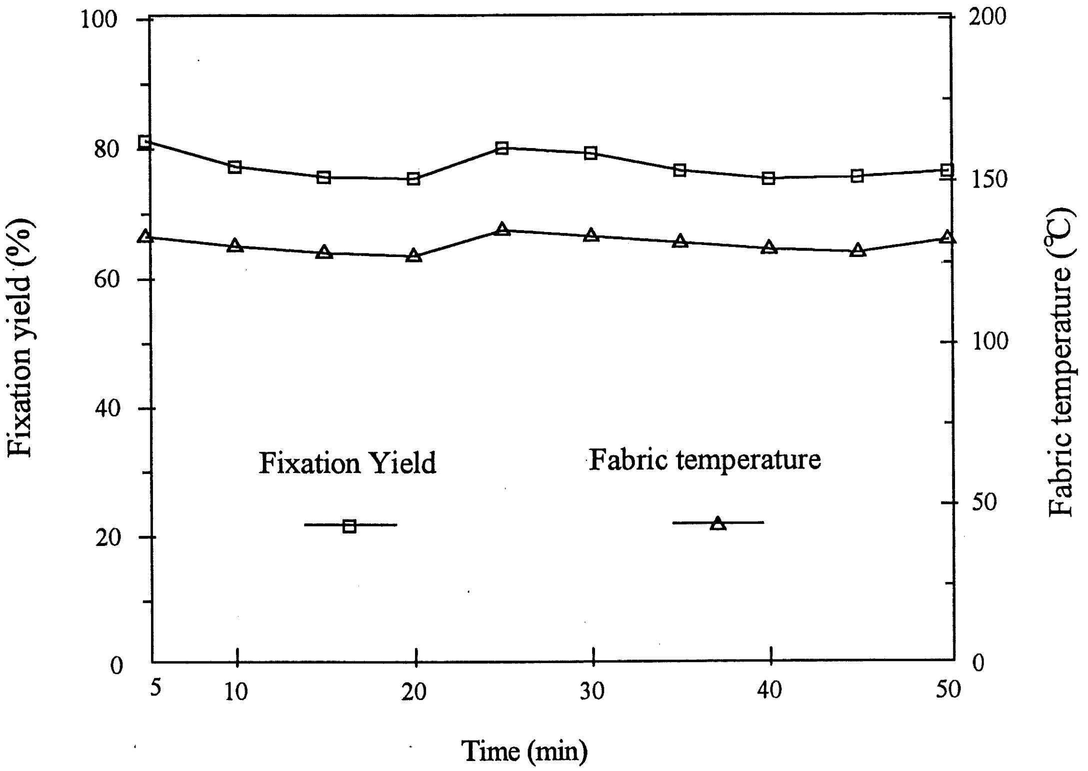


Figure 7.3 Variation of fixation yield and fabric temperature

(Dye solution without urea and with salt)

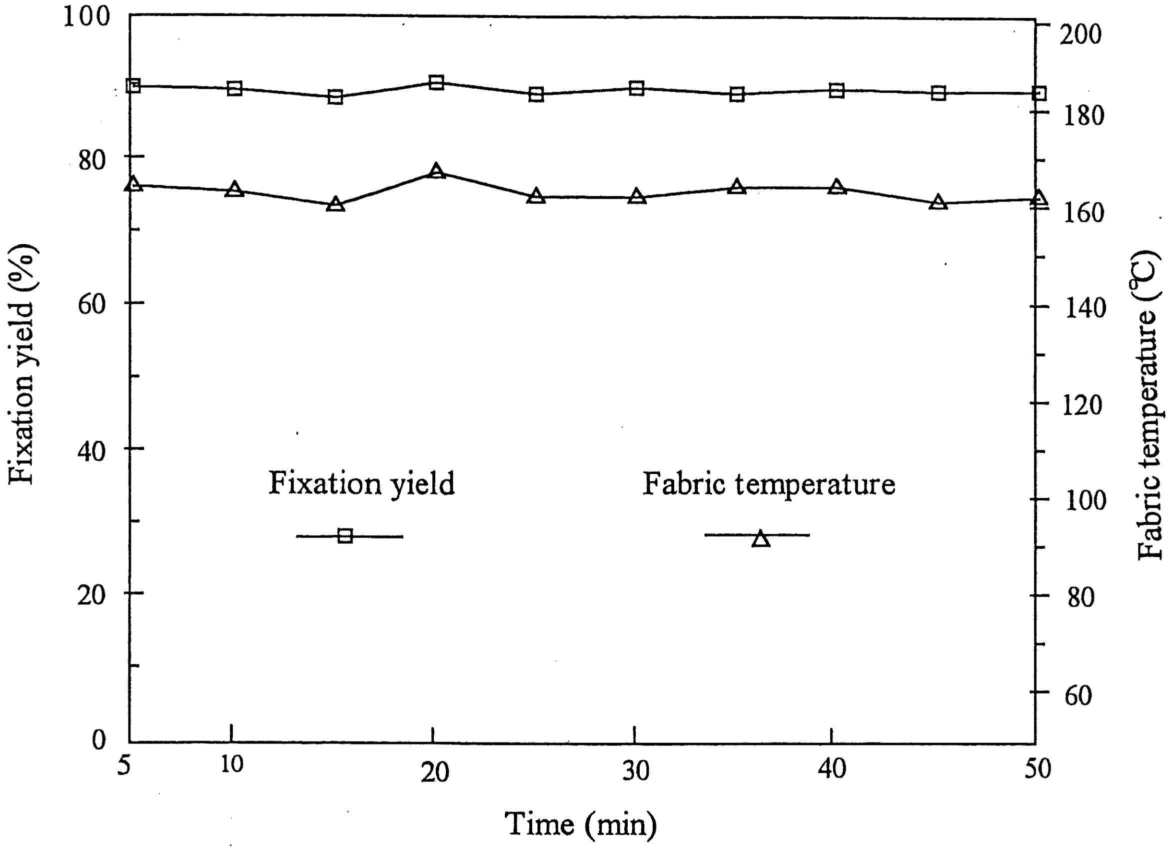


Figure 7.4 Variation of fixation yield and fabric temeprature

(Dye solution with urea and without salt

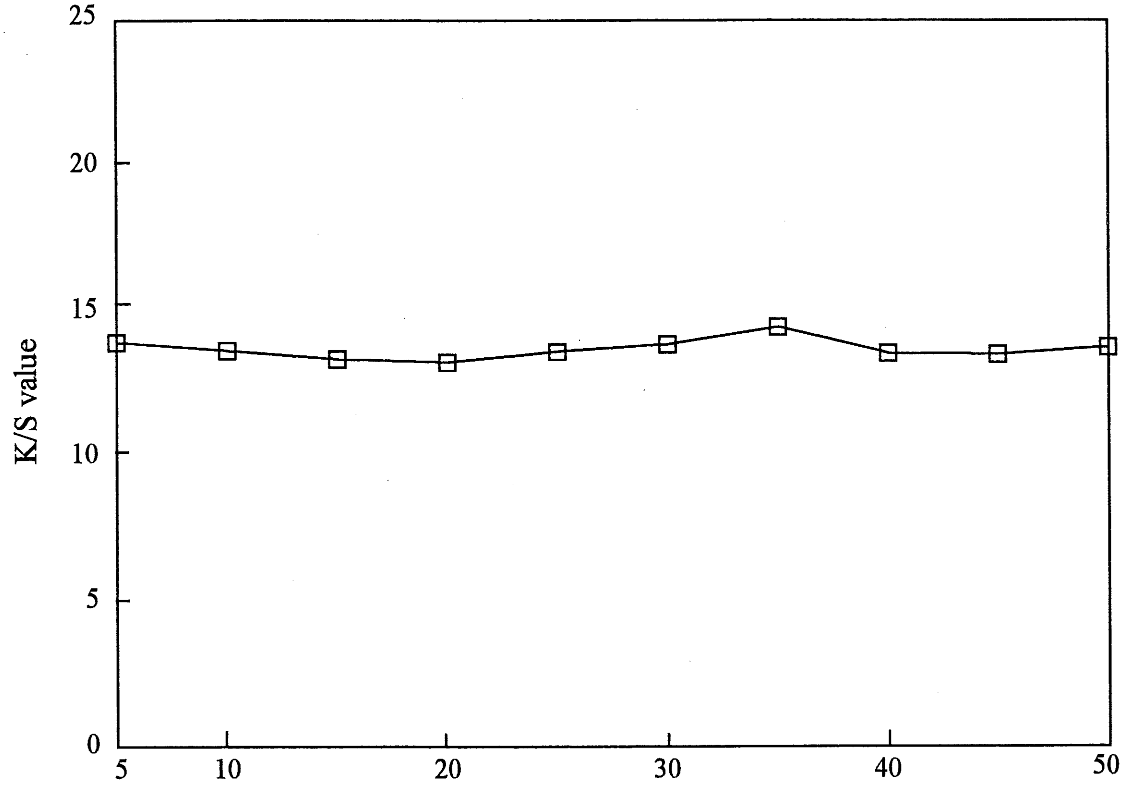


Figure 7.5 Variation of K/S values (Dye solution without urea and with salt)

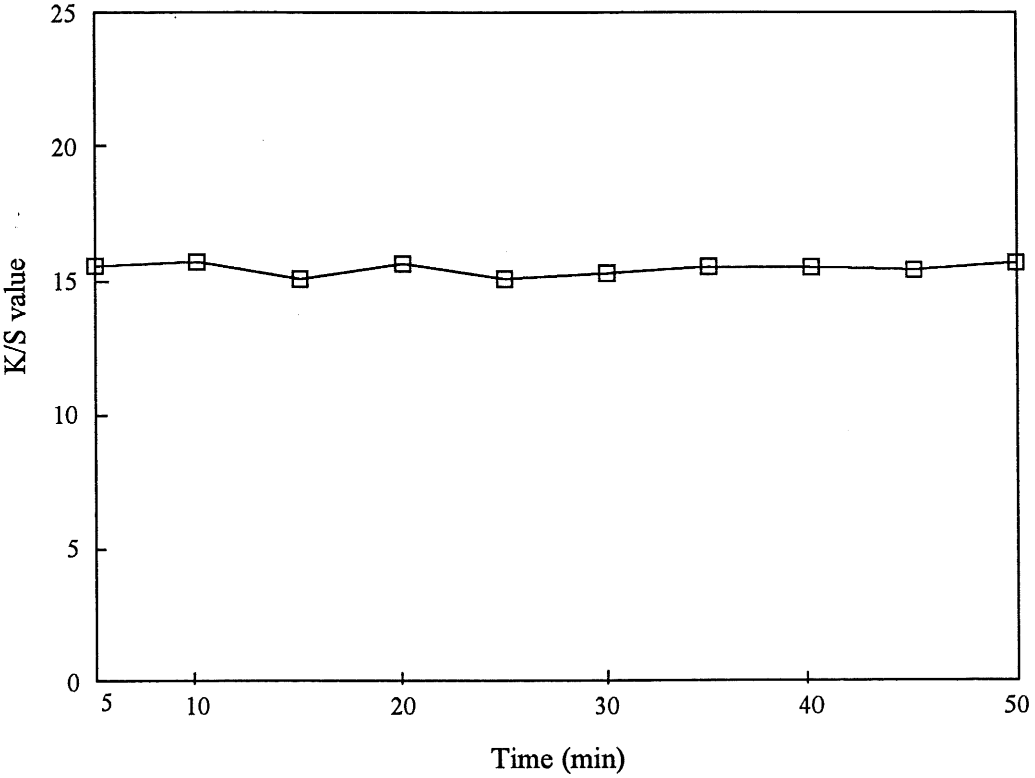


Figure 7.6 Variation of K/S values (Dye solution with urea and without salt)

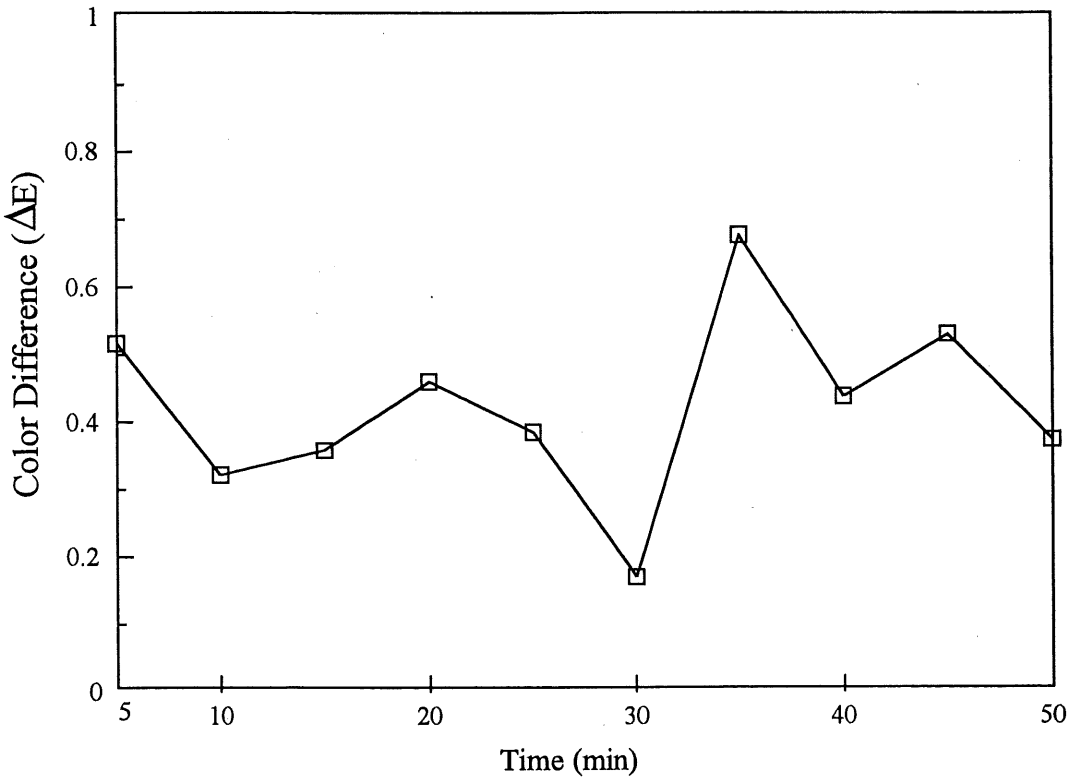


Figure 7.7 Variation of color difference (Dye solution no urea and with salt)

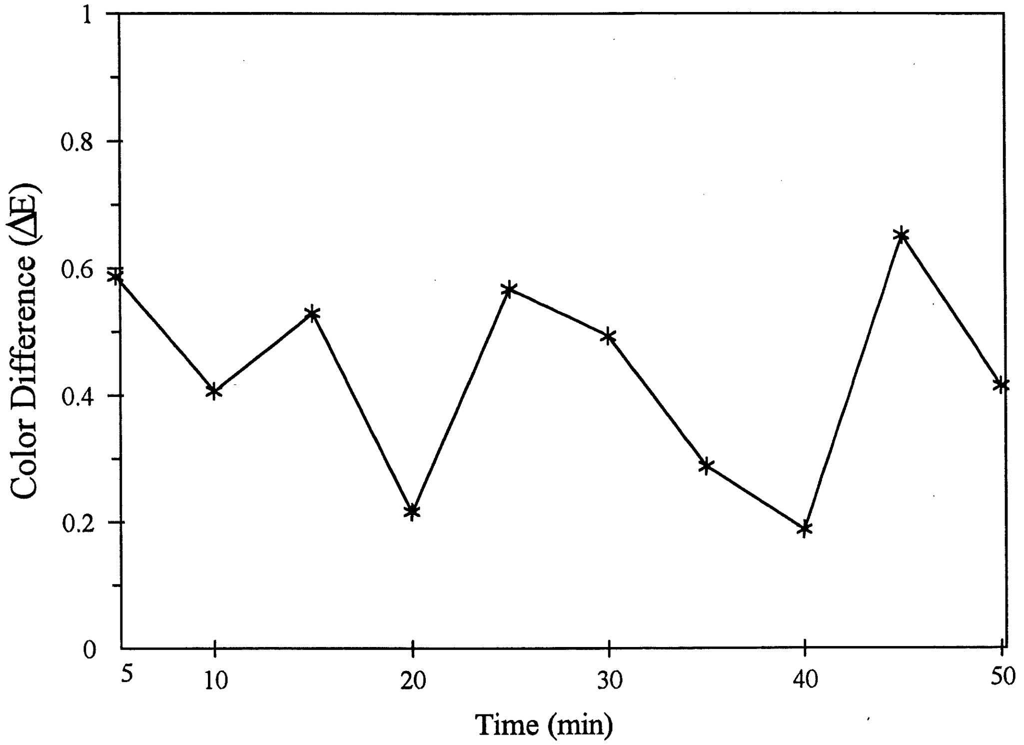


Figure 7.8 Variation of color difference (Dye solution with urea and no salt)

TABLE 7.1 CIELAB COLOR DIFFERENCE VARIABLES

(DYE SOLUTION NO UREA AND WITH SALT)

Time (min)	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔC^*	ΔH^*	ΔE
5	41.96	58.11	-1.68	0.05	-0.08	0.51	-0.10	0.50	0.52
10	42.06	57.94	-2.06	0.15	-0.25	0.13	-0.26	0.12	0.32
15	42.01	58.22	-2.53	0.10	0.03	-0.34	0.04	0.34	0.36
20	41.86	58.46	-2.56	-0.05	0.27	-0.37	0.28	0.36	0.46
25	41.98	57.92	-2.45	0.07	-0.27	-0.26	-0.26	0.27	0.39
30	42.00	58.05	-2.18	0.09	-0.14	0.01	-0.14	0.00	0.17
35	41.68	58.83	-2.22	-0.23	0.64	-0.03	0.64	0.01	0.68
40	41.86	57.80	-2.00	-0.05	-0.39	0.19	-0.40	0.17	0.44
45	41.70	58.21	-1.70	-0.21	0.02	0.49	0.00	0.49	0.53
50	41.97	58.39	-2.50	0.06	0.20	-0.31	0.21	0.30	0.37
Average	41.91	58.19	-2.19	---	---	---	---	---	---

TABLE 7.2 CIELAB COLOR DIFFERENCE VARIABLES

(DYE SOLUTION NO SALT AND WITH UREA)

Time (min)	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔC^*	ΔH^*	ΔE
5	39.43	57.69	-0.67	-0.21	0.04	0.55	0.04	0.55	0.59
10	39.26	57.65	-1.37	-0.38	0.00	-0.15	0.01	0.15	0.41
15	40.01	58.02	-1.17	0.37	0.37	0.05	0.37	0.06	0.53
20	39.79	57.80	-1.23	0.15	0.15	-0.01	0.15	0.01	0.22
25	40.10	57.87	-1.46	0.46	0.22	-0.24	0.23	0.24	0.57
30	39.45	57.20	-1.12	-0.19	-0.45	0.10	-0.45	0.09	0.49
35	39.65	57.37	-1.30	0.01	-0.28	-0.08	-0.27	0.09	0.29
40	39.60	57.80	-1.32	-0.04	0.15	-0.10	0.16	0.10	0.19
45	39.29	57.11	-1.09	-0.35	-0.54	0.13	-0.54	0.12	0.65
50	39.80	57.95	-1.45	0.16	0.30	-0.23	0.31	0.22	0.42
Average	39.64	57.65	-1.22	---	---	---	---	---	---

In order to obtain high fixation yield, an adequately high fixation temperatures must be achieved good fixation for this low reactivity dye without any deleterious thermal damage to the cotton. Temperatures in excess of 140°C without urea or 170°C with urea greatly increase the risk of scorch marks on the fabric.

7.6 Conclusion

The continuous dyeing and fixation process using infrared heating for a low reactivity reactive dye on cotton gave high fixation yields and no visible color variations along the length of dyed fabric. A fixation yield of about 90% was achieved with urea added to the dye solution but without added salt. For a reactive dye of such low reactivity, the key problem is the control of the fabric outlet temperature. The results illustrate that a stable process is possible with the obvious advantages of using infrared heating: high fixation yields, good color consistency, and short dyeing times.

The possibility of obtaining high fixation yields (> 90%) using infrared heat makes this a technologically attractive process for several reasons. Such high yields are possible with dyes of high, medium, and low reactivity, in short processing times, with little migration of the dye to the yarn surfaces during initial drying. Although the suppression of dye migration lowers the color yield of the dyeing, it avoids problems of white fabrics becoming visible if the yarn surface is abraded. Most importantly, very little unfixed dye remains in the cotton fabric so the washing effluent is only slightly colored. This is a current environmental problem for dyehouses using reactive dyes. Two problems, however, must be considered. The high fabric temperatures required for good dye fixation increase the risk of fabric scorching and the emitter power and fabric speed should be automatically controlled (DHIB et al., 1994). Also, at the high NaOH concentration necessary for optimum dye fixation, the dye in the bath is more likely to undergo premature hydrolysis. To avoid this, it would be necessary to mix the dye and NaOH solutions just prior to impregnation, which would require the use of metering pumps as in the cold pad-batch process (FOX and SUMNER, 1986). The dyeings in the continuous process using infrared heating showed high fixation yields and were of uniform color.

8. OVERALL SUMMARY AND CONCLUSIONS

The objective of this project was the development of a continuous process for the dyeing of cotton with reactive dyes using pad impregnation followed by thermofixation using infrared heating.

For the dyes examined, the degree of dye fixation to the cotton was greatest for dyes of high reactivity. Even for dyes of low reactivity, however, high fixation yields were possible using longer residence times in the infrared oven and higher infrared emitter power settings. The fixation yield was quite sensitive to changes in these two variables. Final fabric temperatures not greater than 140^0C avoided any thermal damage to the cotton. The fixation yields of some dyes were quite sensitive to the type and concentration of the alkali used for the fixation reaction. The weaker alkali Na_2CO_3 was suitable for fixation of high reactivity dyes, but for dyes of low reactivity, the stronger NaOH was necessary. Despite the fact that the alkali type and concentration were not optimized, it was possible to obtain fixation yields over 85% for most dyes, and in some cases over 90%. This is remarkable in comparison to typical fixation yields of 75% or less in existing processes.

The small effects of increasing the salt concentration in the pad solution did support the generalization that salt is much less effective at low liquor to goods ratios. Addition of urea to the dye solution had variable effects on the fixation yields obtained using infrared heating. It was effective in increasing the yields of some dyes of lower reactivity. The fixation yield of the reactive dyes to cotton was improved to a certain extent by vacuum extraction, but the effect was not usually significant. Vacuum extraction significantly improves the performance of the operation because the fabric can be dried much more quickly. The key conclusion from the preliminary study was that infrared thermofixation can give remarkably high fixation yields, even for dyes of low inherent reactivity towards the cotton.

In the short time between padding, cutting of the fabric sample for analysis, and extraction of the dye it contains, a small proportion of the dye invariably reacted with the cotton and all the dye initially present in the fabric could not always be removed immediately after padding. The extracted cotton was thus weakly colored rather than being white. This results in a lower value of the measured fixation yield. A new technique for determination of the dye fixation yield was developed with a correction for the non-extractable dye based on measurement of the reflectance spectrum and calculation of the Kubelka-Munk K/S value.

A quantitative examination of the effects of the process variables in infrared fixation was carried out. Relatively simple relationships between the controlled process variables and the output responses were obtained for the fixation of a reactive dye on cotton using two factorial experimental designs. These indicated that the fabric speed through the oven, the infrared emitter power and the NaOH concentration in the dye solution used were the most important variables influencing the dye fixation yield. The fabric speed and emitter power also significantly affected the temperature and water content of the fabric after heating.

A detailed comparison of hot air and infrared thermofixation processes was carried out using four reactive dyes of widely different reactivities. Both quartz and T-3 tubular infrared sources gave high fixation yields. Comparison of the color yields of these dyeing with those obtained by a cold pad-batch method, indicated that infrared drying with T3 tubes and heating did not cause any significant migration of the initially unfixed dye to the yarn surfaces during the initial stage of drying. The fixation yields for hot air thermofixation at two different temperatures were considerably lower and the shapes of the fixation-time profiles were quite different from those of the infrared processes. Dyeings obtained by hot air thermofixation had higher color yields than those from the infrared processes showing evidence of extensive dye migration during drying. Examination of the cross-sections of dyed fibers by optical microscopy showed uniform dyeing and fixation for the fabrics heated using infrared and ring dyeing for fixation by hot air. Unfortunately, the trials carried out using a pre-drying method were not completely successful and did not show that there is a link between the suppression of dye migration and the high fixation yields which are possible in the radiative process.

The infrared thermofixation dyeing process was run on a continuous basis for an extended period using a low reactivity reactive dye on cotton. Again, a high degree of fixation was found and there was no visible color variation along the length of dyed fabric (100 m). A fixation yield of about 90% was achieved with urea added to the dye solution but without added salt. The results illustrated that a stable dyeing process is possible with the obvious advantages of using infrared heating: high fixation yields, good color consistency, and short dyeing times.

The possibility of obtaining high fixation yields (> 90%) using infrared heat makes this a technologically attractive process for several reasons. Such high yields are possible with dyes of high, medium, and low reactivity, in short processing times, with little migration of the dye to the yarn surfaces during initial drying. Most importantly, very little unfixed dye remains in the cotton fabric so the effluent from the subsequent washing process is only slightly colored. This is a current environmental problem for dyehouses using reactive dyes.

Two problems, however, must be considered. The high fabric temperatures required for good dye fixation increase the risk of fabric scorching and the emitter power and fabric speed should be automatically controlled. Also, at the high NaOH concentration necessary for optimum dye fixation, the dye in the bath is more likely to undergo premature hydrolysis. To avoid this, it would be necessary to mix the dye and NaOH solutions just prior to impregnation, which would require the use of metering pumps as in the cold pad-batch process.

The results clearly showed the potential for developing a pad-thermofixation continuous dyeing process for cotton with reactive dyes, using infrared heating, that would allow high fixation yields without salt additions to the dyebath, and possibly without addition of high concentrations of urea. Such a process would reduce the color of the effluent from the post-dyeing washing process and its overall pollution load. The infrared thermofixation dyeing process thus merits further study and possible commercial exploitation. Before scale-up studies are undertaken, however, a number of questions need to be examined which have not been considered in this thesis.

1. Commercial dyeing are invariably produced using a mixture of dyes, usually three and often more. The infrared thermofixation of reactive dye mixtures is thus a necessary pre-requisite before any scale-up studies.

2. For each type of reactive dye it will be essential to establish the dyebath pH that gives optimal dye fixation. This study showed that for dyes of low reactivity, such as those with a monochlorotriazine reactive group, and for the vinyl sulphone reactive dyes, a NaOH concentration of 5 g/L is suitable. However, for other types of dyes the use of a weaker alkali such as sodium carbonate is necessary.

3. The infrared thermofixation process involves high radiant power densities on the fabric surface. On completion of drying, the fabric temperature rises very rapidly. It is thus

difficult to heat a fabric to a particular temperature and then to maintain this at a steady value for a short period. There is a real risk of thermal damage to the fibers if the fabric is overheated. This leads to two further suggestions for future work, neither of which were examined in this thesis.

4. Although the infrared process gave high fixation yields without obvious scorching of the cotton surface when the final fabric temperature was not more than 140°C, it is obvious that for commercial exploitation a full evaluation of the properties of fabrics dyed by this process must be carried out. This will include not only evaluation of the color and its fastness properties, but also its mechanical properties, particularly those related to the handle. Overheating of cotton is known to produce a rather crisp surface, even if there is no sign of any burning.

5. Because of the risk of fabric scorching when extended radiative heating is needed to give high levels of fixation, a somewhat different type of procedure should be examined. In this, the cotton fabric is padded with the alkaline dye solution, dried by infrared radiation and then heated to a suitable temperature, less than 140°C, and then the fabric temperature maintained for a short period by passage through a hot air oven. This type of process is more likely to be acceptable in industry because of the much lower risk of fabric scorching. It is also more in line with the actual industrial equipment set-up with an infrared unit directly in front of a tenter frame.

6. Finally, the results presented here clearly showed that an infrared thermofixation process produces high dye fixation yields with little migration of the unfixed dye to the yarn surfaces during drying. However, there was no concrete evidence supporting the idea that the suppression of the dye migration is responsible for the high levels of fixation, even though this seems like a plausible explanation. Obviously, dye that has migrated to the surface of the yarn is less likely to diffuse into the cotton fibers and react with the cellulose. Unfortunately, the pre-drying trials were not particularly successful and did not provide an answer to this question. If migration suppression using infrared radiation is responsible for the high fixation yields, then a process in which the fabric is dried by infrared and subsequently heated by any method would give equally high fixation. This should be tested. Since vacuum extraction of an

impregnated fabric is also a valuable method of reducing dye migration during drying, a pad - vacuum - infrared process should be compared with a pad- vacuum - hot air process.

If these proposed studies provide acceptable results, the infrared thermofixation process for reactive dyes on cotton will be ready for industrial scale trials.

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