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STUDIES RELATING TO THE CONSERVATION OF MIAO TEXTILES

by

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A thesis submitted in partial fulfilment of the
requirements of The Nottingham Trent University
for the degree of Doctor of Philosophy

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ABSTRACT

Title: Studies relating to the conservation of Miao textiles

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This thesis reports on studies relating to the conservation of Miao textiles, which consist of indigo-dyed cotton decorated with silk-embroidered panels. In many instances the base fabric, indigo-dyed cotton, is given a finishing treatment which involves impregnating with a protein gel obtained from ox hide.

The first part of the study is an investigation of the use of microwave radiation as a means of sterilising these fabrics by destroying fungal spores without damage to the textile fibres, the protein coating, or the various dyes, including natural dyes, likely to have been used in the garments. In addition the effects of laundering and dry cleaning on components of the garments have been examined. The results show that microwave irradiation is a very efficient technique for destroying a number of fungal spores and show that although the protein coating on indigo-dyed cotton had no major effect on the wash fastness of the dye, the material having the same moderate fastness as did the sample of indigo-dyed cotton, the coating itself was resistant to the laundering treatment. The ratings for fastness to dry cleaning of the silk samples dyed with natural dyes were good-to-excellent, across all the natural dyes and dye/mordant combinations except for indigo-dyed silk.

The second part deals with a study of dyeing of chitosan, an amine-containing polysaccharide which has been proposed as both an agent for coating fibres and fabrics and for the production of fibres, with natural dyes. A range of shade have been produced using chitosan in both flake and film form and the hues obtained are, in most cases, similar to those obtained on silk. For two mordants, alum and chromium sulphate, a resist effect is found when chitosan is mordanted and dyed while still adhering to a glass plate. A mechanism involving the formation of interchain crosslinks through two or more amine groups binding to individual metal ions at the film surface. It is proposed that this effect could be used, together with the dyeability of chitosan, for design effects on chitosan fibres or chitosan-coated fibres and fabrics.

In memory of my father
Huang Po-Luen (1917-1997)
and to my dear mother
Hsieh Shii-Mey (1928-)

物格而後知至；
知至而後意誠。

~ 孔子 （551-479 B.C.）

When things are investigated,
then true knowledge is achieved;
When true knowledge is achieved,
then the will becomes sincere.

~ *Confucius (551-479 B.C.)*

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INTRODUCTION

Taiwan is a hot, humid and rainy island, located in the subtropical zone of Asia. The humidity and temperature of Taiwan change greatly according to the seasons. This causes textiles to be easily damaged by insects and fungi if not stored under the proper conditions.

In Taiwan, people customarily use camphor or naphthalene balls for textile preservation. Camphor and naphthalene are also used as moth repellents in museums or by private textile collectors. Appropriate care helps to reduce degradation. In general, the knowledge and practice of textile preservation and management in Taiwan is at an early stage, and some valuable textiles suffer undue degradation. There are many problems, especially in long-term conservation, related to colour change, strength loss, fungal growth, and insects damage. Examples of causes of fabric degradation are heat, light, moisture, and insecticide residues.

The Graduate Institute of Textiles and Clothing at the Fu Jen Catholic University owns various collections of Han Chinese, Chin dynasty, Miao and Taiwan Aboriginal textiles. Miao clothing is among China's most beautiful and is produced by a design conscious minority people. These collections are a source for study, research, and design for faculty and students at the Fu Jen University and related departments of Fashion and Textiles in Taiwan. The sense of responsibility toward the preservation of the vast heritage of research and design resources becomes the main issue that the Institute has to face. To prevent these collections suffering from damage is the first major objective of the Graduate Institute of Textiles and Clothing. This forms the starting point of the current research.

The aims for development of research of the Graduate Institute are to attain the goal of textile conservation. In addition to preventing the old textiles from degrading by light, humidity, and temperature, it is necessary to avoid degradation of Miao textiles by sterilising and laundering. At present, physical techniques may have some advantages over the use of chemicals because, for example, they leave no residue on the treated objects and do not pollute the environment.[1]

The main aim of the Graduate Institute is both to conserve historic textiles and to protect the environment. Therefore, the research presented here concerns the using of microwave irradiation instead of chemical fumigation for killing off fungi which cause degradation of historic textiles. In order to regain the original beautiful and bright colour, laundering is a possible way to attain the goals.

The knowledge and practice of textile preservation and management is also at an early stage of development in the Graduate Institute of Textiles and Clothing at the Fu Jen Catholic University. There are many problems, especially in long-term conservation related to storage, colour change, strength loss, fungal growth, and insect damage. The current research tries to develop a method of killing fungi by microwave radiation without losing strength and without inducing colour change in the fabric. It hopefully would be of considerable help in solving the problems inherent in caring for historic textiles.

For Miao costumes, the dyed silk yarns used in the decorative panels would have been dyed with natural dyes in the older samples although the more recent ones would be dyed with synthetic dyes. Therefore it is necessary to assess the effects of microwave radiation and laundering on naturally-dyed silk and also the base fabric, cotton as well. Silk and wool are amine-containing protein fibres that may be dyed with natural dyes. Chitosan is an amine-containing polysaccharide which is currently being proposed both as an agent for coating fibres and fabrics, and for the production of fibres themselves, and it was of interest to investigate whether or not chitosan may be dyed with natural dyes.

In this research, the results obtained and techniques developed could also be valuable to other related persons and institutes in Taiwan, for instance, the National Palace Museum, the National History Museum, the Provincial Museum, the Lugang Museum and others.

CHAPTER 1 BACKGROUND OF MIAO COLLECTIONS

1.1 Miao people's home country: South-west China and beyond

The Miao people constitute one of the oldest races in China and are scattered throughout the Guizhou, Yunnan, Guangxi, Hunan and Guandong provinces (Figure 1.1). Their many tribal branches have a multitude of names and occupy a multitude of places. A majority of the Miao people call the southeast of Guizhou province their homeland. The Miao people call themselves "Guoxiong," "Muo," "Meng,"etc.[2]

Their ancestors might be traceable to the ancient "San Miao." One legend maintains that the Miaos originated in the Shang Dynasty. During the Chin and Han Dynasties, the Miaos lived in Xiangxi (west Hunan) and Qiandong (eastern Guizhou). After that, they gradually moved and dispersed themselves throughout all southwestern China. Another legend claims that the Miaos originated in the east and that they are probably the founders of the Hemudu civilization.[2]

1.2 Miao people and Miao costumes

The various branches of the Miao people are many and number more than one hundred. Each branch supports its own costume style, language and customs. The Miaos worship gods and ghosts. They live in poor conditions, on mountain ridges all throughout southwestern China. Their professions mainly concern agriculture; some are forest workers; many in the northwestern corner of their homeland engage in animal husbandry. The Miao people plant cotton and flax and spin yarns, weave fabrics and dye these materials themselves. Some cotton fabrics are coated as an after treatment to produce stiffening and a shiny appearance and for this purpose the Miao people use a protein gel from ox hide.

Although they live in poor conditions, they are a naturally happy people. They enjoy singing, dancing and festive dress. This latter pre-occupation has engendered costume styles that exhibit great variety and astonishing technical skill, also some of the best craftmanship in the world [2]. Miao costumes combine creativity and experimentation with styles of dress designs, pattern, colour combination, and ornamentation to satisfy the textile designer's sense and desire for producing beautiful textiles. In 1992, some Taiwan local designers were inspired by Miao costumes and presented an exhibition " Design and Culture "- exploring the relationship between cultural heritage and modern design - , at the Fine Art Museum in Taipei. A variety of textile ideas were adopted from Miao patterns, colours, techniques of embroidery, batik dyeing, and finishing etc..

Owing to the absence of a written language of their own, the Miaos have revealed some of their basic dreams and fantasies about themselves in the beauty, symbolism and design patterns of their textiles arts. In addition to any decorative effect, the cultural functions of Miao costumes are the tribal emblems and for recording history. The Miaos, in order to transmit their own life style and culture from generation to generation, record their history in the decorative patterns of their costumes as well as in poetry, song, stories, and legends. To wear such history-garments is a common culture of minorities in mainland China.[3] Some Miao women spend their entire lives fabricating beautiful clothes that imply deep meaning and the pursuit of fantasy and dreams. The Miaos primarily decorate their costumes with embroidery and batik. Miao women always have decorations on their clothes that are produced using silk yarns. The costumes are very colourful and are the products of outstanding embroidery technical skill (Figures1.2 to 1.6).

A sketch is drawn on a piece of fabric (satin silk or plain cotton fabric) and embroidered with dyed silk yarns which are imported from big cities, such as Beijing, Shanghai, etc.. These pieces of embroidered fabric are then used as decoration by sewing on garments. This technique is very convenient as it is easy to remove the embroidered parts of the garments when the base-fabric garment needs be washed, or transfer the embroidered parts to other garment when the original garment is worn out. However, this manner of decoration makes Miao costumes difficult to identify in terms of the exact time period. Also, it makes it more difficult to conserve Miao costumes in many instances because the very old panels may be too fragile to be conserved using the same treatment as for the base fabric of the garment. In these cases the aged panels should be cleaned using a modified form of the processes used for the newer base fabric.

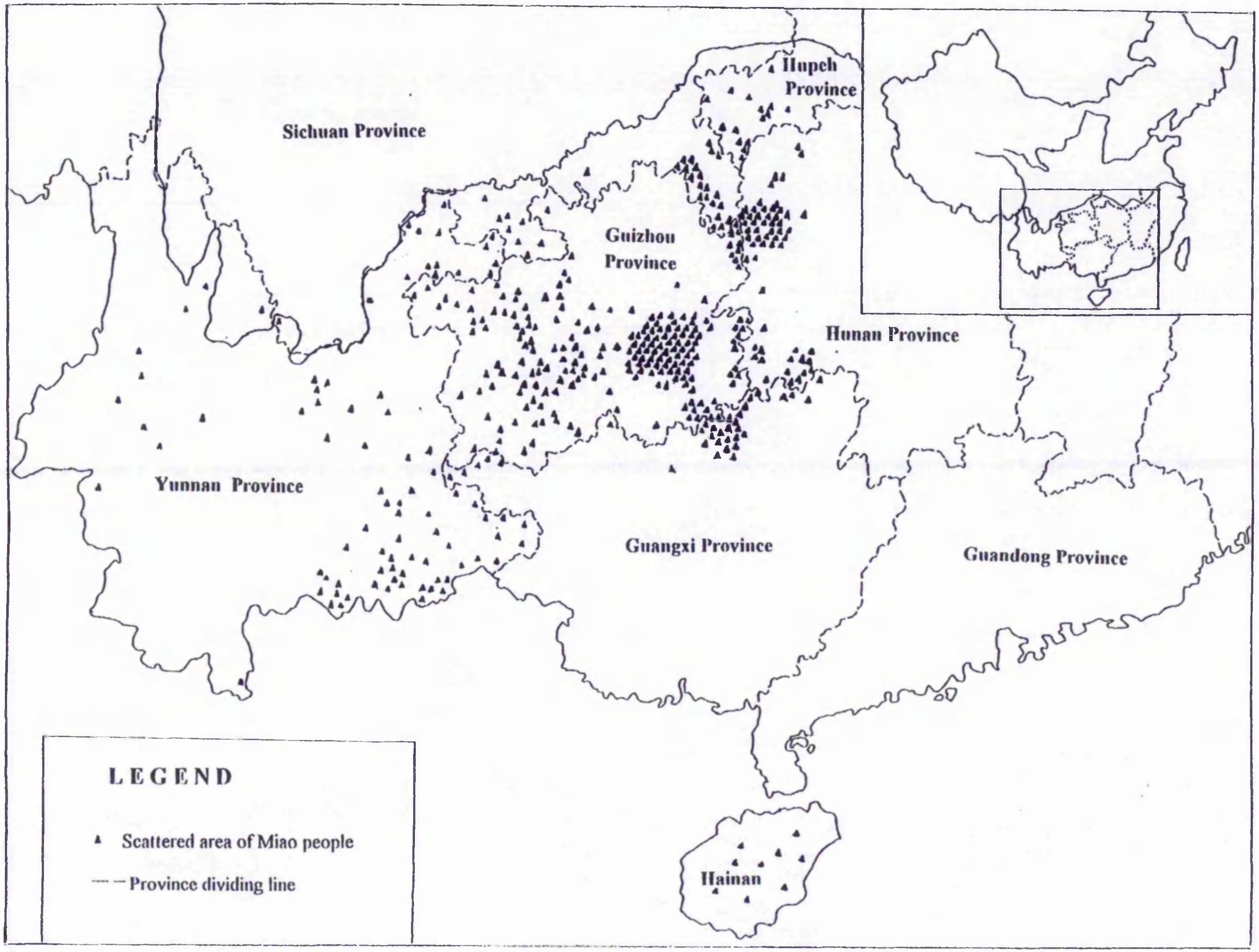

Figure 1.1 Miao people's home country: South-west of mainland China[4]

Figure 1.2 Pleated skirt with design of geometric pattern in applique on the lower part and figure on the upper part. Taijiang County, Guizhou Province.

Figure 1.3 Woman's gala dress with floral embroidery on the front panels and ox-gel coated fabric on the sleeves, together with geometric pattern decoration on the lower part. Danzhai County, Guizhou Province.

Figure 1.4 Knot stitch embroidery on a young woman's upper garment. Design of flower and bird on the shoulder. Kaili County, Guizhou Province.

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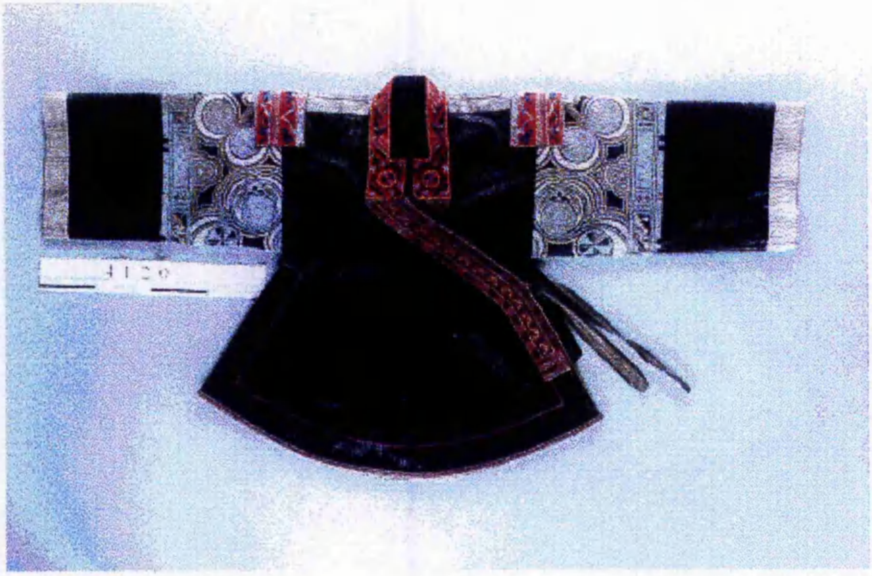


Figure 1.6 Women's upper garment, ox-gel coated fabric, with floral embroidery on the shoulder and neck. Design of spiral and bracken in batik on the sleeves. Paimou in Danzhai, Guizhou Province.

Miao costumes are divided into two general groups: casual wear and gala wear. The casual wear costumes are made of indigo-dyed cotton fabrics, with less decoration. For the basic cloth, they favour blue and brown over other colours and sometimes beat the fabric repeatedly until its texture becomes shiny. These calendered fabrics are used not only for casual wear but also for the basic cloth of gala wear. Brighter hues of red, green, yellow, pink and purple silk yarns will then be embroidered on those fabrics which are to be tailored for gala wear.[5]

1.3 The background of the Miao collections of the Fu Jen University

In 1990 [6] the Department was planning to collect Chinese Ethnic Minority costumes, particularly Miao costumes. Owing to the financial difficulty of there being no budget to collect textiles, garments, and accessories, the Department looked for funding from industry. Fortunately, one of the university's supporters, Mr. Hsing-Chiung Gu, donated generously to the Miao collection project and hence there is a considerable collection of Miao costumes at Fu Jen, comprising over 2500 items including costumes, traditional textiles, and related articles.

The main collecting of Miao costumes was carried out by Mr. Bai-Chung Chen. He and his co-workers entered south-western China in 1990, followed by Mr. Ching-Lin Chen and Mr. Ching-Wei Lou. The department also bought some Miao textiles and garments from private collectors to enhance their own collection.

Some gala dresses in the Fu Jen collections not only assume meticulous and complex patterns, but are also treated with unique finishing treatments. For instance, (1) The dyed fabric of Huangping County is smoked over burning pine and fir logs, then beaten with wooden hammers until it becomes a glistening brown colour[7] (Figure 1.7). (2) In another finishing treatment indigo-dyed fabric is coated with ox hide gel, then beaten with hammers and dried. The coating, beating, and drying processes are repeated several times until the fabric becomes stiff and glistening (Figure 1.8). Nowadays, Miao textiles are rarely treated this way, because the finishing processes are complex and time consuming. However, a considerable number of traditional Miao textiles in the Fu Jen collection were finished in the old manner and need special attention as regards their conservation. Due to the unique character of Miao textiles, together with their beauty and their cultural significance, the garments are of great interest and their conservation is very important.

Figure 1.7 Glistening brown fabric smoked over burning pine and fir logs then beaten with wooden hammers. Huangping County, Guizhou Province.

Figure 1.8 Ox-gel coated fabric, plain embroidery on a young woman's upper garment. Design of flower and bird, mouse, egret, and monkey on the sleeve panels. Shidong in Taijian County, Guizhou Province.

1.4 The textile conservation aims of the Fu Jen Textile and Clothing Culture Center

Educational institutions, such as the Graduate Institute of Textiles and Clothing at Fu Jen, are ideal places to take the initiative in the promotion of cultural awareness and responsibility. The main purposes of conservation of the Fu Jen Textiles and Clothing Culture Center, many of which are already actively pursued, may be summarized as follows [3]:

1). Collection and preservation of traditional textiles, costumes and related articles from Taiwan Aborigines, Taiwanese, Han Chinese, and Chinese Minority cultures (Miao, Yi, etc.).

2). Serve as an educational facility providing audio-visual materials for the teaching of courses in historic and ethnic textiles and clothing (e.g. Conservative Science of Textiles and Clothing).

3). Serve as a practice centre for textile conservation and collection-management for interested students or private collectors.

In the near future, the plan is to execute fund-raising activities for expansion of The Culture Center as follows:

1). For the building of an air-conditioned textile museum of international professional standard, complete with storage space, photographic room, exhibition area, conservation laboratory, and reference library. This is intended to be a "teaching museum" for textiles and costumes, with all the related facilities.

2). For supporting related research and publications.

3). To apply for funding for textile and clothing related projects from government and industry; for instance, the Center has succeeded in its application for a very interesting, future-oriented government-funded project in the textile conservation area.

4). To hold conferences and exhibitions. The Center has signed a contract with the National History Museum on a Miao Historical Costume Exhibition and an International Academic Conference in August 1999.

1.5 Research objectives

The main purposes of this research are to study the degradative effect of microwave irradiation on cellulosic textiles - cotton, indigo-dyed cotton, and indigo-dyed, ox-gel coated cotton - and the effect of laundering on Miao costume. The results will be analysed in terms of colour change, bacterial survival, tensile strength and % elongation, viscosity and staining of the cotton and silk textiles involved.

The objectives of this research are:

1). To determine the effectiveness of sterilising cotton and coated cotton fabrics by microwave irradiation.

2). To determine the degradative effect of microwave irradiation on cotton and ox-gel coated cotton.

3). To determine the colour change induced by microwave irradiation of indigo-dyed and indigo-dyed, ox-gel coated cotton.

4). To assess the colour change and loss of ox-gel of indigo-dyed cotton and indigo-dyed, ox-gel coated cotton on laundering.

5). To assess any colour change due to microwave irradiation on silk dyed with natural dyes.

6). To assess colour fastness to dry cleaning of silk dyed with natural dyes.

7). To assess the potential development of dyeing chitosan with natural dyes, currently being proposed as a suitable material for coating textiles and making fibres.

CHAPTER 2 LITERATURE REVIEW

2.1 Conservation and management of textile collections

In recent years, due to increases in the preservation of old clothing, conservation is becoming more and more sophisticated and specialised. It will normally be carried out by a specialised textile conservator, whose training will have included modern scientific techniques as well as art and textile history, using new technology and materials. It is very important that considerable importance should be attached to the choice of the right approach.

Apart from normal wear and tear, textiles begin to deteriorate as soon as they are made. The most serious cause is light, particularly the ultraviolet radiation from sunlight, which causes both fading of dyes and fibre degradation.[8] Atmospheric pollution, particularly from sulphur dioxide, is another cause of deterioration. Fu Jen is located in Taipei which is the capital and a heavily industrialised city. Recently air pollution is a major concern and although it has improved, there is still the problem that Yang-Ming mountain contains abundant brimstone and sulphur fountains which give rise to sulphur oxide fumes leading to degradation of textile materials, such as cotton and linen. The storage and display of old and valuable textiles will become an major work of conservation and restoration for museums and textile galleries.

Museums contain a wide range of organic materials that may be subject to insect and mildew attack. This biological deterioration is encouraged by high humidity (above 60-65 %), high temperatures (above 25° C), darkness, stagnant air, and poor housekeeping.[9] Several fumigants are used for the disinfection of contaminated art collections, e.g. ethylene oxide, methyl bromide and "Cyphenothrin". Until recently, ethylene oxide and methyl bromide were the preferred fumigants in museums, particularly ethylene oxide which is effective against both insects and mould.[10] However, its hazardous properties will damage museum objects so its use has been restricted. Now most museums tend to avoid using fungicides and insecticides if they can. Many researchers study only non-toxic and residue-free treatments, that can be safely handled with only minor precautions. Recent legislation restricting the number and use of pesticides has led to the pragmatic conclusion that prevention is better than cure. Physical methods give time to treat established infestations in a controlled and planned manner.[11]

2.2 Pest eradication methods in museums

There are many methods and materials with which to control pests. Choice of the eradication method depends on resources, extent of infestation and reaction of infested material to the control method.[12]

2.2.1 Trapping

Trapping systems are only feasible for the mobile stages of insects. Insect traps are usually a combination of two components: a lure or attractant to encourage the insect towards the trap, and a killing or retention system to hold it for disposal. Typical insect traps include: [11-13]

1). Mechanical traps normally use an ultraviolet (UV) light mounted behind a high-voltage grid, which electrocutes and often incinerates the attracted flying insects. These traps are useful for night flying insects.

2). Drowning in an attractant solution or water. The design of the trap allows easy entrance to the insect but denies it exit until it falls exhausted into the solution and drowns.

3). Pheromone trapping with pheromone-baited insect traps can effectively control indoor populations. Gilberg and Roach reported that pheromone traps have tremendous potential as a tool for monitoring insect populations in museum collection.[13] This method requires knowledge of the time and pattern of adult emergence, their lifespan and the duration of their response to the pheromone.

4). Adhesion to a sticky surface, as with fly-paper and sticky blunder traps. Traps for flying insects are not popular, owing to their visual obtrusiveness and exposed sticky surfaces, and because the adult flying stage of many museum insect pests is short-lived.

2.2.2 Vacuum (Low pressure)

The use of low pressure is an effective means of destroying insects. The most effective condition for killing insects is 1 inch of pressure or 29 inches of vacuum. Four days exposure proved 100 % effective against all stages of many stored product pests although the eggs of more species needed to be tested.[14]

Bergh et al.[15] have determined the insect survival after treatment in low pressure(20-100 hPa) for a number of insect species. Insects were kept at varying room temperatures (normally 20 - 40 ° C) and in fairly dry air (20-50 % relative humidity, RH); one set with fixed pressure of 20 hPa, for different time-spans, and another set with a fixed time (24 h) but with different pressures (22-100 hPa). Results showed that none of the animals survived a treatment of 20 hPa for 24 h, and different species showed a mortality rate from 11 % to 98 % during 12 and 6 h tests. The four different pressures tested were chosen so as to get a closer interval in the lowest-pressure region and to investigate the effect of a pressure close to 20 hPa. These results also showed that keeping the pressure below the threshold value is extremely important, thus classifying the vacuum method as vulnerable.

A method for control of museum pest insects must be not only effective in killing the animals but also harmless to the objects. If the vacuum method does turn out to be useful, it will be necessary to check its impact on different types of material. But these two researchers did not check the impact of low pressure on materials.

2.2.3 Thermal control

Thermal methods of pest control can be carried out using natural conditions, or widespread technologies which provide heat or cold.[16] Thermal techniques are presently being widely used for pest control in a variety of applications, both in the museum field and elsewhere. High and low temperatures are effective methods of controlling insect pests.

Low temperature (Freezing) :

A report indicates that more than 140 insect species will be killed by exposure to temperatures between -20°C to -40° C for several days.[16,17] To ensure mortality of *Dermestidae*, one week exposure at -20° C is advised. Sealing the objects in polyethylene bags or a zipper-lock plastic bag is essential to maintain moisture balance and avoid damage from meltwater during power stoppages. However, polymeric materials do become stiffer and more brittle at low temperatures.

High temperature:

At lethal temperatures, 55-60° C, exposure for several hours will kill all stages of insect life.[16] Sealing objects in bags will maintain moisture balance. The advantage of this treatment is that collections could be treated completely in about 4 hours, but the risk factors that need to be considered are : melting and softening of materials, accelerated chemical or physical deterioration at high temperatures, changes in moisture content and dimensional changes due to heating.[16,17]

2.2.4 Low oxygen atmospheres

Until recently, ethylene oxide has been one of the most widely employed chamber fumigants for the control of insect infestations in museum collections. Because of its hazardous properties, and increasing evidence that exposure to ethylene oxide will damage museum objects, its use has been restricted and, in many cases, discontinued by a number of museums and cultural institutions.[18] Studies on stored product pests have shown that prolonged exposure to low oxygen atmospheres (0-1 %) is effective against a wide variety of stored product pests and their various developmental stages. Many researchers have studied the utilisation of low oxygen on museum pests. The major source for finding papers with mortality data for this study was by Gilberg, Grattan, and Valentin *et al.* [19-21]

If 100 % mortality of pests is to be achieved, museum objects must be exposed to oxygen concentrations of 0.4 % or less for at least three weeks at a temperature equal to or greater than 30°C. It can be easily obtained using oxygen scavengers or by purging with nitrogen gas which is commercially available at low cost.[19]

Gilberg and Grattan studied the use of "Ageless", one of the most widely used commercial oxygen absorbers, in 1994.[20] "Ageless" is manufactured in the form of small sachets containing an oxygen absorbent, prepared from finely powdered metallic iron sealed inside a gas-permeable film, which controls the flow of oxygen and moisture to the absorbent. "Ageless" is most efficient and economic when used to scavenge relatively small amounts of oxygen. Recently "Ageless" has found application as an alternative to conventional chemical fumigants for the treatment of insect-infested museum objects.

2.2.5 Microwave heating / radiation

2.2.5.1 Introduction

Microwaves are non-ionizing electromagnetic radiations with wavelengths between one metre and one millimetre. In the electromagnetic spectrum, microwaves are found between the radio frequency at longer wavelengths and infrared radiation at shorter wavelengths. The frequency of microwaves lies between 300 MHz and 30 GHz. The frequency 2450 MHz is authorized for industrial applications.

The properties of microwave irradiation have been widely exploited by the food, [22-25] agriculture and textile industries, notably for the sterilisation of liquid products and the disinfection of cereals [1,26] and drying of textiles. Many researchers have shown significant effects on biological systems using microwave irradiation.[27-29]

2.2.5.2 Microwave irradiation of wool textiles

In 1960-80, the general ways of protecting textiles from damage by insects were by using insecticides, fumigants and mothproofing agents, especially methyl bromide and ethylene oxide, used mostly in museums.[30-31] Some museums also used fungicides to restrain fungal growth in textile conservation. The effect of these chemicals on insects and fungi was to achieve effective control.[26] But at present, museums tend to avoid using them if a better treatment method is available, partly because of health and safety problems, and partly because of possible damage caused by residues if they are left in the object being treated. Therefore, it was decided to study a non-chemical method.

The thermal effects of microwave energy on insects, based on the insects' sensitivity to temperature were studied.[25] Since 1980, there have been three studies on microwave heating to control insect infestation of wool textiles : Reagan *et al*. (1980),[32] Dever *et al*. (1990),[33] and Reyer and chauvin (1992).[26] Regan and Dever studied the effects of microwave radiation on the change of colour and other physical properties of wool. Reyer concluded that microwave heating can provide an effective, non-chemical method of disinfestation. These reports showed that microwave heating can provide an effective, non-chemical method of disinfesting wool and presumably any other protein-containing material. It was sufficiently effective to obtain 100 % mortality at all the stages of the webbing clothes moth, *Tineola bisselliella* and had little effect on the strength of wool materials.

2.2.5.3 Microwave irradiation of paper

From 1960, there have been several researchers studying the effect of electromagnetic radiations for the disinfection of paper but most have focused on gamma rays. [1,34-36] Only one research study by Flieder, *et al*. investigated the use of gamma rays, electron beams and microwaves, to destroy various cellulolytic fungi on several types of paper.[1] The results showed that microwave irradiation is extremely effective at killing all the fungal spores tested and was claimed to have no negative chemical or physical effects on the paper. Chemically paper and cotton are similar, both being cellulose, however, no work has been devoted to the action of microwave radiation on microorganisms, bacteria or fungi, on cotton textiles.

2.2.6 Storage of textile materials

It is sometimes advisable to parcel textiles up so that insects cannot get at them. For wrapping textiles, good quality paper is as effective as transparent plastic, but the latter is stronger, and has the added advantage that the contents are more readily inspected. In the case of susceptible material it is also advisable to put about a cupful of 1,4-dichlorobenzene crystals in the bottom of the bags to ensure against the risk of moth eggs being present and to include a quantity of a volatile insecticide in the parcel.[37]

2.3 Preservation and eradication of microorganisms: bacteria and fungi

Although most microorganisms are killed by exposing them to temperatures greater than 65°C, spores are much more resistant and may require much higher temperatures. Chemical disinfectants may not kill all organisms or spores. Therefore microorganisms are not killed instantly when they are exposed to heat or to chemical disinfectants. In any population there will be some that are more resistant than others. The most satisfactory way of sterilising infected waste for hospitals is by high-pressure steam in an autoclave.[38] This way is not suitable for textile conservation because the high temperature and pressure may damage textile materials. Many researchers have studied the effect of fungal activity on textiles but few have studied the effect of bacteria. The particular attention of the research presented here has been focused on the eradication of microorganisms using physical method which could be a useful treatment for textile collection in museums

The purpose of this review is to concentrate on physical treatments such as temperature and moisture control, freezing, oxygen permeability, and microwave sterilisation. The following information on *conidia* activation and eradication is from Strang,[17] Florian,[18,39] Rosenberg,[22] Daniel, [30] Collins,[17] and Scott. [40,41]

2.3.1 Fungi conidia / activity

Fungi reproduce by forming asexual conidia or sexual spores. The fungi, which cause mould growth on surfaces of dead organic materials such as material fibres, produce asexual conidia and it is these conidia which initiate this growth. It is these fungi that are called the conidial fungi.[18] The main treatments that effect activation for fungi conidia are temperature extremes, drying or wetting, and exposure to chemical activation.

The studies of Florian showed that even if conidia are activated they do not germinate unless there are suitable enviromental conditions. Mild heat treatment may activate dormant conidia or spores of some fungal species. This possibility of activation remains even if the spores are dried or frozen before germination. The optimum temperature for germination is around 26° C.[18]

Upsher[42] has studied the increase in fungal growth which occurred where high humidities prevailed. Rain would have been a greater influence on fungal development had it been permitted to wet the materials.

Florian reports that conidia deactivation occurs with dehydration, and/or low oxygen concentration in the air (less than 2 %) which must occur within six hours after activation by pH or temperature changes. Therefore storing artifacts wet or damp at low but not freezing temperatures will reduce the rate of growth or germination but will not kill the fungi, e.g. hyphae. Heat activation requires temperatures ranging from 40-75°C for varying lengths of times from five minutes to five hours. Different species require a diversity of durations and temperatures.

2.3.2 Bacterial activity

The minimum nutritional requirements for the growth and multiplication of bacteria are water, a carbon source, a nitrogen source and some inorganic salts. All nutrients enter into the cells through water and all waste products are also eliminated through it.

A bacterium is a single cell which is capable of reproducing itself. Most bacteria are free-living, i.e. they do not require other living matter to survive and reproduce and when they grow on solid or semi-solid surfaces that provide the necessary nutrients they form colonies. Most bacteria reproduce asexually by dividing in two but a few reproduce by budding.[38] If favourable conditions of moisture, pH, nutrition, temperature, etc. are present, some bacteria may double in number about every 20 min.

2.3.3 Sterilisation methods

2.3.3.1 Heating and freezing

It is possible that short term heating may activate fungal spores already present on these objects or specimens. According to Florian's study,[18] at temperatures of 36° C or above the conidia may remain viable for a few hours, but then they are usually killed. Dehydration at temperatures around 36° C not only dries the artifact materials, but also often kills the conidia . The average temperature to kill fungi or bacteria is 65° C.

Freezing wet materials may not be suitable because of ice damage. Freezing is also of questionable effectiveness in killing dry conidia. Some artifacts cannot withstand high temperatures (above 36° C) or the low temperatures (between -20 to -40° C) and should not be treated in this way.

2.3.3.2 Microwave sterilisation

Microbial reduction by microwaves, i.e., sterilisation, has been studied in a large number of experiments on many types of foods. Rosenberg and Bögl presented a summary of the relevant literature which shows microwave energy is a good way to control pests and microorganisms in the food industry.[22]

For disinfection of paper, Flieder found that whatever the conditions, the microwave irradiation of fungi cultured on dry papers had no effect on the viability of the spores, but it had a good effect when the irradiation was carried out in the presence of water. Flieder showed that under these latter conditions microwave irradiation is extremely effective at killing all the fungal spores tested on paper using 600 W microwave power.[1] The research presented here considers the potential of a technique for disinfecting cotton textiles using microwave irradiation as a conservative treatment for killing fungi.

Bacterial spores can be inactivated by microwave heating, provided that the temperature and treatment time are sufficient. It is evident from several studies on microwave irradiation, that there is a lack of research studies on the effects of sterilisation of textiles. Only one research report indicated that at the frequency 2450 MHz, low level continuous microwave radiation does not interfere with the growth of bacteria.[43]

2.3.4 Methods of preventing fungal/bacterial growth

2.3.4.1 Moisture control

The water vapour of air, the water content of the conidia, and the water content of the substrate are three aspects of water as it relates to fungal activation and growth. During germination, the water activity or equilibrium moisture content (EMC) in the conidia remains substantially constant. In dormant conidia or spores, the water activity will change in response to changes in environmental parameters.[18]

In the literature, tolerance of fungi is often related to RH. Pitt considers 70 % as the maximum RH to prevent fungal growth and says that if it does occur, it must be due to some microenvironment with a higher RH.[44,45] Scott reported that at a given temperature, a reduction in water activity causes a fall in germination rate.[41] Florian recognised a relationship between the moisture contents of the air and substrate and availability of water for exploitation by fungal conidia. She concluded that the most important aspect of maintaining conidia germination and vegetative growth is the absolute moisture content of the substrate.[18]

2.3.4.2 Oxygen permeability

Oxygen permeability can also play a major part in fungal activity. Positive-pressure display cases in which the air brought into the exhibit case is filtered to remove fungi can prevent surface contamination. Super-filtration in a room with an air-conditioning system will reduce the conidia load in the air. Scott reports that ventilation moves air from the external environment to internal spaces, and circulation moves the air around. If the air is circulating, a much larger volume of air comes into contact with the object and its influence will reduce mould spores settling on the surface of an object.[41]

2.3.4.3 Air flow

Air flow is a simple method for temporary conservation of art objects. Sakamsto *et al.* found that a light air flow restrained fungal growth. The combination of air flow with control of temperature (20-35° C) and humidity makes it possible to prevent the fungal growth in circumstances where art objects are conserved.[46] This study reported that fungal growth can be controlled where the air flow velocity is positive. Thus, in conserving art objects, it is important to create and maintain a "weak air flow" in the storage areas and cabinets.

2.3.4.4 Low humidity and oxygen

Valentin, *et al.*[21] studied methods of preventing microbial growth on parchment through control of RH and oxygen levels, using radioactive tracers to evaluate microbial growth on infected parchment samples. They found that the combination of low RH and low oxygen levels significantly decreases microbial activity on solid supports.

2.3.5 Other methods

Industrial and large scale sterilisation methods include infra red heat and ionizing radiation.[22] Infra red heat is frequently used to sterilise metal, glassware and stored foods since this energy can be readily absorbed by the commodities.[25] As well as their use for sterilising materials, radiation techniques may be used to age new materials in restored antiques. Ionizing radiation, with cobalt-60 as the source, is used for large-scale sterilisation of plastics, foods, medicines, and instruments etc., which would be damaged by heat. Flieder reported that irradiation with gamma rays at 3 KGy under nitrogen destroyed all the fungal spores tested on paper provided that they had been pretreated for 24 hours at 50° C and 95% RH.[1] Justa studied the disinfection of historical archives using gamma radiation as an alternative means in 1993.[36] In Taiwan, the National History Museum is studying the effect on ageing silk of using gamma ray irradiation for restoration.

2.4 Natural dyes

The Chinese had dye-workshops as early as 3000 B.C..[47] Most natural dyes are obtained from plants, and the subject therefore of natural dyeing is often called plant dyeing or vegetable dyeing. It has been shown that certain plant extracts will dye without any further substance being present - non-mordant dyes. However, a large proportion of natural dyes are mordant dyes; these require the presence of additional substances, frequently metal ions. Dyers throughout history also have had a deep interest and a working knowledge of the part that chemistry plays in achieving the colours that are desired. Some beautiful examples of early dyed fabrics still remain in museums and collections. In recent years, many researchers have studied natural dyes in textiles in relation to the conservation and restoration of old textiles. Taylor[48] concluded that the mordant is more important than the dye itself in determining the light fastness of coloured textiles.

Many natural dyes consist of a number of coloured components and the final shade obtained is to some extent dependent on the proportion of these components, a factor which in turn varies according to source, season, and dyeing conditions.[49] It is difficult to duplicate a colour exactly. Despite the above factors, a knowledge of dyeing techniques and recipes may be gleaned from printed books, dyehouse records, and living practitioners, and the processes reconstructed and adapted.

In *The Dictionary of Dyes and Dyeing*,[50] naturals dyes are summarised under their colours: (1) Blacks, (2) Blues, (3) Browns, (4) Greens, and (5) Reds. They also are referred to by their common English names.[48,49,51]

2.4.1 Indigo

Indigo has long been regarded as one of the most valuable and important of all colouring matters. It was used in India and Egypt long before the Christian era. It was introduced into China in the Chou Dynasty over 2000 years ago.

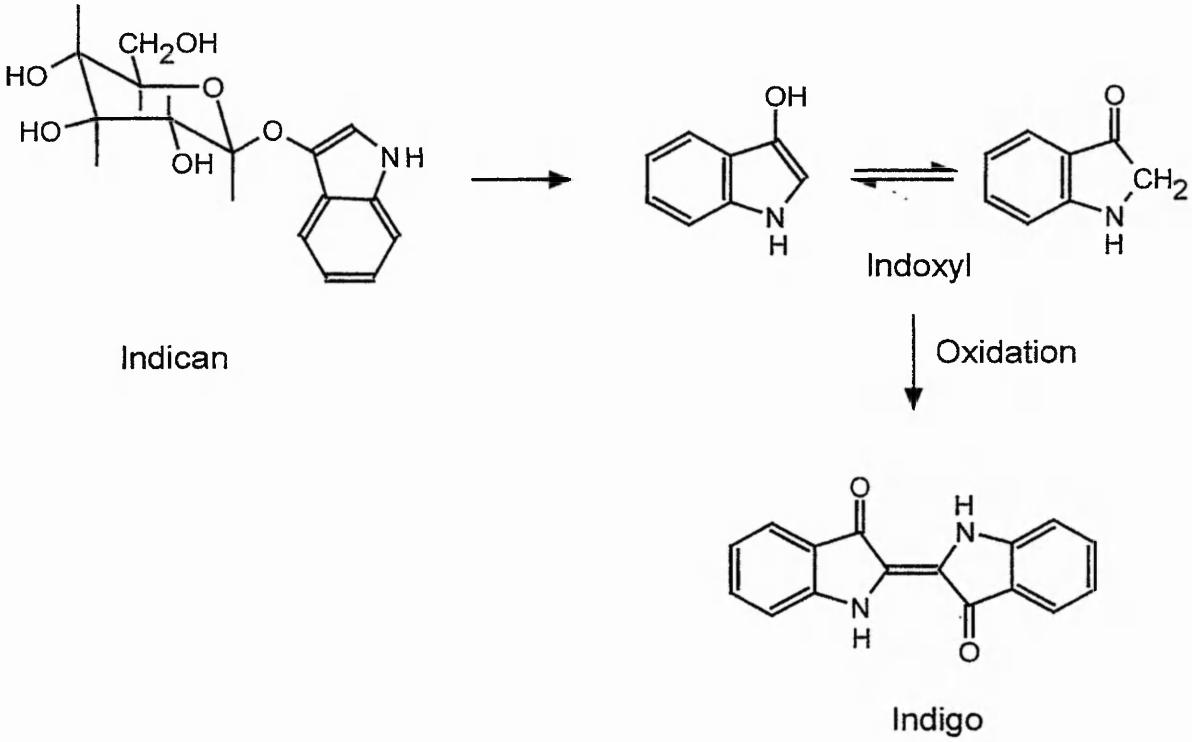
The brilliant colour and good-excellent fastness to washing and rubbing obtained with indigo dyeings made it very important. But compared with other natural dyes, indigo seems to have been among the most complicated. Particular steps are required for the extraction of the dyestuff and its concentration and preparation for storage.

It was certainly in very ancient times that men discovered the strange fact that the yellow juices of the indigo shrub would dye blue on wool, cotton, and many other fibres. The plant, whose use was highly developed in the Orient by Marco Polo's time, was cultivated for its dye centuries before Christ, and indigo-dyed textiles that still hold their colour have been found in Egyptian tombs and in the Inca graves of Peru, as well as from ancient India.[47]

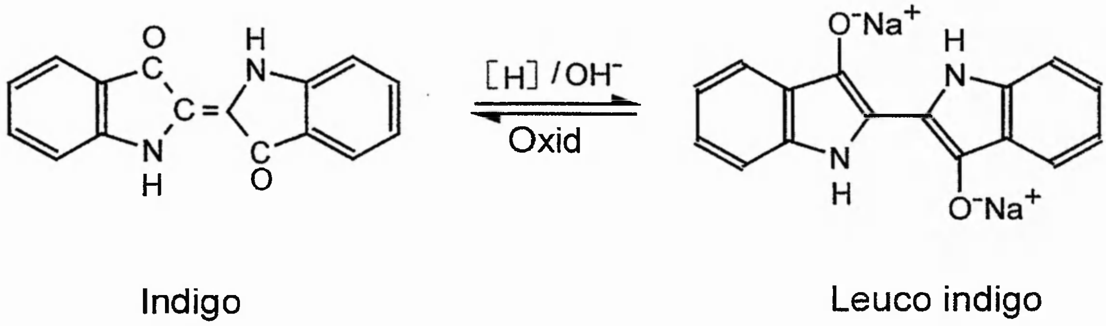
Marco Polo, who lived in the thirteenth century, and who was the earliest European traveller into China and India on record, relates that he saw indigo made in the Kingdom of Coulan, and describes the process by which it was prepared. However, indigo was not introduced into Europe until the sixteenth century.[50,52]

India is the natural home of the indigo plant and is the oldest centre of indigo dyeing in the world.[50] The greatest amount of natural indigo is obtained from India and more especially from Bengal, Oude, and Madras. It is also produced in Java, Manilla, China, Japan, Central America, Brazil, and certain parts of Africa. The principal plants cultivated for the manufacture of this dye are the *Indigofera tinctoria, Indigofera anil, Indigofera disperma*, and *Indigofera argentea.*

Indigo is obtained from the leaves of the plants of the genus *Indigofera.* It occurs in the form of indican which is the ß-D-glucoside of the half molecule indoxyl. Fermentation of the extract hydrolyses the indican to D-glucose and indoxyl, the latter then being oxidised to indigo.



Indigo is insoluble in water and has to be converted to a soluble form in order to be applied to cellulosic fibres; this is achieved by reduction under alkaline conditions using sodium dithionite / sodium hydroxide to produce the so-called leuco compound :



The reduced form is adsorbed by cellulosic fibres and once dyeing has taken place the leuco indigo is oxidised back to the insoluble indigo.

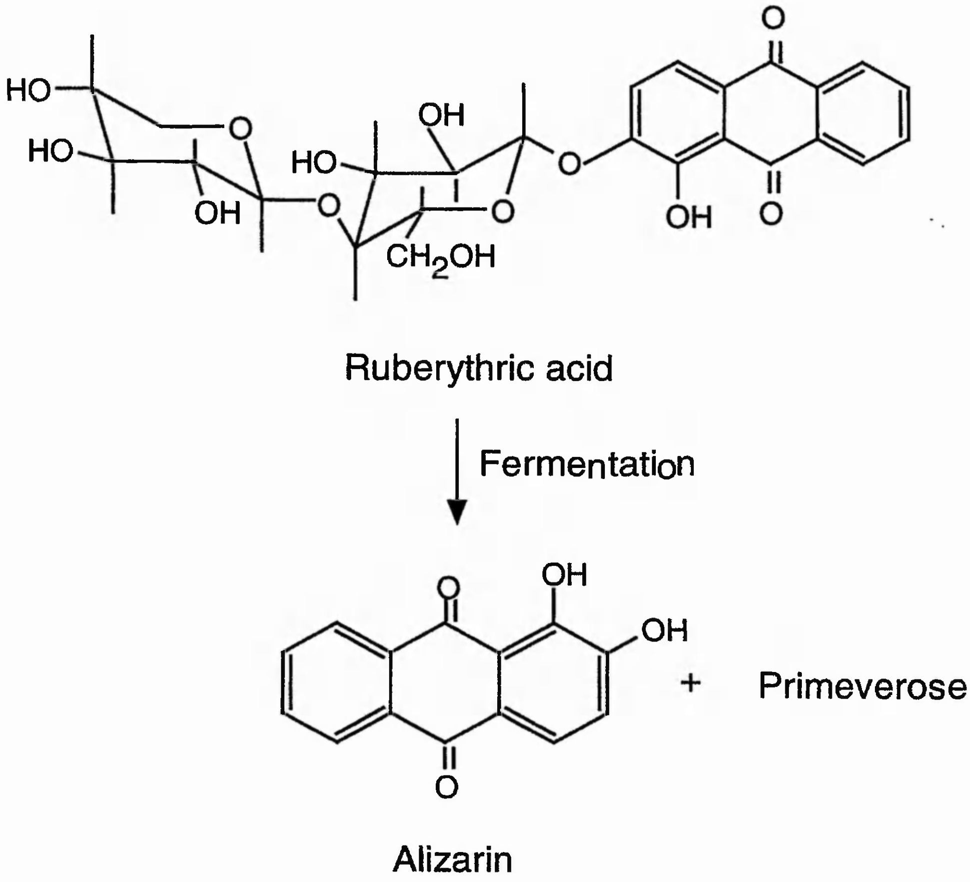
A large proportion of natural dyes are mordant dyes. Indigo is a substantive dye, and consequently requires no mordant. Owing to its modest fastness properties, it remains one of the most popular dyes today. One explanation for this is the fact that fabrics dyed with it retain a clear shade of blue in spite of wear and many washes. Compared with most natural dyes which have poor light stability, the colours of indigo dyed textiles are retained in museums.

Natural indigo contains a red isomer of indigo known as *indirubin* and other impurities in varying proportions. These constituents facilitate preparation of the vat, and were considered to have a desirable effect on the dyed shade. The first commercial synthetic indigo was successfully achieved in 1897 using a process based on the fusion of o-carboxyphenylglycine with caustic potash and oxidation of the resulting indoxyl.[53]

2.4.2 Madder

Madder is the root of the herbaceous perennial plant *Rubia tinctorum* and during its use as a dye was widely cultivated throughout Europe and the Middle East.[50] The earliest references come from the Indus civilization of around 3000 B.C. and it is fitting that India should be the home of the dye.

The colouring constituent of madder is alizarin (1,2-dihydroxyanthraquinone) which is present in the plant in the form of a glycoside called ruberythric acid. This consists of alizarin linked through its 2-hydroxyl group to the disaccharide primeverose (6-0-ß-D-xylopyranose-D-glucopyranose).



Madder yields smaller quantities of closely related dyes, the principal one being purpurin which is 1,2,4-trihydroxyanthraquinone. The structure of alizarin was determined in 1868 and its commercial production began in 1869, closely followed by that of purpurin. Because standardisation is of great importance in dyeing, the fact that the synthetic dyes were so much cheaper and better standardised were the main reasons why they replaced the natural products.

Madder is the classic mordant dye. The crucial property is the ability of madder, together with metallic oxides or hydroxides to produce permanent colours on the fibres. The main mordants that have been used are alum, potassium dichromate, copper sulphate, ferrous sulphate, and stannous chloride, and of these the first is historically the most important.[50] Mordants produce variations of red, pink, black, violet, lilac and puce colours with madder.

The most famous use of madder was for producing Turkey red where a complicated process of using madder with Turkey red oil and alum in the presence of lime gave one of the fastest colours.[50] In *A Weaver's Garden*,[54] Buchanan mentioned that Turkey red was imbued with ritual and full of magical and mystical overtones, especially in the East. Perhaps the notorious complexity and secrecy of the process was a marketing ploy to enhance the value of the product. Robertson also mentioned that the brightest and most lasting dye derived from madder was Turkey red. In this long and complicated process, the fibres were prepared by boiling, tanning, and mordanting with alum and calcium salts before dyeing.[55] However in her recipe for madder dyeing on wool, Robertson just used alum as the mordant, which gives Chinese lacquer red rather than Turkey red. However the traditional Turkey red technique is rarely used today and it is likely that the technique is not known to the scientists and technologists in the dyeing industry.

2.4.3 Other natural dyes

The commonest material in North America and Europe in earlier days was wool. This was in contrast to India and much of Asia, where cotton and silk were more appropriate for wearing apparel. Before synthetic dyes were produced, all colouring matters were derived directly from plant or animal sources. Natural dyes developed over the centuries were mainly for these fibres, and the sources were mainly from grasses, flowers, seeds, berries, trees, and lichens, etc..

A number of yellows were obtained from saffron, turmeric, gardenia, and weld. In addition the madder plant afforded the most important red dye, though three reds from insect sources, kermes, lac and cochineal, were also widely used. Brown was produced from walnut, tea leaves, onion skin, and lichens. Beautiful purple shades were obtained from certain lichens in the presence of a nitrogen donor (ammonia or stale urine).[49] Logwood was by far the most important black dye from the 16th century to give black and violet shades on a number of fibres. Most plant extracts give green shades when applied in the presence of copper sulphate.

China's climate covers the range from tropical to temperate. The different climates lead to the cultivation of a variety of plants. Originally the natural dyes developed were based on the sources of local plants. Basically, the use of natural dyes in China is similar to western countries, but some fruits in the south of China are difficult to cultivate in the west, e.g. lichee, mango, and mulberry (leaves afford food for the silkworm). Lichee leaves, mango and mulberry fruits are also sources of dyes. In China, gardenia and green tea are widely spread and used as natural dyes since extraction of the colouring matter is easy and they are good colourants. The application class of gardenia is that of a direct dye,[51] that means gardenia gives a bright yellow on cellulosic or protein fibres without a mordanting treatment. In the current research gardenia and green tea are two sources of natural dyes for dyeing silk and chitosan materials.

Before synthetic dyes were produced, all of natural fibres were dyed by natural dyes. Even nowadays, just a few synthetic fibres can take natural dyes, for instance, nylon could be dyed with logwood.[49] With the advent of synthetic dyes, the use of natural dyes decreased dramatically, and this was accentuated by the development of synthetic fibres. However chitosan-coated synthetic fibres should be dyeable with natural dyes.

2.4.4 Mordants

Some of the more common mordants found in the recipes included in books on natural dyes are: [47,54,56]

1. Aluminum potassium sulphate (alum, $AlK(SO_4)_2.12H_2O$), which is usually combined with cream of tartar (potassium hydrogen tartrate) in a ratio of 3 parts of alum to 1 part of cream of tartar. It is used for mordanting light, pure colours.
2. Cupric sulphate (blue vitriol, copper sulphate, $CuSO_4.5H_2O$), which is often used to help make colours in the green range as it itself imparts a bluish-green colour to the fibre.
3. Ferrous sulphate ($FeSO_4.7H_2O$). In the natural dye field iron is called a "saddening" agent because it makes a colour darker or duller.
4. Potassium dichromate (Chrome, $K_2Cr_2O_7$) or chromium sulphate ($Cr_2(SO_4)_3.15H_2O$) used to deepen the colours achieved and to make them more lasting.
5. Stannous chloride ($SnCl_2$), often used as a brightening agent to make a colour sharper or lighter.

6. Calcium acetate ($Ca(CH_3COO)_2$), often used as a brightening agent to make a colour brighter.

2.5 Chitin and chitosan

Chitin is a naturally occurring polysaccharide present in the exoskeleton of crustaceans, molluscs and insects and in the cell wall of certain fungi. It is one of the most abundant organic materials being second only to cellulose in the amount produced each year by biosynthesis. Structurally it is similar to cellulose except that an acetamido group replaces the C(2)-hydroxyl group of cellulose.

Alkaline treatment of chitin converts it to chitosan in which the C(2)-hydroxyl group of cellulose is replaced by a primary amine group - Unlike chitin, which is only soluble in complex organic solvent systems, chitosan is readily soluble in dilute aqueous acids such as 0.1 M acetic acid, due to the formation of protonated amine groups along the polymer chain.

In most cases samples of chitin and chitosan are copolymers rather than homopolymers. Chitin normally contains a proportion of deacetylated sugar residues while most commercial chitosan materials have only 80-85 % of the acetamido groups hydrolysed to amine groups.

The first study of the uptake of dyes on chitin was carried out in 1958 by Giles and Hassan.[57,58] Since then several researchers have studied the topic with the intention of improving dye coverage and dyeability of natural and synthetic fibres by pretreating them with chitosan solutions.[59,60] Furthermore in recent years there has been considerable work carried out on the production of fibres from chitin, chitosan and chitin/cellulose blends.[61]

The principal mechanism of dye uptake on chitosan is ion exchange.

$\text{Chit-N}^{+}\text{H}_{3}\text{X}^{-}$ +Dye-SO_{3}^{-} Chit-$\text{N}^{+}\text{H}_{3}\text{O}^{-}_{3}$S-Dye + X^{-}

Additional dye ions may be adsorbed through other attractive forces - van der Waals' forces, hydrophobic bonding and hydrogen bonding, depending on the nature of the dye ion - so that the plateau may be in excess of that expected from an ion exchange process alone. With low molecular weight dyes where these additional attractive forces will be also minimum, there is a 1:1 stoichiometry between the $-\text{N}^{+}\text{H}_{3}$ groups in the chitin/chitosan substrate and the $-\text{SO}^{-}_{3}$ groups of the adsorbed dye when the system is allowed to reach equilibrium in the presence of an excess of dye.[62] The dyes used to dye chitin and chitosan have been mainly acid, direct and reactive dyes. No work has been carried out to date on the dyeing behaviour of natural dyes on these materials. However since many natural dyes involve the use of metal ions as mordants, and chitosan readily adsorbs many metal ions, it is likely that chitosan would be a suitable substrate for many natural dyes.

Chitosan/metal ion complex formation

Roberts pointed out that chitosan-metal ion complex formation occurs primarily through the amine groups functioning as ligands, so that the extent of deacetylation of the chitosan is a critical factor in controlling the level of metal ion uptake. However, it is not the total concentration but the concentration of accessible amine groups that is important, since these are the ones available for complex formation. [63]

The measurement of metal ion complexation were obtained at equilibrium as follows: (1) Muzzarelli and Tubertini studied the rate of uptake of a number of transition metal ions by an excess of chitosan and their results indicated that equilibrium had been reached in all cases after 45 h contact time, or after 30 h with a number of the metal ions. (2) Koshijima *et al*. found that equilibrium was reached in the chitosan-Cu(II) system after 50 h at 30°C. (3) McKay *et al*. used contact times of 168 h to ensure equilibrium conditions in the same system.[64]

2.6 Colour fastness and mechanical properties of textile fabrics

2.6.1 The effect of laundering on the mechanical properties and colour fastness of cotton

It has long time been known by laundering researchers all over the world that test pieces of cotton fabric offer a valuable means of evaluating wear in commercial laundering. In the literature, reviews of many results indicated that the decrease in tensile strength can be taken as a measure of the wear that occurs during laundering. This is affected by chemical degradation (mainly by oxidising agents) and mechanical abrasion.[65,66] Vaeck carried out a comprehensive study of chemical damage that included determination of the relationship between tensile strength loss and fluidity increase for bleaching of different degrees of severity.[65]

The mechanical properties and colour fastness are very important characteristics for museum textiles. During laundering for conservation, the fabric has to withstand potential loss of colour and mechanical damage which would damage the treasures. When considering the decrease in tensile strength caused by chemical degradation of the cellulose in laundering, it is necessary to know, for the fabric concerned, the relationship between loss in tensile strength and the soap or detergent concentration, for soaps and detergents differ in their cleaning power. Phillips, et al.[67] concluded that the colour fading of cotton fabrics has led to significant changes in wash product formulation, whilst maintaining the cleansing power and disinfection properties of the wash liquor.

According to Munshi, the function of the laundry is to restore soiled fabrics to a state of newness by removing the maximum amount of dirt, soil and stains with minimum changes in colour, dimensions and strength of the laundered articles.[66] The success of the laundry in doing this depends mainly upon three factors :

1). the launderability of the fabrics;
2). the procedure used for washing the textile materials;
3). the type of detergent and soap used.

Most of the researches in laundering use laboratory machines which have been produced to simulate conditions occurring in actual wear to provide an assessment of the fabric performance.

Venkatesh, *et al.*[68] studied soiled fabrics that were washed in a detergent solution in a Tergotometer, Launder-O-meter, or in any standard home washing machine at a suitable temperature. These experimental washing machines offer different agitation on fabrics. Mechanical abrasion should be avoided with old textiles and fragile fabrics; hand washing or spray cleaning are considered to be suitable cleansing techniques to preserve museum textiles.[8,37,69]

2.6.2 The effect of dry cleaning on colour change

2.6.2.1 History of dry cleaning

According to the CIBA Review 1964/1,[70] legendary references to the start of the dry cleaning industry say it began in France in the 1840s with an accidental discovery that camphene (spirits of turpentine), a lamp fuel then in common use, had excellent cleansing powers. Another new insight into the early history of the industry was gained from a paper published in 1957 by Dr. Sidney M. Edelstein. He mentioned an early reference to the solvent in a book, published in 1716, under a chapter on “The Secrets of Removing Spots and Stains” where there appears, along with several older methods using water, a “ special secret for removing grease and oil spots from silk stuff ”. This book indicated that the start of using spirits of turpentine was before 1716. The history of dry cleaning might be nearly 300 years old.

2.6.2.2 Types of dry cleaning solvent

Modern dry cleaning of clothing makes use of organic solvents such as perchloroethylene and trichloroethylene, which remove oil-borne soil and stains. Since these organic solvents do not cause fibre swelling, no shrinkage occurs on this account, although inherent relaxation shrinkage in the fabric may occur.[71]

1. Camphene (Turpentine)

The lingering odour of turpentine in garments cleaned with camphene was doubtless one of the major factors that slowed the acceptance of this solvent for immersion cleaning in the transitional period of the 1840s and 1850s. This is the earliest organic solvent for dry cleaning.

2. Benzene

Its solvent power for fats and oils enables it to be used with advantage for removing grease stains from articles of silk and wool. In addition to its superior solvent power it has the advantage over turpentine of leaving no odour behind it. However benzene is unlikely to be used nowadays since it is known to be a powerful carcinogen.

3. White petroleum

This third organic solvent also became available in the late 1800s. It grew out of the great industrial developments which took place in the United States at that time. By 1928 the use of white petroleum in dry cleaning was so wide spread that it had become popularly known as "Standard solvent", and was listed as Commercial Standard 3-28 (CS 3-28) by the US Bureau of Standards.

4. 140° F solvent

Camphene and benzene were not specifically made for dry cleaning. They were both highly explosive and extremely dangerous in use. The petroleum products and oil companies co-operated willingly in the adoption of a solvent specification which would minimize the hazard of fire and eliminate complaints of odour. 140° F solvent is a safety type petroleum solvent, having a flash point of 140° F (60° C) as compared with Standard solvent's 100° F (38° C).

5. Chlorinated hydrocarbons

The two major advantages of a chlorinated hydrocarbon are that it is non-flammable and fast drying. Perchloroethylene is more commonly used than trichloroethylene, which has the disadvantage that triacetate is damaged by it. Today, perchlorethylene and Standard solvent

(white petroleum) are the basic solvent systems in use throughout the world for dry cleaning apparel and household furnishing.

2.6.2.3 Colour fastness in dry-cleaning

The term "colourfastness" as it relates to dry cleaning and wet cleaning methods means : (1) retention of shade and (2) absence of staining.[71] In the terminology of the AATCC "colorfastness that it is the resistance of a material to change in any of its colour characteristics, to transfer of its colourant(s) to adjacent materials, or both, as a result of the exposure of the material to any enviroment that might be encountered during the processing, testing, storage or use of material".[72]

Dry cleaning solvents do not penetrate the surface of the fibre and do not come in contact with the colouring material. A dyed fabric may exhibit no loss of shade strength and produce no staining of the water or solvent when tested. In dry cleaning tests, if the test is a simulation of laundering conditions, this would mean that the fabric could be laundered with a white fabric without danger of contaminating it with dissolved dye.

CHAPTER 3 EXPERIMENTAL

3.1 Materials

3.1.1 Cotton fabrics

A number of different cotton fabrics were used in the research.

Fabric C1: Scoured and bleached 69×42 plain weave, weighing 211 g/m^2.

Fabric C2: Scoured and bleached 116×96 plain weave test fabric (Testfabric Co. USA), weighing 88 g/m^2.

Fabric C3: Unscoured and unbleached 56×38 plain weave greige, weighing 48.5 g/m^2.

Fabric C4: Unbleached 66×60 plain weave test fabric, weighing 166 g/m^2.

Fabric C5: Scoured and unbleached calico 67×66, weighing 140 g/m^2.

Fabric CD1: Cotton fabric 62×43 indigo-dyed by Miao people in mainland China, weighing 160 g/m^2.

Fabric CDG1: Cotton fabric indigo-dyed then treated with ox skin gel, 55×76 dobby weave, weighing 269 g/m^2, beaten with hammers and dried. The coating, beating and drying steps are repeated several times. Produced from the Miao people.

3.1.2 Silk fabric

Degummed and bleached silk, 128×111 plain weave, weighing 33.6 g/m^2.

3.1.3 Wool fabric

Scoured and unbleached 75×74 twill woollen fabric, weighing 164 g/m^2.

The specifications of textile fabrics used in the research are shown in Table 3.1.

Table 3.1 The specifications of textile fabrics used in the research

Textile Fabrics	*Fabric count* *(Yarns / per in)*	*Fabric weight* *(g/m^2)*
C1	69×42	211
C2	116×96	88
C3	56×38	48.5
C4	66×60	166
C5	67×66	140
CD1	62×43	160
CDG1	55×76	269
Silk	128×111	33.6
Wool	75×74	164

3.1.4 Chitosan materials

3.1.4.1 Starting chitosan

The chitosan used was supplied by Aber Technologies, France, and had 2 % residual *N*-acetylation (DA=0.02). This was used to prepare samples having different molecular weights and DA values. A sample (10 g) was bleached by treating at 95-100° C for 1 hr in distilled water (200 mL) containing $NaBH_4$ (1 g) and Na_2CO_3 (1 g).

3.1.4.2 Production of lower molecular weight chitosan

To a solution of chitosan in 0.1 M acetic acid was added sodium nitrite ($NaNO_2$) and the mixture stirred overnight at room temperature.[73,74] The solution was then used directly for coating cotton fabric without isolation of the degraded chitosan.

3.1.4.3 Production of chitosan having varying DA values

A solution of chitosan in 0.1 M acetic acid was diluted with 2.5 volumes of methanol and a solution of acetic anhydride in methanol added with stirring. After stirring overnight at room temperature the chitosan was precipitated by addition of concentrated NH_4OH, filtered off, washed well and dried at 55-58° C under vacuum. The DA value was determined by CI Acid Orange 7 adsorption.[75]

3.1.4.4 Production of chitosan films

Chitosan (2 g) either bleached or unbleached, was dissolved in 2 % (vol./vol.) acetic acid (50 mL) by stirring overnight at room temperature. The solution was spread on a glass plate using a coating table then allowed to dry overnight at room temperature. The dried film was then neutralised using either NH_4OH or NaOH solution, rinsed with distilled water until neutral, then dried at room temperature.

3.1.5 Natural dyes

Stock solutions of natural dyes were prepared from a range of materials.

3.1.5.1 Alizarin (madder)

Alizarin powder (6 g) was added to distilled water (1 L), the mixture raised to the boil over 20 minutes and heating continued at the boil for 30 minutes. After cooling the mixture was filtered and the extraction process repeated and two filters were combined to give 1010 mL of a yellow stock solution. Weaker or more concentrated stock solutions could be prepared by using smaller or greater quantities respectively of alizarin powder.

3.1.5.2 Green tea

Dry tea leaves (10 g) were added to distilled water (500 mL), the mixture raised to the boil over 20 minutes and heating continued at the boil for 30 minutes. After cooling the mixture was filtered and the extraction process repeated on the residue using 300 mL distilled water. The two filtrates were combined to give 600 mL of a brown stock solution. A less concentrated stock solution was prepared from 5 g tea leaves.

3.1.5.3 Turmeric

Turmeric root (10 g) was added to distilled water (500 mL), the mixture raised to the boil over 20 minutes and heating continued at the boil for 30 minutes. The mixture was then cooled and filtered to give 400 mL of a yellow stock solution.

3.1.5.4 Silver birch

Fresh silver birch leaves (20 g) were added to distilled water (500 mL), the mixture raised to the boil over 20 minutes and heating continued at the boil for 60 minutes. The mixture was then cooled and filtered to give 400 mL of a light brown stock solution.

3.1.5.5 Nettle

Dried nettle stems with leaves (10 g) were added to distilled water (500 ml), the mixture raised to the boil over 20 minutes and heating continued at the boil for 30 minutes. After cooling the mixture was filtered and the extraction process repeated on the residue using 300 mL distilled water. The two filtrates were combined to give 400 mL of a brown stock solution.

3.1.5.6 Gardenia

Dried gardenia seeds (20 g) were added to distilled water (500 mL), the mixture raised to the boil over 20 minutes and heating continued at the boil for 30 minutes. After cooling the mixture was filtered and the extraction process repeated on the residue using 300 ml distilled water. The two filtrates were combined to give 600 mL of an orange-yellow stock solution.

3.1.5.7 Onion skin

Onion skin (5 g) was added to distilled water (500 mL), the mixture raised to the boil over 20 minutes and heating continued at the boil for 30 minutes. After cooling the mixture was filtered to give 370 mL of a yellow-brown stock solution.

3.1.5.8 Thistle

Dried thistle stems with leaves (10 g) were added to distilled water (500 mL), the mixture raised to the boil over 20 minutes and heating continued at the boil for 30 minutes. After cooling the mixture was filtered to give 400 mL of a light brown stock solution.

3.1.5.9 Plantain

Dried plantain leaves (10 g) were added to distilled water (500 mL), the mixture raised to the boil over 20 minutes and heating continued at the boil for 30 minutes. After cooling the mixture was filtered to give 400 mL of a light brown stock solution.

3.1.5.10 Natural indigo

Natural indigo dye was obtained from the "Natural Dyes" shop in Kyoto, Japan.

3.1.6 Chemical solutions

All chemicals and solvents were General Purpose Reagent grade and were used as supplied.

3.2 Dyeing

3.2.1 Preparation of indigo-dyed cotton fabric

Fabric C4 was dyed with natural indigo, with vatting being carried out at 40° C and dyeing at 20° C. During dyeing the dyebath was checked frequently to ensure that it was still alkaline and reducing, using Congo Red and Caledon Yellow GN indicator paper respectively. After dyeing the leuco dye was oxidised back to the insoluble form by exposure to air, then soaped at the boil to develop the correct shade and fastness properties.

3.2.2 Dyeing of wool with natural dyes

Unbleached twill woollen fabric was used to pretest the natural dyes. Samples of wool (2.5 g) were mordanted using either 4 % or 20 % of mordant o.w.f. and a liquor ratio of 40:1. The mordants used were alum, copper sulphate, ferrous sulphate, potassium dichromate, stannous chloride, and calcium acetate and were applied at the boil for 30 minutes. The samples were then removed from the bath, squeezed, and cooled in air.

The cooled mordanted samples were placed in dyebaths containing 150-200 mL of the extracts set at room temperature, raised to the boil over 20 minutes and dyed at the boil for 30 minutes. The samples were then removed, rinsed well in cold water and air dried.

3.2.3 Dyeing of silk

3.2.3.1 Dyeing of silk with natural dyes

Degummed and bleached silk was used in this work. Samples (2 g) were mordanted at a liquor ratio of 100:1 using 5 % mordant o.w.f.. The mordants used were alum, copper sulphate, ferrous sulphate, potassium dichromate, stannous chloride, and calcium acetate and were applied at the boil for 30 minutes. After mordanting the samples were removed from the bath, squeezed, and cooled in air.

The cooled mordanted samples were placed in dye baths containing 150 mL of the extract plus 75 ml distilled water set at room temperature, raised to the boil over 20 minutes and dyed at the boil for 30 minutes. The samples were removed, rinsed well and air dried.

3.2.3.2 Dyeing of silk with indigo

A mordanted sample of silk (2 g) was dyed at a liquor ratio of 150:1 using 3 % natural indigo, 2 % sodium dithionite, 1 % gelatin solution (40 mL/L) and concentrated ammonia (10 mL/L) by the following procedure.

The ammonia and approximately half the sodium dithionite were added to the water at 55° C and the solution allowed to stand for 5 minutes. The gelatin solution was then added, followed by the indigo, the mixture stirred well and the remainder of the sodium dithionite added.

3.2.4 Dyeing chitosan

3.2.4.1 Dyeing chitosan in flake form

Chitosan flake was mordanted at the boil for 30 minutes at a liquor ratio of 150:1 and 10 % mordant (on weight of flake). After filtering off the mordanted chitosan flake was cooled, then placed in a natural dye solution (LR 250:1) and dyed at the boil for 30 minutes. The flake was then filtered off, rinsed well with water and air dried at room temperature.

3.2.4.2 Dyeing chitosan in film form

Mordanting and dyeing were carried out on films still adhering to the glass plates on which they had been cast and neutralised. This was to ensure ease of handling, both during these operations and during subsequent measurements.

The film was mordanted in 300 mL of the appropriate mordanting solution. The glass plate and chitosan film combination was entered at room temperature, the solution raised to the boil over 20 minutes, and held at the boil for 30 minutes. After cooling the plate was removed and the film rinsed with distilled water and dried.

The combination (plate + film) was then placed in 150 mL of the required natural dye extract diluted with an equal volume of distilled water, dyed at the boil for 30 minutes, then rinsed in water and air dried at room temperature.

3.2.5 Measurement of dyed materials

Reflectance measurements of dyed fabrics were carried out on an I.C.S. Micromatch 16-point reflectance spectrophotometer using the normal technique.

To determine the “reflectance” spectra of the chitosan films, each of the dyed films, still adhering to the glass plates, was backed with a white tile and measurements carried out using the I.C.S. Micromatch.

Colour strength values and colour difference values were also determined, where appropriate, using the I.C.S. Micromatch.

3.2.6 SEM Measurements

Film cast on glass was mordanted with chromium sulphate and another film was peeled off completely then mordanted under the same conditions. The air surface and glass surface of a non-mordanted film and the two mordanted films were mounted on a SEM specimen holder then coated with gold-palladium. The surface morphology of the films was observed with a Cambridge Stereoscan 600 Instrument at an accelerating voltage of 20 kv.

3.3 Production of chitosan-coated cotton fabrics

Chitosan solutions containing 20 g chitosan/L and 60 g chitosan/L were prepared in 1 % aqueous acetic acid. Cotton fabric was steeped in the selected solution then run through a pad mangle set to give 100 % expression. The padded fabric was then dried in a circulating air oven at 60° C. The % coating obtained was calculated from the % pick-up, obtained by weighing the fabric dry and after padding, and the known concentration of chitosan in the pad liquor. Higher weights of coating were obtained by repeating the steep-pad-dry cycle the required number of times.

3.4 Microwave irradiation

3.4.1 Irradiation conditions

Microwave irradiation was carried out in a Sharp Carousel Model R-3A64 domestic microwave oven operating on a wave frequency of 2450 MHz. Heating times of 30 seconds-2.0 minutes were used at high, medium high and medium power levels. Longer irradiation times were achieved by multiple irradiation treatments, allowing the microwave oven to cool down between each treatment. All measurements were performed under the same environmental conditions.

3.4.2 Tests for determining possible damage due to microwave irradiation

3.4.2.1 Tensile strength

Tensile strength tests were carried out according to the ASTM Standard Test-D 1682-64, ravelled strip method and British Standard BS 2576.[76,77]

3.4.2.2 Fluidity

The fluidity in cuprammonium hydroxide was measured using the modified rapid method.[78]

3.4.2.3 Methylene Blue adsorption

The measurement was carried out as follows:[79]

(1) Preparation of Methylene Blue solution

Accurately weighed potassium dihydrogen phosphate (KH_2PO_4 , 1.361 g) was dissolved in distilled water and made up to 100 mL in a volumetric flask with distilled water. In a 1 litre graduated flask place Methylene Blue (1.280 g), 50 ml of potassium dihydrogen phosphate solution, and 46.7 ml of 0.1 M sodium hydroxide solution. Add distilled water, dissolve the contents, make up to the mark with distilled water and shake to ensure uniform mixing. Then take 100 mL of this solution and dilute to 1 litre with distilled water to give a 0.4 mM solution of Methylene Blue.

(2) Calibration of 551S UV/VIS (Perkin-Elmer) Spectrophotometer

Measure accurately 10, 25, 50, and 75 mL portions of the 0.40 mM Methylene Blue solution and dilute each to 100 mL with distilled water in volumetric flasks. These solutions have concentrations of 0.04, 0.10, 0.20, and 0.30 mM respectively. Dilute 10.0 mL of each solution, including the undiluted 0.40 mM solution, to 100 mL in a volumetric flask with approximately 0.1 N-hydrochloric acid (8.9 mL conc. acid made up to 1 litre) and determine the optical density in the UV/VIS Spectrophotometer using a 1 cm glass cell.

(3) Absorption of Methylene Blue by cellulose

Weigh accurately 1.0 g of cotton, cut the sample into small pieces, place in a volumetric flask with 100 mL 0.4 mM Methylene Blue solution, shake for 2 h and stand overnight. Filter through a filter paper, take exactly 10 ml of the filtrate and dilute to 100 ml in a volumetric flask. Measure the absorbance at 600 nm and determine the concentration of Methylene Blue from the calibration graph.

3.4.2.4 Colour change

Reflectance measurements were carried out using an I.C.S. Micromatch 16-point reflectance spectrophotometer. To even out any non-uniformity in the samples the values used were the average from eight measurements. Both colour strength and colour difference (Δ E) values were recorded.

3.5 Sterilisation of cotton bv microwave irradiation

3.5.1 Selected fungi

The fungal flora tested on the textiles were :

1. *Aspergillus niger* : reference IMI 091855
2. *Aspergillus terreus* : referenceIMI 045543
3. *Penicillium funiculosum* : reference IMI 087160

4. *Mucor hiemalis* + & – strains, mated NTUCC 146 & NTUCC 147

The fungi selected were based on Aranyanak's study,[80] and on fungal species commonly found on cotton and silk textiles and known to contain cellulases. These fungi were obtained from the Department of Life Sciences, TNTU.

3.5.2 Preparation of ten-fold dilutions

Most spore suspensions contain large numbers of viable spores and have to be suitably diluted before a known volume is applied to a plate for counting.

Dilutions were prepared as follows :

(1) Pour 9.0 mL of sterilised 3 % Tween into a Universal bottle containing an agar slant with mature fungal colonies to release fungal spores.

(2) Using a sterile 1 mL pipette, pipette 1.0 mL of the Tween culture into the 10^{-1} sterilised distilled water (SDW) bottle, which contains 9.0 mL sterile distilled water. Reject the pipette into the disinfectant. Shake the bottle gently.

(3) Using a fresh, sterile 1 mL pipette, pipette 1.0 mL of the 10^{-1} mixture into the 10^{-2} bottle. Reject the pipette into the disinfectant and shake the bottle gently.

3.5.3 Measurement of the numbers of spores

To count the numbers of spores of each fungal dilution (10^{-2}) a counting slide and microscope were used. The concentration of spores was adjusted to make sure the concentration of each fungal suspension used is as equivalent as possible.

3.5.4 Preparation of material

A laminar flow cabinet at safety range was used to keep all materials away from contamination. 1.0 mL of standard fungal suspension was pipetted into a 100 mL SDW bottle to make a pure fungal suspension. The fungal suspension was poured into sterilised metal dish and the material soaked in this suspension. The material was drip dried before microwave irradiation.

Two drip dried single layer fabrics were prepared for sterilising. Fabric was soaked in fungal suspension and drip dried then was put as the middle layer of sample, either 3 or 5 layers. The top and bottom layers were dried and had been sterilised by high-pressure steam in an autoclave at 121°C.

Soaked and dried fabric was put in a petri dish and covered. Petri dishes were put in a constant temperature room at 30° C or in an oven controlled at 40° C or 50° C for drying overnight until dried completely. The same treated samples were put in a vacuum oven (Townson & Mercer Ltd, made in UK), a vacuum of 500 mm. Hg and 30, 40, 50° C were used. All petri dishes were left overnight until dried completely.

3.5.5 Sterilising

The single or multilayers samples were placed on a glass plate then immediately moved into microwave oven (Matsui carousel model with 2450 MHz , made in UK) and placed on the carousel plate. The fungal suspension treated samples were irradiated at full power, 850 W, for a range of exposure times, 0-300 seconds. In the laminar flow cabinet, each petri dish was uncovered and the dried sample was taken out then irradiated for 0, 20, 40, and 60 seconds.

3.5.6 Spread plate for fungal growth

The numbers of viable fungal spores were determined following suitable dilution by the spread plate cotton. Incubation was at 25°C. The colonies which would develop over the whole surface if fungal spores were not killed off by microwave irradiation were estimated carefully to give a viable count of the numbers of living cells.

3.6 Dry cleaning of silk

The modified test method of dry cleaning are based on the British Standard Method BS 1006-D 01 and Marks & Spencer methods[81,82] (Appendix I).

3.7 Laundering of cotton

Colour fastness to laundering on cotton fabrics was carried out using the British Standard BS 1006-C06[83] and assessed for colour change, staining, and where appropriate loss of gel. The samples were laundered under appropriate conditions of temperature, additive ($NaBO_3$), and abrasion action (number of steel balls) such that the result was obtained in a conveniently short time.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Preliminary experiments on microwave irradiation of cotton

4.1.1 Initial trials

It was first necessary to establish suitable procedures for irradiating the cotton samples without obvious damage occurring. In the first experiments samples of C2 cotton fabric were placed directly on the carousel glass plate and irradiated. Under these conditions char spots appeared at the edges of the sample after 2 minutes irradiation, becoming darker with increase in the exposure time. After 8 minutes irradiation the spots had become black. These results suggested that the microwave distribution in the oven was non-uniform.

To check this non-uniformity the carousel glass plate was covered with a circular layer of C4 cotton fabric and irradiated in 1 minute periods. A char spot was observed after 6 minutes treatment, the number and intensity increasing with increase in treatment time. Eventually after 10 minutes the spots had connected to form a continuous charred circle (Figure 4.1). These results supported the concept that the microwave radiation is not uniformly distributed.

In a further test the carousel glass plate was covered with two layers of C4. Again irradiation produced similar results on the bottom layer of fabric in contact with the glass plate, while the effect was less noticeable on the top layer after each period of irradiation (Figure 4.1). It was concluded that localised "hot spots" were being produced in the glass-plate itself and that charring was being caused by direct transfer of heat from these hot spots to the fabric.

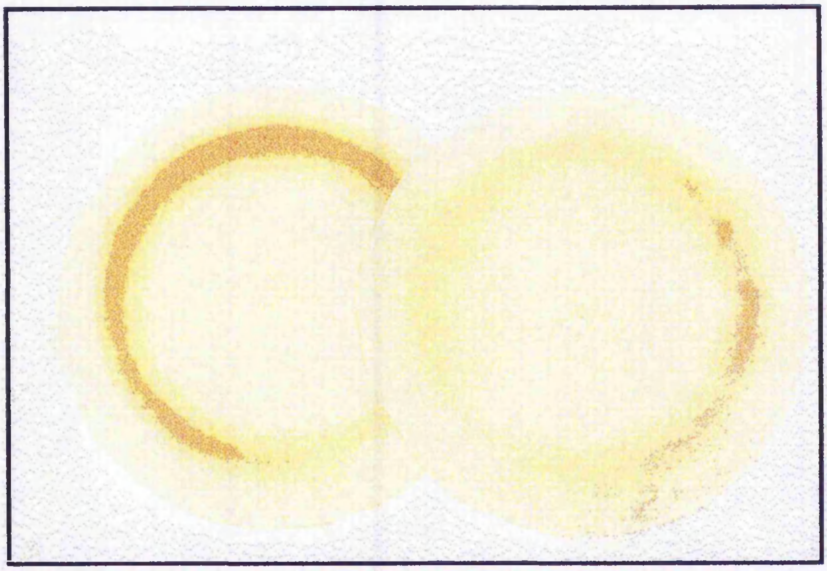


Figure 4.1 Charred spots connected to form a circular ring on irradiated cotton: upper layer (right) and bottom layer (left).

4.1.2 Use of different support systems

Since the above results indicate that charring is caused by contact between the cotton sample and the glass plate, various methods of avoiding this direct contact were examined.

4.1.2.1 Use of a microwaveable box

Samples of cotton fabrics C1, C2, C3 and C4 were all tested in a commercial plastic box sold as suitable for use in microwave ovens, and irradiated at maximum power for 8 minutes. The box was found to have warmed up slightly while the carousel glass plate was much hotter. However, on irradiating for 10 minutes the bottom of the box melted although the samples were free from charring. Obviously the base of the box dissipates the heat from the localised hot spots to some extent, but in view of the damage suffered by the box itself this technique was not pursued further.

4.1.2.2 Use of paper balls and microwaveable box

Paper balls were used to raise the microwaveable box so preventing direct contact between the box and the glass plate. However, on irradiating for 10 minutes at maximum power the paper balls caught fire and the box melted, and this technique was not pursued further.

4.1.2.3 Use of glass wool

Glass is a non-flammable fibre, although it loses strength at 315° C and softens at 815° C, and has a moisture regain of 0 %.[142] In view of its stability to high temperatures it was decided that glass fibre might be a suitable material to prevent direct contact between the sample and the carousel glass plate.

A sample of cotton fabric C4 was supported on a layer of glass fibre and irradiated at full power for 10, 20 and 30 minutes. Although the glass plate was too hot to touch by hand there was no evidence of charring of the fabric even after 30 minutes treatment time. This method of supporting the sample was therefore used in all subsequent microwave irradiation treatments.

4.2 Study of the effects of microwave irradiation on the properties of cotton

4.2.1 Introduction

Although no charring was observed for suitably supported cotton samples irradiated at full power for up to 30 minutes, it was necessary to try to establish whether or not more subtle changes in properties are brought about by such treatment. The important factors in respect of the current research are tensile strength and elongation, molecular weight, oxidative damage, and colour stability.

4.2.2 Effect of microwave irradiation on the tensile properties of cotton

Samples of cotton fabric C4, indigo-dyed cotton fabric CD1, and indigo-dyed, ox-gel coated cotton fabric CDG1, were irradiated at full power for 10, 20 and 30 minutes and their tensile strength and % elongation measured using a H. T. E. M-Series Machine. The results are given in Table 4.1 and show that irradiation at full power for up to 30 minutes had no effect on either the tensile strength or the % elongation of any of the samples of cotton fabric. The values of both the tensile strength and the % elongation are greater for C4 than for the indigo-dyed fabric CD1 obtained from it. This is due to the shrinkage occurring during dyeing which leads to a more dense fabric. The tensile strength of CDG1 was increased because the ox-gel coating increased the strength of the fabric. The tensile strength of wet C4 was increased slightly compared to dried C4 after exposure times of 0 and 1 minutes, but decreased by about 2.5-3 % after 2 minutes irradiation.

Table 4.1 Tensile strength and elongation of cotton irradiated at full power

Fabrics and microwave exposure time (min)	*Tensile strength (Kg)*	*Elongation (%)*
C4		
0	28.80	7.42
10	29.03	7.40
20	29.37	7.33
30	29.60	7.18
CD1		
0	34.90	13.00
10	32.00	12.68
20	34.05	12.90
30	33.67	12.82
CDG1		
0	47.80	7.18
10	48.20	7.14
20	47.40	7.53
30	47.80	7.34

4.2.3 Effect of microwave irradiation on the molecular weight of cotton

The molecular weight of cotton may be determined from dilute solution viscosity measurements using a solvent such as cuprammonium hydroxide. A simpler and more rapid technique which indicates trends without giving molecular weights *per se* is measurement of fluidity. This is an inverse measure of the length of the cellulose chains since the larger the chains the greater the resistance to flow, that is the greater the viscosity and the lower the fluidity.

The results are given in Table 4.2 and show that there was no change in the fluidity for irradiation times of up to 30 minutes. This confirms the results of the tensile strength measurements since any reduction in molecular weight, as indicated by an increase in fluidity, would give rise to a decrease in the tensile strength.

Table 4.2 The cuprammonium fluidity of irradiated cotton fabrics

Microwave exposure time (min)	*C4*	*CDG1*
0	27.22	69.24
10	28.68	70.40
20	28.33	71.66
30	28.30	70.46

4.2.4 Effect of microwave irradiation on the chemical structure of cotton

Cellulose chains may undergo oxidation without any reduction in chain length and hence without any reduction in tensile strength. The sites available for oxidation are the primary hydroxyl group at C(6) and the secondary hydroxyl groups at C(2) and C(3). The former may be oxidised to either a –CHO group or –COOH group and either or both of the secondary hydroxyl groups may be oxidised to a >C=O group. The presence of –CHO or >C=O groups makes the chains susceptible to breakdown on treatment with alkali hence their presence would have led to an increased fluidity in cuprammonium hydroxide solution. Since this was not the case (Table 4.2) it can be assumed that these groups were not produced under the conditions used in the microwave irradiation.

The presence of carboxylic acid groups may be detected by the adsorption of Methylene Blue, a basic dye which has no affinity for pure cellulose. Table 4.3 gives the absorbance values of Methylene Blue solutions of various concentrations after steeping samples of non-irradiated C4 cotton fabric, and C4 cotton fabric irradiated at full power for 30 minutes. It can be seen that there was no significant decrease in the absorbance values of the solutions used to steep samples of irradiated cotton, strongly suggesting that there is no significant increase in the concentration of carboxylic acid groups due to the irradiation treatment.

Table 4.3 Absorbance values, measured at 600 nm, of Methylene Blue solutions after steeping samples of irradiated cotton fabric C4

Microwave exposure time (min)	*Concentration of Methylene Blue*				
	0.4×10^{-3}M	*0.8×10^{-3}M*	*0.12×10^{-3}M*	*0.16×10^{-3}M*	*0.20×10^{-3}M*
0	0.075	0.135	0.232	0.309	0.380
30	0.078	0.136	0.220	0.284	0.387

4.2.5 Effect of microwave irradiation on the colour stability of indigo-dyed cotton

Although microwave irradiation does not damage the cotton substrate, its use as a disinfecting process for Miao textiles would only be acceptable if it also has no effect on the dyes themselves. To test this, samples of CD1 were irradiated at full power for 10, 20 and 30 minutes, after which they were checked against untreated CD1 using an ICS Micromatch reflectance spectrophotometer and their colour strength and ΔE values determined. The results are given in Table 4.4. The error limit of the Micromatch for measuring colour strength, determined using untreated CD1, was found to be ± 0.02 and so the results in Table 4.4 suggest that at the maximum irradiation time used (30 minutes) there is a slight loss of colour strength. This is supported by the approximate doubling of the value of ΔE (the colour difference) at the maximum treatment time compared to either 10 or 20 minutes treatment times.

A similar check was carried out on indigo-dyed and ox-gel coated cotton fabric CDG1 and the results are given in Table 4.5. Both colour strength and ΔE values show that there is no change in colour on irradiating for up to 30 minutes at full power. This was confirmed by visual evaluation of the irradiated samples using the AATCC Gray Scales for colour change and D_{65} illuminant. All the samples were given a rating of 5.

Table 4.4 Colour strength and colour difference values of irradiated CD1 compared with the untreated material

Microwave exposure time (min)	*Colour strength*	*Colour difference (ΔE)*
10	1.02	0.32
20	0.99	0.28
30	0.97	0.72

Table 4.5 Colour strength and colour difference values of irradiated CDG1 compared with the untreated material

microwave exposure time (min)	*Colour strength*	*Colour difference (ΔE)*
10	1.00	0.23
20	1.00	0.21
30	1.01	0.27

4.3 Study of the effects of microwave irradiation on the properties of silk

4.3.1 Introduction

Although the base material used in Miao garments is indigo-dyed cotton, with or without subsequent application of an ox-gel coating, the decorative effects are mainly due to the addition of embroidered silk panels. It was therefore important to determine the effects of microwave irradiation on both the physical properties of silk and the colour stability.

4.3.2 Effect of microwave irradiation on the tensile properties of silk

Samples of silk fabric were irradiated for periods of up to 30 minutes at full power, after which their tensile strength and % elongation were measured. The results, which are given in Table 4.6, show that there was no significant change in either property even with the maximum level of treatment.

Table 4.6 Tensile strength and elongation of silk irradiated at full power

Microwave exposure time (min)	*Tensile strength (Kg)*	*Elongation (%)*
0	26.85	15.26
10	27.33	15.25
20	25.73	15.23
30	27.43	16.05

4.3.3 Effect of microwave irradiation on the colour stability of natural dyes on silk

Although the Miao people nowadays would use silk dyed with synthetic dyes to produce the embroidered panels, many of the panels in the Fu Jen collection of garments will have been produced using natural dyes and it was considered important to assess the stability of such dyeings to microwave irradiation. Nine different natural dyes were examined, the selection being based on materials available in south-west China. The nine dyes are: gardenia; green tea; alizarin (madder); nettle; onion skin; plantain; silver birch; thistle and turmeric, and each was applied on six mordants (see Section 4.7.3). The colour strength and colour difference values relative to non-irradiated samples were determined after 10, 20 and 30 minutes irradiation at full power. These determinations were carried out using an ICS Micromatch reflectance spectrophotometer, and in addition the samples were visually assessed using the AATCC gray scales for assessing colour change and illuminant D_{65}.

The results (Tables 4.7 - 4.15) show that for irradiation times of up to 20 minutes only one of the 55 dye/mordant combinations - alizarin on a stannous chloride mordant - showed any shade change when assessed visually. However, instrumental assessments indicated that a greater number of combinations show a colour change. (A colour strength outside the limits of 1.00 ± 0.02, and a ΔE value greater than 1.0, were taken as indicators of a change in colour). There is not necessarily a correlation between colour strength and ΔE values; for example turmeric on a calcium acetate mordant, on irradiating for 10 minutes, has a colour strength of 0.99, indicating no colour change within the limits of accuracy of the measurement, but a ΔE value of 1.86, indicating a clear difference in shade following microwave irradiation. However it must be understood that the ΔE value is a measure of change in all three components of colour: hue, brightness and chroma and not just depth of shade as in measurement of the colour strength. In view of the excellent colour stability when assessed visually and the subsequently determined fact, discussed in Section 4.4, that irradiation times as short as 2 minutes are sufficient to destroy fungal spores, it may be concluded that microwave irradiation would be a suitable disinfection technique for Miao textiles.

Table 4.7 The visual and instrumental assessment of the effect of microwave irradiation of silk dyed with gardenia and various mordants

Mordants	*10 minutes*			*20 minutes*			*30 minutes*		
	Rates	*Strength*	*ΔE*	*Rates*	*Strength*	*ΔE*	*Rates*	*Strength*	*ΔE*
No mordant	5	0.98	0.73	5	1.05	1.26	5	1.01	0.79
Alum	5	1.00	0.32	5	1.03	0.65	5	0.95	0.84
Copper sulphate	5	1.03	0.69	5	1.03	0.82	5	1.03	0.95
Potassium dichromate	5	1.00	0.80	5	1.03	0.59	5	1.03	1.00
Ferrous sulphate	5	0.97	0.90	5	0.99	0.91	5	0.97	0.73
Stannous chloride	5	1.01	0.55	5	1.00	0.85	5	1.02	0.80
Calcium acetate	5	1.01	0.40	5	1.04	0.72	5	1.06	0.72

Table 4.8 The visual and instrumental assessment of the effect of microwave irradiation of silk dyed with green tea and various mordants

Mordants	*10 minutes*			*20 minutes*			*30 minutes*		
	Rates	*Strength*	ΔE	*Rates*	*Strength*	ΔE	*Rates*	*Strength*	ΔE
No mordant	5	1.05	0.79	5	1.06	0.83	5	1.07	0.97
Alum	5	1.04	0.69	5	0.96	0.59	5	0.96	0.84
Copper sulphate	5	1.03	0.41	5	0.95	0.79	5	1.03	0.52
Potassium dichromate	5	1.01	0.27	5	1.09	1.06	5	1.10	1.39
Ferrous sulphate	5	0.99	0.36	5	0.99	0.37	4-5	0.98	0.93
Stannous chloride	5	0.99	0.42	5	1.01	0.27	5	1.00	0.40
Calcium acetate	5	1.02	0.28	5	1.03	0.56	5	1.05	0.64

Table 4.9 The visual and instrumental assessment of the effect of microwave irradiation of silk dyed with alizarin and various mordants

Mordants	*10 minutes*			*20 minutes*			*30 minutes*		
	Rates	*Strength*	ΔE	*Rates*	*Strength*	ΔE	*Rates*	*Strength*	ΔE
No mordant	5	0.96	0.69	5	0.96	0.83	5	0.97	0.74
Alum	5	1.01	0.38	5	1.02	0.55	5	1.01	0.13
Copper sulphate	5	1.00	0.50	5	1.01	0.31	5	0.97	0.64
Potassium dichromate	5	1.01	0.29	5	0.98	0.32	5	0.95	0.68
Ferrous sulphate	5	1.01	0.20	5	1.01	0.18	4-5	1.01	0.35
Stannous chloride	4-5	1.00	0.25	4-5	1.07	0.97	4-5	1.04	0.50
Calcium acetate	5	1.02	0.49	5	0.96	0.58	5	1.02	0.28
Alum→ Calcium acetate	5	0.98	0.87	5	0.96	1.25	5	1.00	1.11

Table 4.10 The visual and instrumental assessment of the effect of microwave irradiation of silk dyed with nettle and various mordants

Mordants	*10 minutes*			*20 minutes*			*30 minutes*		
	Rates	*Strength*	*ΔE*	*Rates*	*Strength*	*ΔE*	*Rates*	*Strength*	*ΔE*
No mordant	5	1.01	0.13	5	0.99	0.10	5	1.00	0.24
Alum	5	1.05	0.82	5	1.03	0.65	5	1.05	0.65
Copper sulphate	5	1.01	0.39	5	0.95	0.68	4-5	0.93	1.00
Potassium dichromate	5	1.04	0.57	5	1.01	0.16	5	1.01	0.17
Ferrous sulphate	5	1.02	0.51	5	1.06	0.87	5	1.03	0.45
Stannous chloride	5	1.04	0.62	5	1.02	0.37	4-5	1.05	0.76
Calcium acetate	5	0.99	0.20	5	1.05	0.57	5	1.04	0.47

Table 4.11 The visual and instrumental assessment of the effect of microwave irradiation of silk dyed with onion skin and various mordants

Mordants	*10 minutes*			*20 minutes*			*30 minutes*		
	Rates	*Strength*	*ΔE*	*Rates*	*Strength*	*ΔE*	*Rates*	*Strength*	*ΔE*
No mordant	5	0.95	0.92	5	0.97	0.80	4-5	1.00	0.38
Alum	5	1.05	0.85	5	1.02	1.03	5	1.10	1.45
Copper sulphate	5	0.94	0.90	5	0.92	1.44	5	0.94	1.18
Potassium dichromate	5	1.02	0.67	5	1.01	0.56	5	0.92	1.34
Ferrous sulphate	5	1.04	0.65	5	1.02	0.57	4-5	1.06	0.88
Stannous chloride	5	1.02	0.87	5	1.05	0.78	5	1.01	1.09
Calcium acetate	5	0.97	0.50	5	0.98	0.59	5	0.97	0.43

Table 4.12 The visual and instrumental assessment of the effect of microwave irradiation of silk dyed with plantain and various mordants

Mordants	<u>*10 minutes*</u>			<u>*20 minutes*</u>			<u>*30 minutes*</u>		
	Rates	*Strength*	ΔE	*Rates*	*Strength*	ΔE	*Rates*	*Strength*	ΔE
No mordant	5	0.97	0.43	5	0.94	0.72	5	0.95	0.63
Alum	5	1.01	0.11	5	1.01	0.18	5	0.98	0.38
Copper sulphate	5	1.00	0.20	5	1.01	0.26	5	0.97	0.45
Potassium dichromate	5	0.97	0.49	5	0.97	0.34	5	0.98	0.23
Ferrous sulphate	5	0.92	1.19	5	0.93	1.01	5	0.96	0.82
Stannous chloride	5	1.03	0.46	5	1.02	0.59	5	1.02	0.37
Calcium acetate	5	0.95	0.58	5	1.01	0.25	5	0.96	0.54

Table 4.13 The visual and instrumental assessment of the effect of microwave irradiation of silk dyed with silver birch and various mordants

Mordants	<u>*10 minutes*</u>			<u>*20 minutes*</u>			<u>*30 minutes*</u>		
	Rates	*Strength*	ΔE	*Rates*	*Strength*	ΔE	*Rates*	*Strength*	ΔE
No mordant	5	1.01	0.20	5	1.01	0.40	5	1.03	0.44
Alum	5	1.00	0.12	5	0.98	0.27	5	1.03	0.50
Copper sulphate	5	1.00	0.29	5	1.02	0.64	5	1.04	0.84
Potassium dichromate	5	0.95	0.67	5	0.98	0.42	5	0.97	0.47
Ferrous sulphate	5	0.98	0.25	5	0.96	0.48	5	0.98	0.38
Stannous chloride	5	0.99	0.08	5	1.01	0.31	5	1.01	0.66
Calcium acetate	5	0.98	0.29	5	0.96	0.44	5	0.96	0.48

Table 4.14 The visual and instrumental assessment of the effect of microwave irradiation of silk dyed with thistle and various mordants

Mordants	*10 minutes*			*20 minutes*			*30 minutes*		
	Rates	*Strength*	*ΔE*	*Rates*	*Strength*	*ΔE*	*Rates*	*Strength*	*ΔE*
No mordant	5	0.95	0.71	5	0.99	0.64	5	1.01	0.33
Alum	5	0.98	0.43	5	1.01	0.24	5	1.01	0.26
Copper sulphate	5	0.99	0.24	5	0.98	0.34	5	1.04	0.65
Potassium dichromate	5	0.99	0.33	5	1.02	0.42	5	0.98	0.26
Ferrous sulphate	5	0.99	0.74	5	1.01	0.66	5	1.05	1.02
Stannous chloride	5	1.03	0.92	5	1.01	1.08	5	1.02	1.28
Calcium acetate	5	1.03	0.50	5	0.98	0.77	5	1.02	0.71

Table 4.15 The visual and instrumental assessment of the effect of microwave irradiation of silk dyed with turmeric and various mordants

Mordants	*10 minutes*			*20 minutes*			*30 minutes*		
	Rates	*Strength*	*ΔE*	*Rates*	*Strength*	*ΔE*	*Rates*	*Strength*	*ΔE*
No mordant	5	0.92	1.62	5	0.92	1.77	5	0.89	2.78
Alum	5	0.99	0.75	5	1.00	0.57	5	0.99	0.67
Copper sulphate	5	0.97	0.45	5	0.98	0.30	5	0.97	0.50
Potassium dichromate	5	0.97	0.73	5	0.99	0.75	5	0.95	1.20
Ferrous sulphate	5	0.91	1.60	5	0.92	1.15	5	0.94	1.16
Stannous chloride	5	0.98	0.47	5	0.97	0.57	5	0.94	0.88
Calcium acetate	5	0.99	1.86	5	1.01	1.37	5	0.98	1.59

4.4 Sterilisation of cotton fabric by microwave irradiation

4.4.1 Introduction

Having established that microwave irradiation for times of up to 20 minutes had no appreciable effect on either the physical properties or shade of a range of components and potential components of Miao textiles, its effectiveness for sterilising these materials was examined.

4.4.2 Sterilisation of single layers of cotton fabric

Initial experiments were carried out using single layers of cotton fabrics (C4, CD1, CDG1) inoculated with four fungal spores. Irradiation times of up to 5 minutes were used and the results are given in Tables 4.16 - 4.20. These show that almost all the fungi were killed by irradiation times of 60 seconds and that there was a considerable decrease after as short an irradiation time as 20 seconds. Any remaining fungi were destroyed on doubling the irradiation time to 120 seconds. These results are shown as histograms in Figures 4.2 - 4.5.

Table 4.16 Numbers of *Penicillium funiculosum* surviving on each plate after microwave irradiation

Microwave exposure time (Sec)	*C4*	*CD1*	*CDG1*
0	71	170	28
20	4	7	3
40	1	5	3
60	0	2	1
120	0	1	0
300	0	0	0

The initial concentration of *Penicillium funiculosum* suspension was [3.2×10^4 cells/ml].

Table 4.17 Numbers of *Aspergillus niger* surviving on each plate after microwave irradiation

Microwave exposure time (Sec)	*C4*	*CD1*	*CDG1*
0	512	430	174
20	36	55	4
40	10	8	1
60	5	2	0
120	1	0	0
300	1	0	0

The initial concentration of *Aspergillus niger* suspension was [1.2×10^5 cells/ml].

Table 4.18 Numbers of *Mucor hiemalis* surviving on each plate after microwave irradiation

Microwave exposure time (Sec)	*C4*	*CD1*	*CDG1*
0	37	179	74
20	2	3	26
40	0	0	15
60	0	0	2
120	0	0	0
300	0	0	0

The initial concentration of *Mucor hiemalis* suspension was [3.9×10^4 cells/ml].

Table 4.19 Numbers of *Aspergillus terreus* surviving on each plate after microwave irradiation

Microwave exposure time (Sec)	*C4*	*CD1*	*CDG1*
0	357	414	215
20	47	38	2
40	7	5	0
60	6	0	1
120	1	1	0
300	1	1	0

The initial concentration of *Aspergillus terreus* suspension was [1.2×10^5 cells/ml].

Table 4.20 Summary of the numbers of the four species of fungi surviving after microwave irradiation

Time (Sec)	***Penicillium funiculosum***			***Aspergillus niger***			***Mucor hiemalis***			***Aspergillus terreus***		
	C1	*CD1*	*CDG1*	*C1*	*CD1*	*CDG1*	*C1*	*CD1*	*CDG1*	*C1*	*CD1*	*CDG1*
0	71	170	28	512	430	174	37	179	74	357	414	215
20	4	7	3	36	55	4	2	3	26	47	38	2
40	1	5	3	10	8	1	0	0	15	7	5	0
60	0	2	1	5	2	0	0	0	2	6	0	1
120	0	1	0	1	0	0	0	0	0	1	1	0
300	0	0	0	1	0	0	0	0	0	1	1	0

The initial concentration of *Penicillium funiculosum* suspension was [3.2×10^4 cells/ml], *Aspergillus niger* suspension was [1.2×10^5 cells/ml], *Mucor hiemalis* suspension was [3.9×10^4 cells/ml] and *Aspergillus terreus* suspension was [1.2×10^5 cells/ml].

Figure 4.2 Numbers of *Penicillium funiculosum* surviving on each plate after microwave irradiation

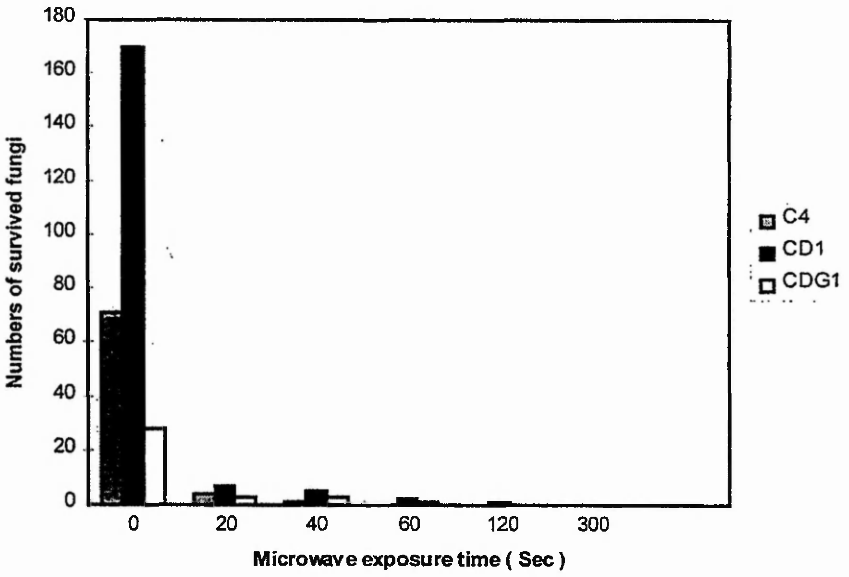


Figure 4.3 Numbers of *Aspergillus niger* surviving on each plate after microwave irradiation

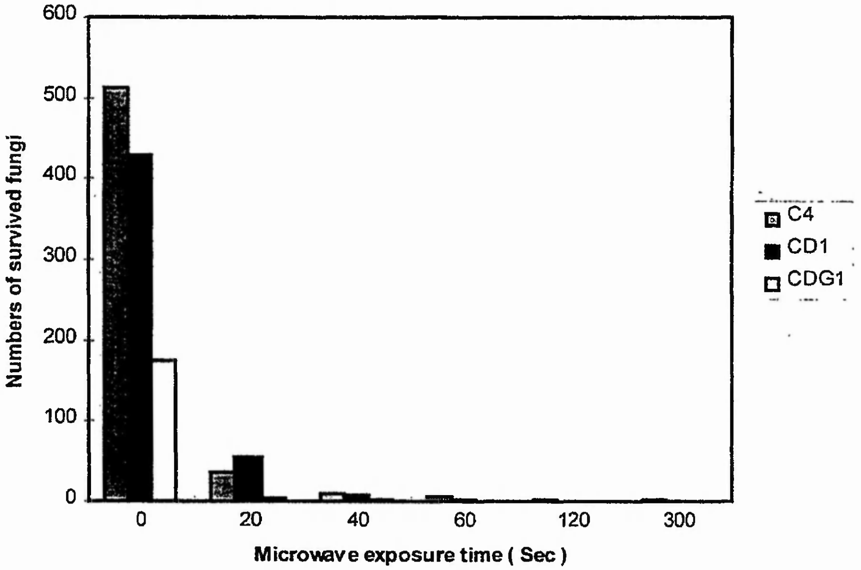


Figure 4.4 Numbers of *Mucor hiemalis* surviving on each plate after microwave irradiation

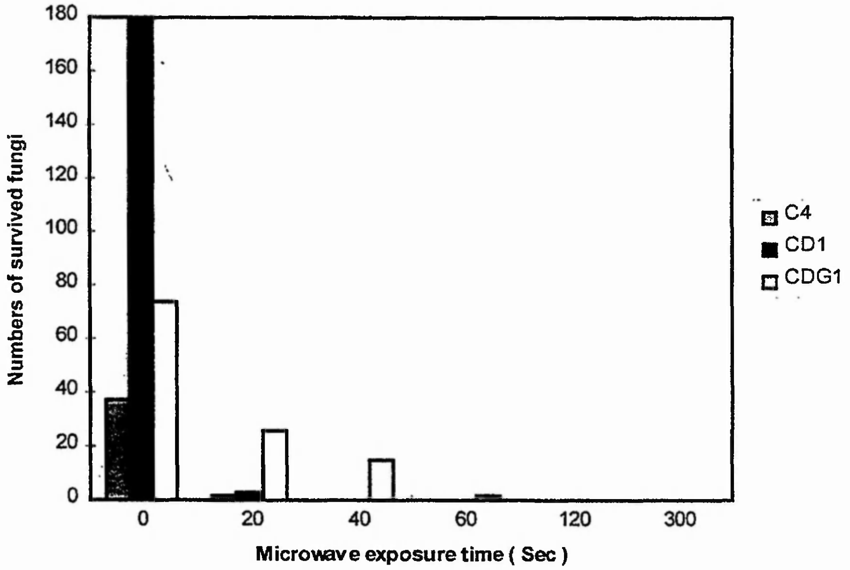
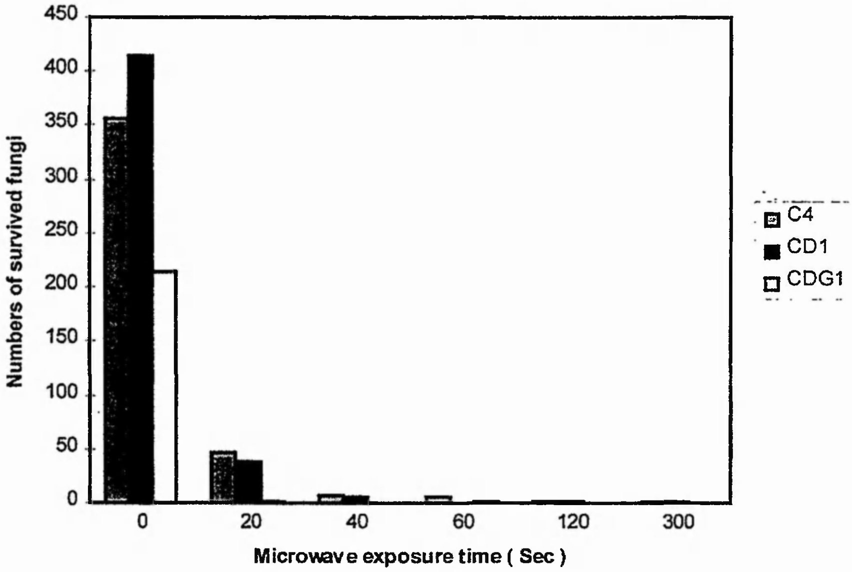


Figure 4.5 Numbers of *Aspergillus terreus* surviving on each plate after microwave irradiation



4.4.3 Sterilisation of multiple layers of cotton fabric

In the treatment of garments with microwave radiation the material would be present in the form of multi-layers of fabric, rather than a single layer. The influence of multi-layers on the effectiveness of microwave radiation for sterilising textile fabrics was therefore investigated using two fungal species. The results obtained using three and five layers are given in Tables 4.21 and 4.22 and show that the treatment was more effective with increase in the number of layers. This may be explained by the multiple layers being more efficient at retaining the heat generated by absorption of the microwave radiation.

Table 4.21 Numbers of *Aspergillus niger* surviving on each plate of multi-layers of irradiated cotton

Microwave exposure time (sec)	*Three layers*	*Five layers*
0	40	40
20	1	0
40	1	1
60	0	0

The initial concentration of *Aspergillus niger* suspension was [1.8×10^5 cells/ml].

Table 4.22 Numbers of *Penicillium funiculosum* surviving on each plate of multi-layers of irradiated cotton

Microwave exposure time (sec)	*Three layers*	*Five layers*
0	192	192
20	1	0
40	1	0
60	0	0

The initial concentration of *Penicillium funiculosum* suspension was [1.1×10^5 cells/ml].

4.4.4 Effect of drying in air or under vacuum

Samples of inoculated fabric were air-dried at three temperatures: 30°C, 40°C and 50°C, then irradiated at full power for a range of times up to 1 minute. The results show (Tables 4.23 and 4.24) that there was very little decrease in the fungal concentration of the samples dried at 30°C and 40°C even at the maximum exposure time. This show clearly that the presence of water is essential during microwave irradiation to ensure that the microorganisms are killed, and the decrease in concentration with increase in irradiation time found with *Penicillium funiculosum* air dried at 30°C may be attributed to the small but crucial moisture regain value of the fabric. However no surviving fungi were found on the sample air-dried at 50°C, even at the 0 second exposure level. This shows that a temperature of 50°C is in itself a sufficient treatment to kill off *Aspergillus niger* and *Penicillium funiculosum.*

Table 4.23 Numbers of *Aspergillus niger* surviving on each plate of irradiated air dry unbleached cotton

Exposure time(sec)	*30° C air dry*	*40° C air dry*	*50° C air dry*
0	>500	455	0
20	>500	147	0
40	>500	547	0
60	>500	409	0

The initial concentration of *Aspergillus niger* suspension was [$1.1\text{-}1.4\times10^5$ cells/ml].

Table 4.24 Numbers of *Penicillium funiculosum* surviving on each plate of irradiated air dry unbleached cotton

Exposure time(sec)	*30° C air dry*	*40° C air dry*	*50° C air dry*
0	235	>500	0
20	230	>500	0
40	136	>500	0
60	85	>500	0

The initial concentration of *Penicillium funiculosum* suspension was [1.5×10^5 cells/ml].

Similar results (Tables 4.25 and 4.26) were obtained when inoculated samples were dried under vacuum (500 mm.Hg) at 40°C and 50°C, the former samples showing no decrease in fungal survival numbers after irradiation times of up to 1 minute, and the latter showing no fungal survival even without a microwave irradiation treatment. These results agree in general with these of Florian[18] who studied the dehydration of materials at temperatures equal to or above 36°C, and reported that the drying process frequently killed the fungal conidia. The average temperature required to kill fungi or bacteria was found by Florian to be 65°C, which suggests that the two fungal species investigated in the current research are more heat sensitive than many.

Table 4.25 Numbers of *Aspergillus niger* surviving on each plate of irradiated vacuum dry unbleached cotton

Exposure time (sec)	*40° C vacuum dry*	*50° C vacuum dry*
0	>500	0
20	>500	0
40	>500	0
60	>500	0

The initial concentration of *Aspergillus niger* suspension was [$1.1\text{-}1.4\times10^5$ cells/ml].

Table 4.26 Numbers of *Penicillium funiculosum* surviving on each plate of irradiated vacuum dry unbleached cotton

Exposure time(sec)	*40° C vacuum dry*	*50° C vacuum dry*
0	84	0
20	116	0
40	129	0
60	119	0

The initial concentration of *Penicillium funiculosum* suspension was [1.5×10^5 cells/ml].

4.5 Stability of indigo-dyed and indigo-dyed, ox-gel coated cotton to laundering

4.5.1 Introduction

Conservation of Miao textiles requires them to be laundered in addition to being sterilised and it was important to determine how the various components can withstand the laundering treatment.

4.5.2 Effect of temperature, agitation and additives on colour stability

The various conditions used in the evaluation are shown in Table 4.27 and have been used each with and without the addition of sodium perborate. Other variables examined are the effect of increased agitation provided by the addition of steel balls, the liquor ratio and the pH. The washing process was carried out in a Launder-O-meter. The results are given in Tables 4.28 - 4.30 for both visual and instrumental assessments.

As would be expected the colour fastness and fastness to staining decreased with increasing temperature. Addition of sodium perborate reduced the colour fastness and the presence of steel balls either had no effect on the colour fastness or increased it by half a point. In general the nylon section of the multifibre fabric was the most heavily stained regardless of conditions. One interesting observation was that in a number of cases, notably with CD1 and CDG1, the colour strength was increased by the laundering process. It is possible that in both these commercially produced samples the soaping process, required after dyeing to develop the true shade, had been omitted.

Table 4.27 Test conditions for colour fastness to laundering

Test No.	*Temp. (°C)*	*Liquor volume (mL)*	*Sodium perborate (g/L)*	*Time (min)*	*Steel balls*	*Adjust pH to*
A1S	40	150	None	30	0*/10	Not adjusted
A2S	40	150	1	30	0*/10	Not adjusted
B1S	50	150	None	30	25	Not adjusted
B2S	50	150	1	30	25	Not adjusted
C1S	60	50	None	30	25	10.5±0.1
C2S	60	50	1	30	25	10.5±0.1

* Steel balls were not used in these tests.

Table 4.28 The visual and instrumental assessment of colour fastness to laundering of CD1

Test No	*Strength & ΔE*	*Colour Change*	*Staining*					
			Wool	*Acrylic*	*Poly-ester*	*Nylon 66*	*Cotton*	*Acetate*
A1S		4-5	4-5	4	4-5	2	4	3
A1S*		4	4-5	4	4-5	2-3	4	3
A2S		4	4-5	5	4-5	2-3	4-5	3
A2S*		3-4	4-5	5	5	5	4-5	5
B1S		3	4-5	5	4-5	3-4	5	4
B2S		3	4-5	5	4-5	4	5	4-5
C1S		3-4	3-4	4	4	1-2	3	2-3
C2S		3	4	4-5	4	1-2	4-5	2-3
A1S	S	1.31	1.19	1.60	1.16	1.87	1.80	1.91
	ΔE	4.88	2.80	4.20	1.76	10.77	4.11	9.58
A1S*	S	1.10	1.16	1.32	1.12	1.68	1.89	1.67
	ΔE	4.18	2.56	2.42	1.62	9.60	4.42	8.22
A2S	S	1.09	1.02	1.22	1.17	1.70	1.45	1.85
	ΔE	6.63	1.22	1.52	1.62	9.23	2.66	8.86
A2S*	S	1.18	1.10	1.11	1.09	1.93	1.58	1.72
	ΔE	6.23	1.93	0.75	1.58	11.48	3.20	8.75
B1S	S	1.14	1.24	1.17	1.27	2.43	1.87	2.20
	ΔE	4.18	3.30	1.27	2.62	15.32	4.56	13.81
B2S	S	0.92	1.14	1.17	1.10	2.05	1.40	1.94
	ΔE	8.74	2.36	1.27	1.72	12.59	2.39	10.43
C1S	S	1.06	1.62	1.74	1.73	5.13	3.25	3.74
	ΔE	4.74	7.05	4.43	5.55	27.80	9.17	21.84
C2S	S	0.88	1.30	1.66	1.41	4.51	2.06	3.34
	ΔE	9.96	4.56	3.77	4.38	25.91	5.33	20.00

* Steel balls were not used in the test.

Table 4.29 The visual and instrumental assessment of colourfastness to laundering of CD2

Test No	*Strength & ΔE*	*Colour Change*	*Staining*					
			Wool	*Acrylic*	*Polyester*	*Nylon 66*	*Cotton*	*Acetate*
A1S		4	4-5	5	5	4	5	4-5
A1S*		4	4-5	5	5	4-5	5	4-5
A2S		4	5	5	5	4	5	4-5
A2S*		4	4-5	5	5	4-5	5	4-5
B1S		3-4	4	5	4	2-3	4	3
B2S		3-4	4-5	5	4-5	2-3	5	3
C1S		2-3	4-5	4-5	4-5	2-3	5	3
C2S		3	4-5	5	4-5	2-3	5	3
A1S	S	0.93	1.04	1.14	1.13	1.08	1.07	1.13
	ΔE	1.21	0.43	1.09	0.80	1.66	0.46	1.39
A1S*	S	0.95	1.03	1.13	1.06	1.08	1.06	1.24
	ΔE	1.05	0.51	0.86	0.50	1.23	0.36	1.99
A2S	S	0.95	0.99	1.10	0.96	1.07	1.17	1.09
	ΔE	1.49	0.60	0.57	0.47	1.28	0.64	1.23
A2S*	S	0.96	0.93	1.08	1.03	1.01	1.07	1.08
	ΔE	1.31	0.70	0.59	0.32	0.84	0.75	1.32
B1S	S	0.94	1.01	1.14	1.08	1.16	1.16	1.16
	ΔE	1.36	0.30	0.80	0.62	2.74	0.89	2.29
B2S	S	0.82	0.97	1.21	1.08	1.14	1.06	1.23
	ΔE	2.86	0.42	1.29	0.62	2.39	0.61	2.58
C1S	S	0.85	1.04	1.41	1.32	1.64	1.16	1.76
	ΔE	2.35	0.54	2.44	2.00	6.71	1.06	6.67
C2S	S	0.82	1.05	1.34	1.13	1.54	1.18	1.81
	ΔE	2.98	0.53	1.89	1.07	5.95	1.27	6.91

CD2: Indigo-dyed cotton was prepared by the researcher.

* Steel balls were not used in the tests.

Table 4.30 The visual and instrumental assessment of colourfastness to laundering of CDG1

Test No	*Strength & ΔE*	*Colour Change*	*Staining*					
			Wool	*Acrylic*	*Poly-ester*	*Nylon 66*	*Cotton*	*Acetate*
A1S		4	4-5	4-5	5	4-5	4-5	4-5
A1S*		4	4-5	4-5	5	4-5	4	5
A2S		4	5	5	5	4-5	4-5	4-5
A2S*		4	4-5	5	5	5	4-5	5
B1S		3-4	4-5	4-5	5	3	3	4-5
B2S		3	4-5	5	4-5	4	3-4	5
C1S		3	4	4	5	2-3	2-3	4
C2S		3-4	4-5	5	4-5	3	2-3	4-5
A1S	S	1.02	0.99	1.22	1.08	1.07	1.32	0.99
	ΔE	3.01	0.36	2.08	0.57	1.94	2.94	0.79
A1S*	S	0.99	1.02	1.22	1.12	1.13	1.38	0.97
	ΔE	2.56	0.37	2.14	0.69	2.41	3.13	1.01
A2S	S	1.27	0.87	1.12	1.03	1.08	1.36	0.95
	ΔE	5.06	1.21	0.87	0.34	1.41	2.82	0.62
A2S*	S	1.30	1.01	1.15	1.15	1.14	1.44	1.03
	ΔE	5.48	0.49	1.05	0.85	2.43	3.60	1.18
B1S	S	1.24	1.14	1.29	1.14	1.50	1.86	1.11
	ΔE	5.29	1.83	2.06	0.91	7.41	6.89	1.81
B2S	S	1.29	1.01	1.12	1.07	1.35	1.77	1.00
	ΔE	5.49	0.62	0.81	0.44	4.39	6.83	1.23
C1S	S	1.40	1.28	1.61	1.20	2.39	3.90	1.45
	ΔE	6.24	4.87	4.13	1.52	14.21	14.76	5.46
C2S	S	1.38	1.23	1.35	1.22	2.07	3.14	1.29
	ΔE	6.48	2.81	2.04	1.43	8.58	12.91	3.13

* Steel balls were not used in the tests.

4.5.3 Effects of temperature, agitation and additives on the ox gel coating

In addition to colour change there is the possibility of loss of the ox-gel coating during laundering and this factor was studied using the same range of washing conditions as those given in Table 4.27. Loss of ox-gel was determined by the weight of ox-gel coated cotton fabric before and after washing and the results (Table 4.31) show that the loss was fairly constant at about 1.2 % regardless of the conditions used in laundering, even in the case of a temperature of 60°C. It may therefore be assumed that laundering Miao textiles will not cause an unacceptable loss of gel coating.

Table 4.31 Loss of gel of CDG1 on laundering

Test No.	*Before laundering (g)*	*After laundering (g)*	*Loss of gel (%)*
A1S	0.82	0.81	1.21
A1S*	0.82	0.81	1.21
A2S	0.82	0.81	1.21
A2S*	0.78	0.77	1.28
B1S	0.84	0.83	1.19
B2S	0.84	0.83	1.19
C1S	0.83	0.82	1.20
C2S	0.83	0.82	1.20

* Steel balls were not used in the tests.

4.6 Stability to dry cleaning of natural dyes on silk

4.6.1 Introduction

As described earlier (Section 1.2) the decorative silk panels may be removed from the base cotton fabric and cleaned separately. It was thought that dry cleaning might be a less aggressive treatment than laundering and so the stability of natural dyes on silk to dry cleaning was investigated.

4.6.2 Stability tests

A total of nine natural dyes, including alizarin, were dyed on silk on a range of mordants and tested for stability to dry cleaning using both visual and instrumental methods of assessment. The results are given in Tables 4.32 - 4.40.

Table 4.32 The visual and instrumental assessment of colour fastness to dry cleaning of silk dyed with silver birch

Mordants	*Strength & ΔE*	*Used Solvent*	*Colour Change*	*Staining*					
				Wool	*Acrylic*	*Polyester*	*Nylon 66*	*Cotton*	*Acetate*
No mordant			4-5	5	5	5	5	5	5
Alum			4-5	4-5	5	5	5	5	5
Copper sulphate			4-5	4-5	5	5	5	5	5
Dichromate			4-5	5	5	5	5	5	5
Ferrous sulphate			4-5	4-5	5	5	5	5	5
Stannous chloride			4-5	4-5	5	5	5	5	5
Calcium acetate			4-5	4-5	5	5	5	5	5
No mordant	S	1.00	0.98	0.94	1.22	1.30	1.02	0.93	0.99
	ΔE	0.03	0.33	0.92	1.73	1.67	0.70	1.05	0.30
Alum	S	1.00	0.94	0.94	1.27	1.30	1.02	0.88	0.98
	ΔE	0.09	0.93	1.24	1.83	1.65	1.62	0.80	0.62
Copper sulphate	S	1.00	0.99	0.98	1.29	1.36	0.98	0.95	1.01
	ΔE	0.04	0.84	0.37	1.66	1.99	1.20	0.32	0.63
Dichromate	S	1.00	0.92	0.97	1.23	1.29	0.99	0.94	0.98
	ΔE	0.06	1.43	0.52	1.68	1.57	1.48	0.59	0.49
Ferrous sulphate	S	1.00	0.97	1.07	1.32	1.39	1.02	0.94	1.04
	ΔE	0.04	0.41	1.17	1.92	2.10	1.31	0.85	0.93
Stannous chloride	S	1.00	1.04	0.94	1.26	1.34	1.08	0.93	1.01
	ΔE	0.05	0.37	1.21	1.68	1.79	1.46	0.63	0.53
Calcium acetate	S	1.00	0.96	0.95	1.25	1.25	0.99	0.95	0.94
	ΔE	0.05	0.55	0.69	1.75	1.37	1.31	0.33	0.64

Table 4.33 The visual and instrumental assessment of colour fastness to dry cleaning of silk dyed with plantain

Mordants	*Strength & ΔE*	*Used Solvent*	*Colour Change*	*Staining*					
				Wool	*Acrylic*	*Polyester*	*Nylon 66*	*Cotton*	*Acetate*
No mordant			4-5	5	5	5	5	5	5
Alum			4-5	5	5	5	5	5	5
Copper sulphate			4-5	5	5	5	5	5	5
Dichromate			4-5	5	5	5	5	5	5
Ferrous sulphate			4-5	4-5	5	5	5	5	5
Stannous chloride			4-5	4-5	5	5	5	4-5	5
Calcium acetate			4	5	5	5	5	4-5	5
No mordant	S	1.00	0.98	0.99	1.05	1.06	0.91	1.07	0.95
	ΔE	0.03	0.24	0.17	0.62	0.35	0.66	0.78	0.38
Alum	S	1.00	1.01	1.01	1.12	1.17	1.06	1.14	0.96
	ΔE	0.11	0.39	0.15	0.82	0.85	0.40	0.99	0.34
Copper sulphate	S	1.00	0.96	0.99	1.06	1.19	0.92	1.08	0.94
	ΔE	0.10	0.59	0.33	0.48	0.97	0.60	0.92	0.42
Dichromate	S	1.00	0.96	0.97	1.00	1.06	1.01	1.11	0.94
	ΔE	0.08	0.47	0.51	0.39	0.43	0.28	0.95	0.50
Ferrous sulphate	S	1.00	0.96	1.04	1.01	1.15	1.03	1.07	0.92
	ΔE	0.06	0.59	0.91	0.23	1.07	0.74	1.23	0.75
Stannous chloride	S	1.00	1.00	0.96	1.00	1.01	1.00	1.03	0.88
	ΔE	0.08	0.36	1.00	0.26	0.58	0.38	1.07	1.21
Calcium acetate	S	1.00	0.93	0.97	1.14	1.12	1.00	1.08	0.90
	ΔE	0.21	0.92	0.64	1.09	0.66	0.21	1.22	0.77

Table 4.34 The visual and instrumental assessment of colour fastness to dry cleaning of silk dyed with alizarin (madder)

Mordants	*Strength & ΔE*	*Used Solvent*	*Colour Change*	*Staining*					
				Wool	*Acrylic*	*Poly-ester*	*Nylon 66*	*Cotton*	*Acetate*
No mordant			5	5	5	5	5	5	5
Alum			4-5	5	5	5	5	5	5
Copper sulphate			5	5	5	5	5	5	5
Dichro-mate			4-5	5	5	5	5	5	5
Ferrous sulphate			5	4-5	5	5	5	5	5
Stannous chloride			5	4-5	5	5	5	5	5
Calcium acetate			5	5	5	5	5	5	5
Alum→ Calcium acetate			4-5	4-5	5	5	5	5	5
No mordant	S	1.00	0.92	0.99	0.94	1.02	0.95	0.98	0.97
	ΔE	0.04	1.47	0.03	0.37	0.19	0.37	0.21	0.24
Alum	S	1.00	0.99	1.02	0.96	1.09	1.03	1.08	0.91
	ΔE	0.10	1.04	0.78	0.49	0.88	0.84	0.88	0.92
Copper sulphate	S	1.00	0.95	0.96	1.05	1.15	1.06	1.02	0.98
	ΔE	0.06	1.03	0.38	0.28	0.91	0.48	0.34	0.24
Dichro-mate	S	1.00	0.92	0.93	0.94	1.06	1.03	1.01	0.98
	ΔE	0.09	1.13	0.63	0.45	0.38	0.38	0.25	0.19
Ferrous sulphate	S	1.00	0.95	1.08	1.00	1.09	1.04	1.00	1.00
	ΔE	0.09	0.91	1.01	0.34	0.72	0.59	0.32	0.38
Stannous chloride	S	1.00	0.99	1.00	0.98	1.23	1.07	0.48	0.98
	ΔE	0.09	0.54	0.71	0.40	1.39	0.81	0.49	0.84
Calcium acetate	S	1.00	0.91	1.04	0.97	1.13	0.98	0.99	0.92
	ΔE	0.08	1.25	0.59	0.21	0.71	0.39	0.32	0.56
Alum→ Calcium acetate	S	1.00	0.96	0.96	0.92	1.06	1.00	1.04	0.92
	ΔE	0.05	1.16	0.39	0.52	0.44	0.43	0.34	0.59

Table 4.35 The visual and instrumental assessment of colour fastness to dry cleaning of silk dyed with turmeric

Mordants	*Strength & ΔE*	*Used Solvent*	*Colour Change*	*Staining*					
				Wool	*Acrylic*	*Polyester*	*Nylon 66*	*Cotton*	*Acetate*
No mordant			4-5	5	5	5	5	5	5
Alum			4	5	5	5	4	4-5	4-5
Copper sulphate			4-5	5	5	5	4	4-5	4-5
Dichromate			4	5	5	5	4	4-5	4-5
Ferrous sulphate			4-5	5	5	5	5	5	5
Stannous chloride			4	5	5	5	4	4-5	4-5
Calcium acetate			3-4	5	5	5	3-4	4-5	4-5
No mordant	S	1.00	0.95	1.02	1.04	1.09	1.01	1.03	1.02
	ΔE	0.05	0.71	0.25	0.24	0.48	1.00	0.54	0.70
Alum	S	1.00	0.73	1.01	1.05	1.07	1.31	1.08	1.04
	ΔE	0.25	6.30	0.43	0.51	0.50	7.33	1.91	2.47
Copper sulphate	S	1.00	0.88	0.98	1.00	1.09	1.09	1.02	0.95
	ΔE	0.22	1.74	0.56	0.60	0.62	4.84	2.22	1.39
Dichromate	S	1.00	0.87	1.01	1.08	1.07	1.29	1.10	1.17
	ΔE	0.24	2.94	0.30	0.94	0.89	11.78	2.63	4.38
Ferrous sulphate	S	1.00	0.96	1.04	1.02	1.09	1.04	0.98	0.93
	ΔE	0.09	2.25	0.94	0.33	1.04	1.44	0.69	0.89
Stannous chloride	S	1.00	0.85	0.95	1.04	1.02	1.21	1.12	1.04
	ΔE	0.27	2.42	0.68	0.72	0.69	8.29	2.29	3.05
Calcium acetate	S	1.00	0.78	1.03	0.97	1.02	1.49	1.20	1.12
	ΔE	0.50	7.05	0.39	0.88	0.86	14.81	3.04	5.69

Table 4.36 The visual and instrumental assessment of colour fastness to dry cleaning of silk dyed with thistle

Mordants	*Strength & ΔE*	*Used Solvent*	*Colour Change*	*Staining*					
				Wool	*Acrylic*	*Polyester*	*Nylon 66*	*Cotton*	*Acetate*
No mordant			4	5	5	5	5	5	5
Alum			3-4	5	5	5	5	5	5
Copper sulphate			4-5	5	5	5	4-5	5	5
Dichromate			4	5	5	5	4-5	5	5
Ferrous sulphate			4	4	4	4	4	4	4
Stannous chloride			3-4	5	5	5	5	5	5
Calcium acetate			4	5	5	5	4-5	5	5
No mordant	S	1.00	0.85	0.96	1.24	1.32	0.99	1.01	0.98
	ΔE	0.28	2.31	0.61	1.67	1.74	1.03	0.26	0.65
Alum	S	1.00	1.00	0.95	1.29	1.40	1.06	1.02	1.01
	ΔE	0.07	3.24	1.64	1.86	2.11	1.85	0.42	0.74
Copper sulphate	S	1.00	1.01	0.95	1.31	1.39	1.08	1.03	1.02
	ΔE	0.09	0.19	0.90	1.89	2.08	1.28	0.34	0.69
Dichromate	S	1.00	0.98	1.00	1.34	1.35	1.02	0.97	1.04
	ΔE	0.16	0.34	0.48	1.91	1.87	0.99	0.26	0.52
Ferrous sulphate	S	1.01	0.97	1.14	1.43	1.56	1.11	1.12	1.12
	ΔE	0.28	0.42	4.00	2.78	3.64	2.68	1.43	1.79
Stannous chloride	S	1.00	0.89	0.95	1.26	1.34	1.04	1.01	1.07
	ΔE	0.18	2.58	0.76	1.59	1.82	0.91	0.21	0.94
Calcium acetate	S	1.00	1.05	0.90	1.24	1.30	1.01	0.96	0.96
	ΔE	0.10	2.23	1.41	1.81	1.60	0.99	0.26	0.75

Table 4.37 The visual and instrumental assessment of colour fastness to dry cleaning of silk dyed with green tea

Mordants	*Strength & ΔE*	*Used Solvent*	*Colour Change*	*Staining*					
				Wool	*Acrylic*	*Polyester*	*Nylon 66*	*Cotton*	*Acetate*
No mordant			4-5	5	5	5	5	5	5
Alum			4-5	4-5	4-5	4-5	4-5	4-5	4-5
Copper sulphate			5	5	5	5	5	5	5
Dichromate			4-5	5	5	5	4-5	5	5
Ferrous sulphate			4-5	5	5	5	5	5	5
Stannous chloride			4-5	5	5	5	5	5	5
Calcium acetate			4-5	5	5	5	5	5	5
No mordant	S	1.00	1.02	0.95	1.19	1.40	0.91	0.93	0.98
	ΔE	0.19	0.58	0.69	1.60	2.17	0.99	0.45	0.78
Alum	S	1.00	0.89	1.00	1.35	1.50	1.05	1.05	1.02
	ΔE	0.23	1.94	0.41	2.13	2.61	0.67	0.60	1.42
Copper sulphate	S	1.00	1.02	0.96	1.19	1.34	0.98	0.98	0.91
	ΔE	0.19	0.44	0.56	1.19	1.88	0.69	0.23	0.89
Dichromate	S	1.01	0.98	1.03	1.20	1.38	1.01	1.06	0.98
	ΔE	0.64	0.29	0.25	1.52	2.04	0.83	0.41	1.07
Ferrous sulphate	S	1.00	0.98	0.99	1.19	1.28	1.00	1.03	0.96
	ΔE	0.14	0.38	0.82	1.22	1.50	0.91	0.43	1.21
Stannous chloride	S	1.00	0.95	0.93	1.18	1.39	1.03	0.98	1.19
	ΔE	0.13	0.69	0.76	1.30	2.06	0.40	0.20	1.22
Calcium acetate	S	1.00	0.98	0.93	1.21	1.40	0.96	0.97	1.02
	ΔE	0.13	0.36	0.75	1.53	2.16	0.71	0.29	0.67

Table 4.38 The visual and instrumental assessment of colour fastness to dry cleaning of silk dyed with gardenia

Mordants	*Strength & ΔE*	*Used Solvent*	*Colour Change*	*Staining*					
				Wool	*Acrylic*	*Polyester*	*Nylon 66*	*Cotton*	*Acetate*
No mordant			4	5	5	5	5	5	5
Alum			4-5	5	5	5	4-5	5	4-5
Copper sulphate			5	5	5	5	4-5	5	5
Dichromate			4-5	5	5	5	4-5	5	5
Ferrous sulphate			4	4	4-5	4-5	4-5	4-5	4-5
Stannous chloride			4-5	4-5	5	5	5	5	5
Calcium acetate			5	4-5	5	5	5	5	5
No mordant	S	1.00	0.99	0.92	1.02	1.08	0.99	0.96	0.91
	ΔE	0.08	0.83	0.79	1.38	0.64	0.38	0.63	1.11
Alum	S	1.00	0.77	0.89	1.19	1.26	0.98	0.95	0.93
	ΔE	0.10	4.08	1.70	1.44	1.47	0.77	0.29	0.91
Copper sulphate	S	1.00	0.97	0.94	1.25	1.30	0.97	0.96	0.92
	ΔE	0.09	0.56	1.90	1.51	1.64	1.40	0.31	1.18
Dichromate	S	1.00	0.99	0.90	1.21	1.30	1.01	1.00	0.95
	ΔE	0.11	0.84	1.46	1.65	1.66	1.19	0.17	0.95
Ferrous sulphate	S	1.00	0.92	1.01	1.35	1.40	1.04	1.06	0.94
	ΔE	0.18	2.04	3.18	2.19	3.05	2.77	1.33	1.90
Stannous chloride	S	1.00	1.00	0.96	1.26	1.30	0.95	0.96	0.81
	ΔE	0.15	0.61	0.51	1.73	1.64	1.77	0.76	1.87
Calcium acetate	S	1.00	1.18	0.90	1.23	1.31	1.01	0.99	0.96
	ΔE	0.19	3.34	1.55	1.64	1.72	0.75	0.22	1.00

Table 4.39 The visual and instrumental assessment of colour fastness to dry cleaning of silk dyed with nettle

Mordants	*Strength & ΔE*	*Used Solvent*	*Colour Change*	*Staining*					
				Wool	*Acrylic*	*Poly-ester*	*Nylon 66*	*Cotton*	*Acetate*
No mordant			4-5	5	5	5	5	5	5
Alum			4	5	5	5	5	5	5
Copper sulphate			4	5	5	5	5	5	5
Dichromate			4-5	5	5	5	5	5	5
Ferrous sulphate			4-5	5	5	4-5	5	5	5
Stannous chloride			4-5	5	5	5	5	5	5
Calcium acetate			4-5	5	5	5	5	5	5
No mordant	S	1.00	0.93	1.02	1.11	1.20	1.02	1.01	0.95
	ΔE	0.19	0.82	1.09	0.67	1.08	0.19	0.23	0.37
Alum	S	1.00	0.99	1.02	1.05	1.11	1.02	1.01	0.98
	ΔE	0.16	0.39	0.23	0.35	0.65	0.25	0.23	0.21
Copper sulphate	S	1.00	0.95	1.06	1.03	1.08	1.01	1.01	0.87
	ΔE	0.15	0.78	0.52	0.18	0.55	0.23	0.14	0.99
Dichromate	S	1.00	0.93	1.12	1.04	1.14	1.09	1.02	0.87
	ΔE	0.17	0.89	1.07	0.29	0.85	0.69	0.29	0.96
Ferrous sulphate	S	1.00	1.01	1.06	1.05	1.04	1.00	1.06	0.92
	ΔE	0.15	0.16	0.53	0.31	0.37	0.06	0.43	0.69
Stannous chloride	S	1.00	0.97	1.04	1.04	1.11	1.01	0.91	0.81
	ΔE	0.16	0.51	0.76	0.31	0.61	0.14	0.73	1.49
Calcium acetate	S	1.00	0.96	1.14	1.06	1.14	1.10	0.97	0.92
	ΔE	0.14	0.48	1.20	0.36	0.79	0.75	0.18	0.61

Table 4.40 The visual and instrumental assessment of colour fastness to dry cleaning of silk dyed with onion skin

Mordants	*Strength & ΔE*	*Used Solvent*	*Colour Change*	*Staining*					
				Wool	*Acrylic*	*Polyester*	*Nylon 66*	*Cotton*	*Acetate*
No mordant			4	4-5	5	5	4-5	5	4-5
Alum			5	4-5	5	5	4-5	5	4-5
Copper sulphate			4	4-5	5	5	5	4-5	5
Dichromate			4-5	5	5	5	5	4-5	5
Ferrous sulphate			4-5	4	4-5	4-5	4-5	4-5	4-5
Stannous chloride			5	4-5	5	5	4-5	4-5	5
Calcium acetate			4-5	4-5	5	5	4-5	4	5
No mordant	S	1.00	0.92	0.88	1.14	1.39	6.98	0.97	0.92
	ΔE	0.05	1.26	1.59	1.38	2.02	1.37	0.29	1.17
Alum	S	1.00	0.97	0.92	1.15	1.53	1.06	0.99	0.97
	ΔE	0.09	0.92	1.19	1.14	2.69	2.01	0.22	1.71
Copper sulphate	S	1.00	0.89	0.93	0.99	1.15	0.96	1.02	0.96
	ΔE	0.06	1.54	1.29	0.22	1.15	0.54	1.25	0.41
Dichromate	S	1.00	0.93	0.91	1.00	1.14	0.99	1.05	0.93
	ΔE	0.09	0.96	1.61	0.16	0.83	0.19	0.74	0.53
Ferrous sulphate	S	1.00	1.00	0.94	1.18	1.48	1.06	1.00	0.92
	ΔE	0.10	0.12	2.79	1.20	2.57	2.14	0.63	1.70
Stannous chloride	S	1.00	0.99	0.96	1.11	1.14	1.06	1.12	1.05
	ΔE	0.07	1.09	2.15	0.73	1.17	1.45	2.29	1.26
Calcium acetate	S	1.00	0.94	0.92	0.94	1.11	1.05	1.04	1.00
	ΔE	0.12	1.33	1.31	0.45	0.75	1.00	2.12	0.21

Visual assessments suggests that most of the dye/mordant combinations show excellent fastness to dry cleaning, the ratings being 4-5 → 5 for colour change and 5 for staining on each of the components of the multifibre fabric. The main exception to this was the dye obtained from thistles, where ratings of 3, 3-4 and 4 were obtained with some of the mordants. In fact the highest rating obtained for fastness to colour change in the case of turmeric, 4-5, was also obtained for the dye in the absence of any mordant. The instrumental assessment included assessment of the amount of colour extracted into the solvent by measuring the colour strength and ΔE values, taking the used solvent as batch and fresh solvent as standard. These results suggest that in nearly all cases no colour was retained in the solvent and that any colour removed during dry cleaning must be adsorbed on the multifibre fabric. Overall the fastness ratings were good-to-excellent, both for colour change and staining, confirming that dry cleaning is a suitable technique for use with the silk embroidered panels of Miao textiles.

In addition to the above dyes the fastness to dry cleaning of indigo on silk, cotton (CD1) and indigo-dyed, ox-gel coated cotton (CDG1) was assessed (Table 4.41).

Table 4.41 The visual and instrumental assessment of colour fastness to dry cleaning of indigo-dyed silk, CD1, and CDG1

Mor-dants	*Strength & ΔE*	*Used Solvent*	*Colour Change*	*Staining*					
				Wool	*Acrylic*	*Poly-ester*	*Nylon 66*	*Cotton*	*Acetate*
Silk			3-4	3-4	4-5	4	4	4-5	4-5
CD1			4	3-4	4-5	4	4-5	4-5	4-5
CDG1			5	5	5	5	5	5	5
Silk	S	1.02	0.83	1.40	1.24	1.49	1.16	1.26	1.09
	ΔE	3.21	3.28	5.46	2.07	3.27	2.04	2.09	1.70
CD1	S	1.07	1.10	1.91	1.65	2.66	1.35	1.62	1.44
	ΔE	7.23	1.15	7.51	4.01	7.28	2.83	3.74	3.51
CDG1	S	1.02	1.24	0.99	0.93	1.05	1.01	1.51	1.77
	ΔE	3.04	2.64	0.42	3.36	0.78	0.42	2.70	4.76

The results show that the overall fastness ratings were in the order:

Silk < CD1 << CDG1

with indigo-dyed silk having only moderate fastness and CDG1 having very good fastness by visual assessment. However the instrumental assessment does not show the same clear difference in fastness properties.

4.7 Dyeing wool, silk and chitosan with natural dyes

4.7.1 Introduction

Silk and wool are amine-containing protein fibres that have a long history of being dyed with natural dyes. Although nowadays the full colour gamut may be produced using synthetic dyes, which normally have better all-round fastness properties than natural dyes, there is a small but expanding niche market for textile fabrics dyed with natural dyes. A large proportion of natural dyes are mordant dyes; these require the presence of additional substances, frequently metal ions, to impart affinity for the fibre and/or to develop the true colour and maximum fastness properties. With such mordants it is likely that the amine groups act as ligands and bind the metal ions to the fibre. Chitosan, although a polysaccharide, also has amine side-groups and so should be able to be dyed with many natural dye/mordant combinations.

4.7.2 Dyeing wool with natural dyes

Dyeings were carried out using a range of dye/mordant combinations. In studies using the gardenia extract it was observed that there was an increase in the depth of shade obtained both with increase in the concentration of the gardenia solution at constant mordant concentration, and with increase in mordant concentration at constant gardenia solution concentration. However, when using stannous chloride as mordant it was found that at mordant concentrations greater than 4 % the wool fabric was stiffened and shrank during the dyeing process. Figure 4.6 shows wool fabric mordanted with 20 % o.w.f. stannous chloride; it has become stiff, highly shrunken and brittle. Also, with calcium-based mordants only calcium acetate is suitable as a mordant for wool, as calcium oxide (lime), being alkaline, causes considerable damage to the wool.

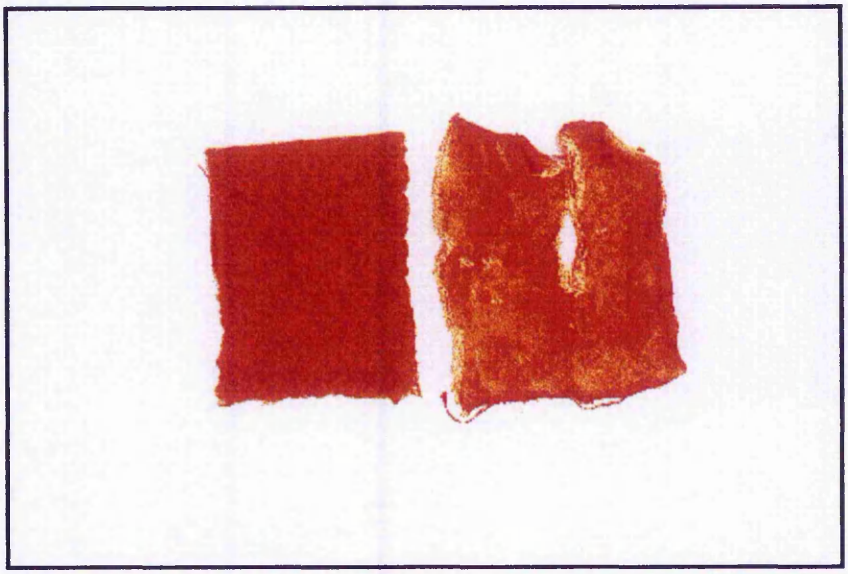


Figure 4.6 The stiff and shrunk wool was damaged by high concentration of stannous chloride. (a) L.h.s.- wool mordanted with 4 % $SnCl_2$ o.w.f. (half sample), (b) R.h.s.- wool mordanted with 20 % $SnCl_2$ o.w.f. (full sample).

4.7.3 Dyeing silk with natural dyes

4.7.3.1 Preparation of dyed samples

The range of shades obtained with the natural dye/mordant combinations is given in Table 4.42. Again, as with wool, deeper shades were obtained on increasing either the dye concentration or the mordant concentration, while keeping the concentration of the other component constant.

Table 4.42 Colours of dyed silk fabrics treated with or without mordants and dyed with natural dyes

Mordants & Dyes	No mordant	Alum	Copper sulphate	Dichro-mate	Ferrous sulphate	Stannous chloride	Calcium acetate
Gardenia	gold yellow	yellow	greenish yellow	yellow	greenish yellow	yellow	yellow
Green Tea	pinkish brown	cream	brown	light brown	gray	cream	light brown
Alizarin (Madder)	purple	orange red	dark purple	pink purple	gray purple	orange yellow	purple *
Nettle	cream white	greenish brown	greenish gray	brownish cream	gray	light brown	cream white
Onion Skin	orange brown	gold brown	dark brown	brown	gray	gold yellow	light brown
Plantain	cream white	cream white	gray green	cream	dark green	cream yellow	cream white
Silver Birch	pinkish brown	light brown	dark brown	brown	gray	cream yellow	light brown
Thistle	cream white	cream white	gray green	greenish gray	greenish brown	cream	cream white
Turmeric	light yellow	yellow	gray yellow	yellow	brownish yellow	yellow	yellow

* Mordanted with alum then calcium acetate, a orange pink was obtained.

4.7.3.2 Reflectance measurements of dyed samples

As shown in Table 4.42 a range of colours can be obtained on silk using natural dyes without mordants. Compared to non-mordanted dyed silk, the used of alum as a mordant gives softer colours and better colour fastness. Copper sulphate is used to produce colours in the green range and ferrous sulphate normally makes a colour darker or duller. Dichromate tends to deepen the colour while stannous chloride frequently makes a colour sharper or brighter and calcium salts soften colours. Tables II-1 to II-9 give the reflectance values for silk dyed with a range of natural dye/mordant combinations, and Table II-10 for indigo-dyed silk (see Appendix II).

The reflectance values are shown in the form of reflectance curves in Figures 4.7 - 4.15 and in most cases similar reflectance curves were obtained for a given dye regardless of the mordant. Exceptions are the dyeings obtained using copper sulphate and ferrous sulphate in the case of most of the dyes.

Figure 4.7 The reflectance curves of silk fabric dyed with gardenia using different mordants

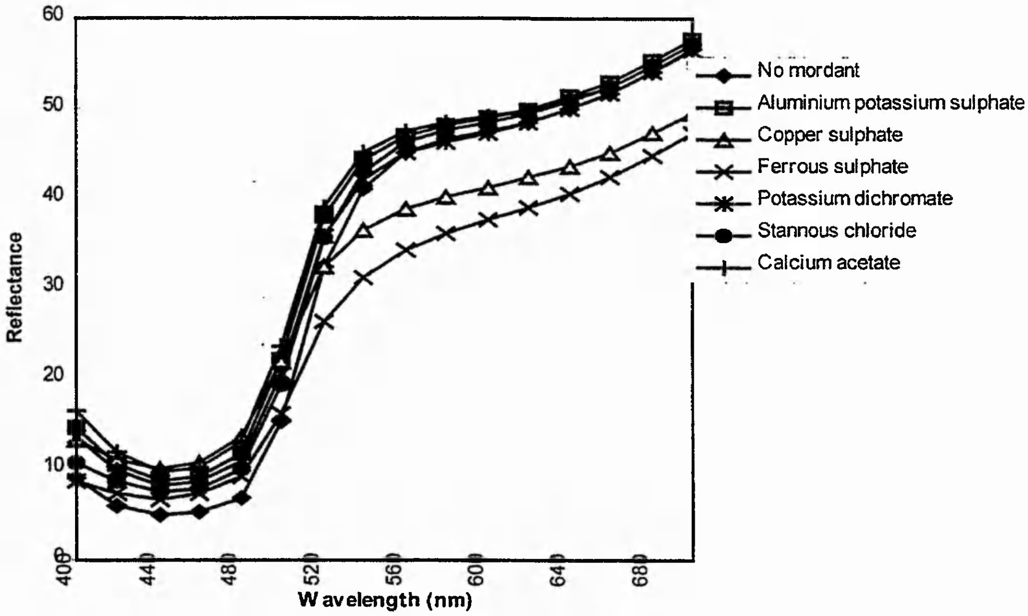


Figure 4.8 The reflectance curves of silk fabric dyed with green tea using different mordants

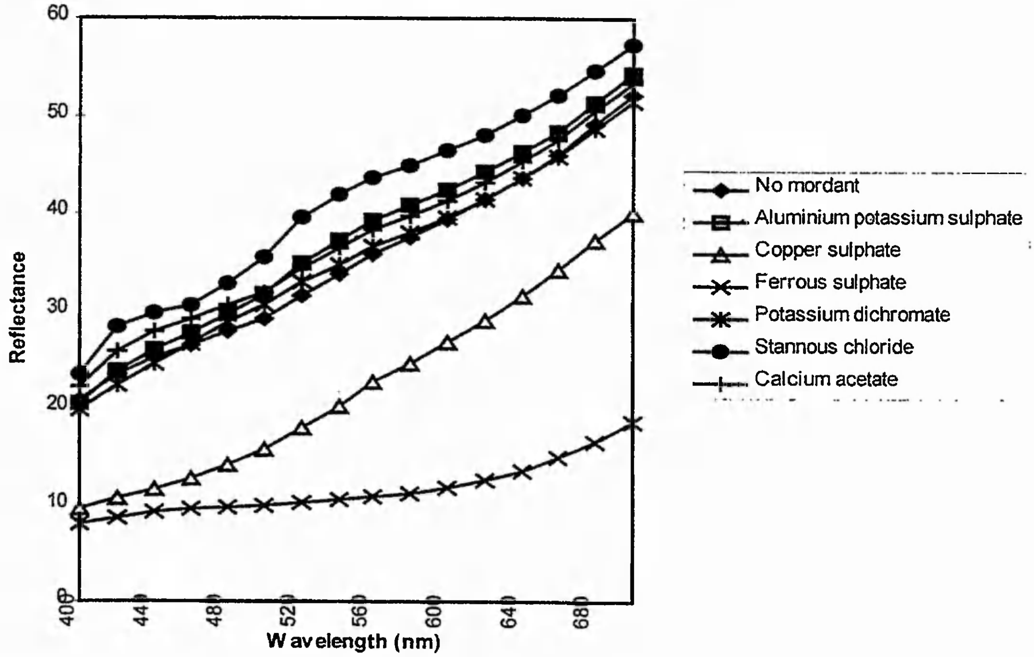


Figure 4.9 The reflectance curves of silk fabric dyed with alizarin (madder) using different mordants

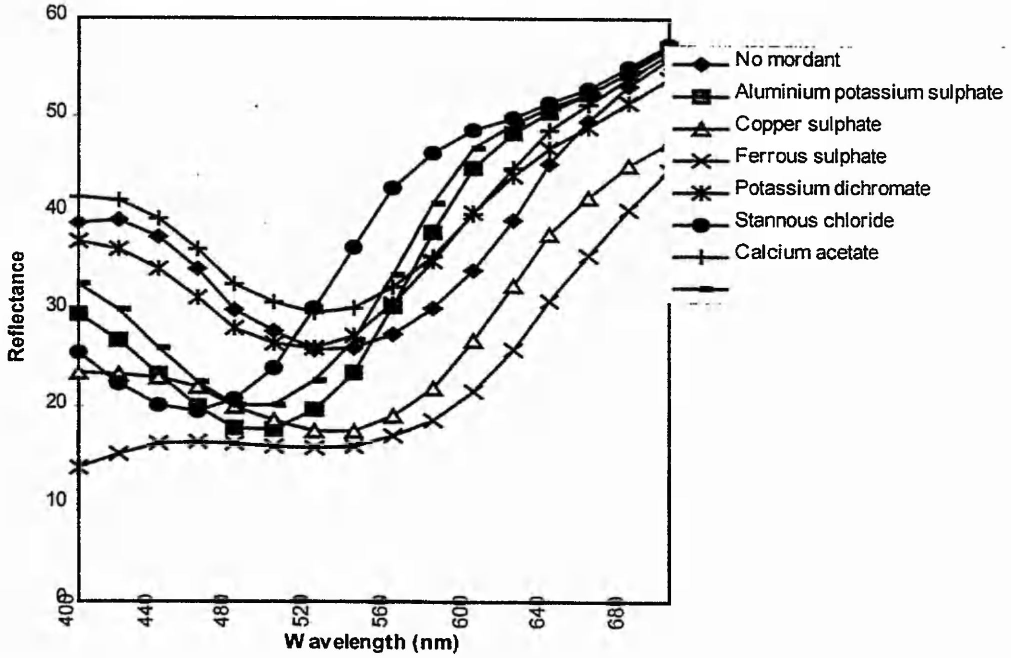


Figure 4.10 The reflectance curves of silk fabric dyed with nettle using different mordants

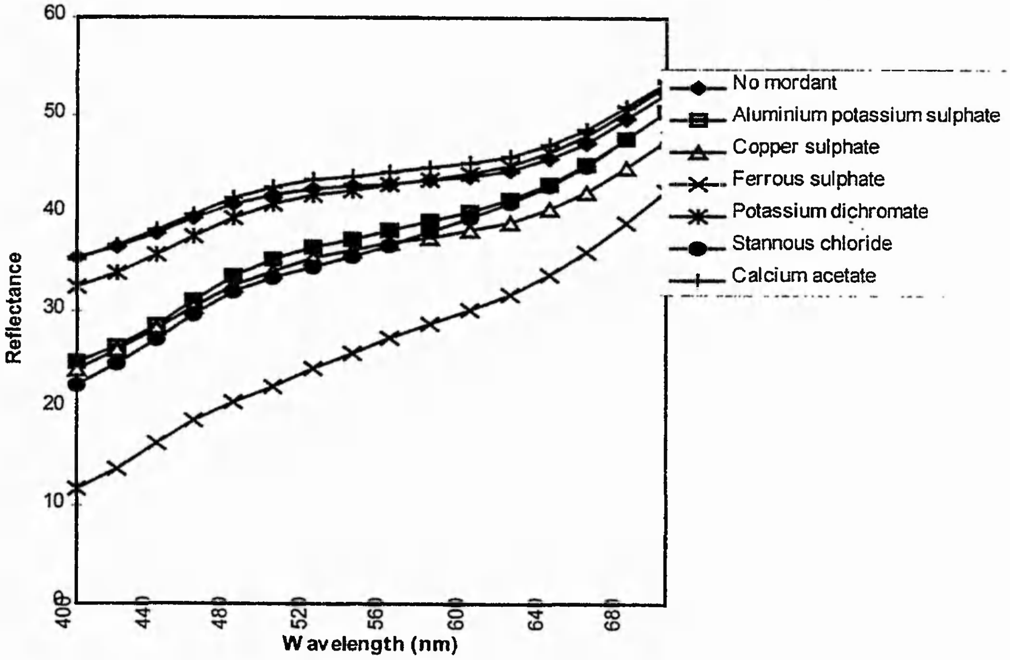


Figure 4.11 The reflectance curves of silk fabric dyed with onion skin using different mordants

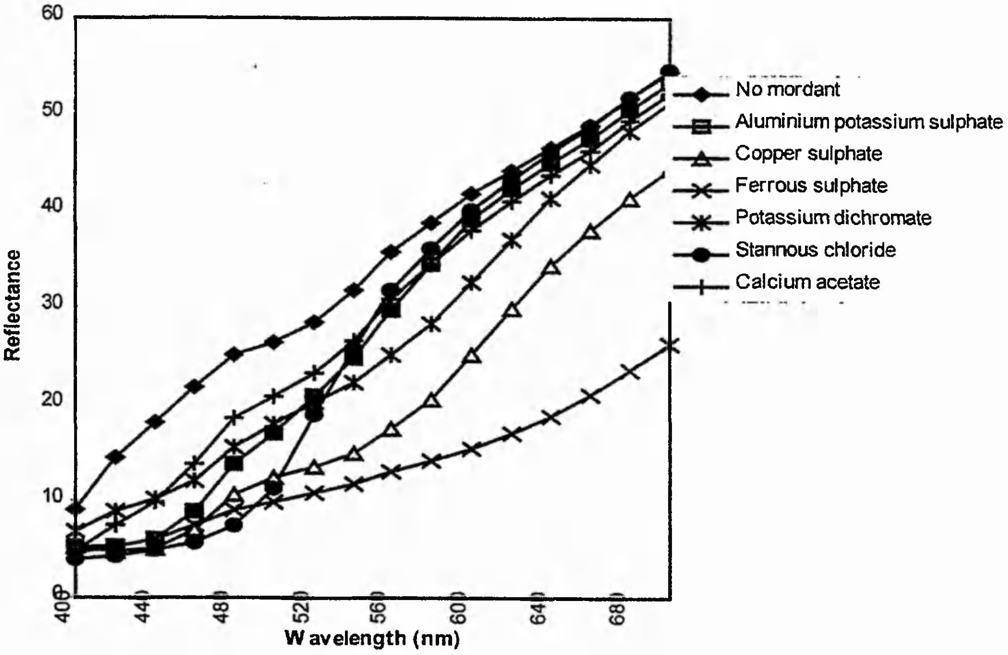


Figure 4.12 The reflectance curves of silk fabric dyed with plantain using different mordants

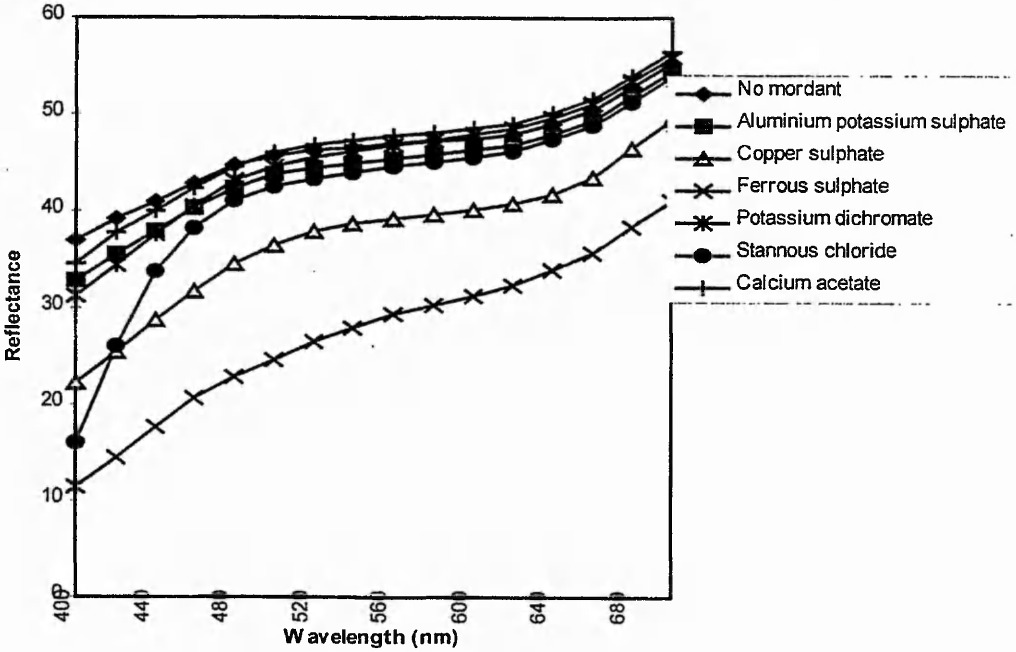


Figure 4.13 The reflectance curves of silk fabric dyed with silver birch using different mordants

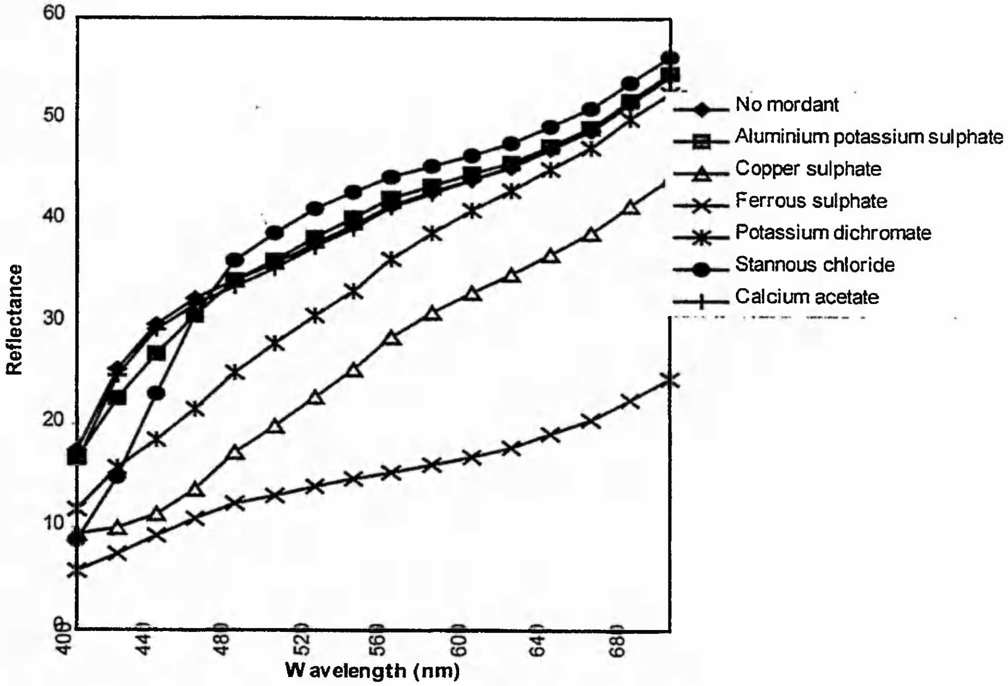


Figure 4.14 The reflectance curves of dyed silk with thistle using different mordants

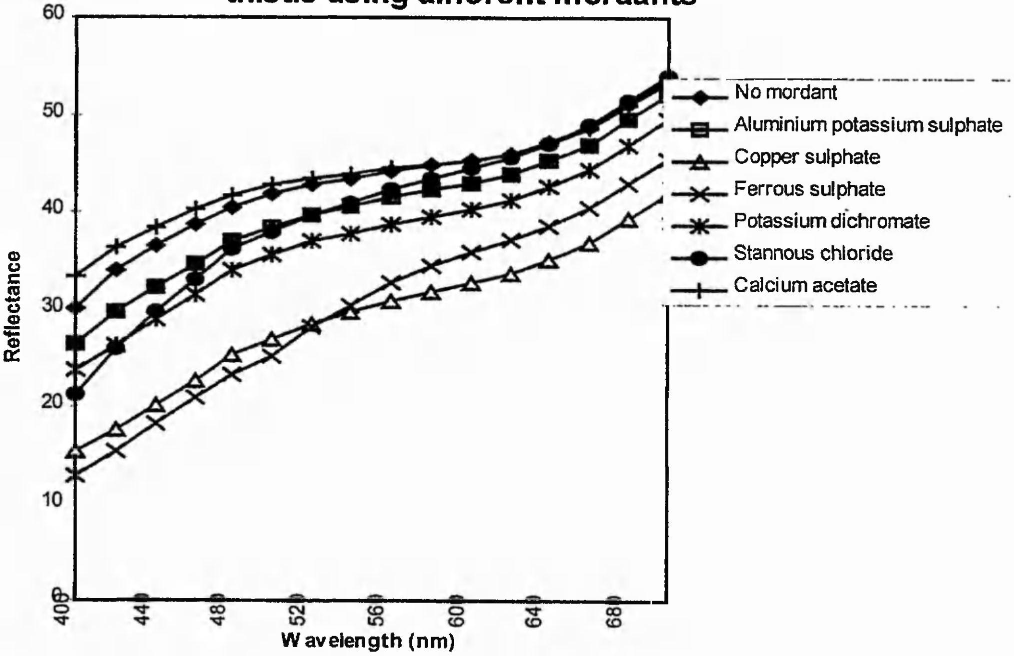
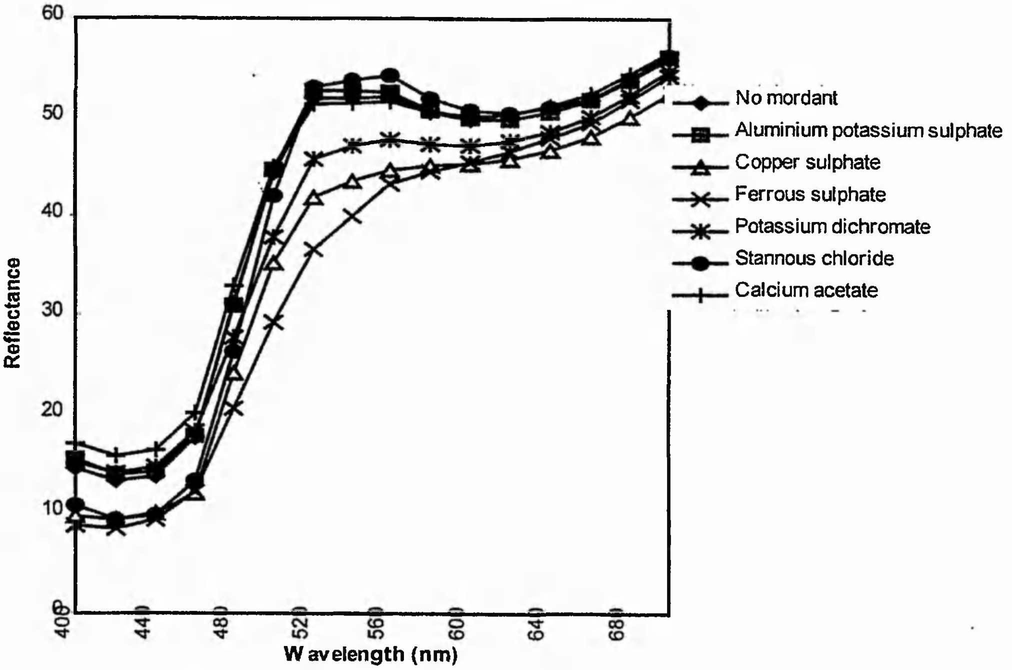


Figure 4.15 The reflectance curves of silk fabric dyed with turmeric using different mordants



4.7.4 Dyeing chitosan with natural dyes

4.7.4.1 Dyeing chitosan in flake form

For the initial studies chitosan in the form of flake was used and again a wide range of colours was obtained (Table 4.43 and Figures 4.16 - 4.21). Again the greatest range was obtained using alizarin (the active component of the natural dye obtained from madder) which is the most important source of red shades from natural dyes.

A second series was produced for the natural dye gardenia using chitosan flake that had previously been given a reduction bleach using sodium borohydride. It is necessary to avoid the use of oxidising bleaching agents, e.g. sodium hypochlorite or hydrogen peroxide since these cause rapid and extensive breakdown of chitosan through attack on the amine group. The use of bleached chitosan flake gave brighter shades.

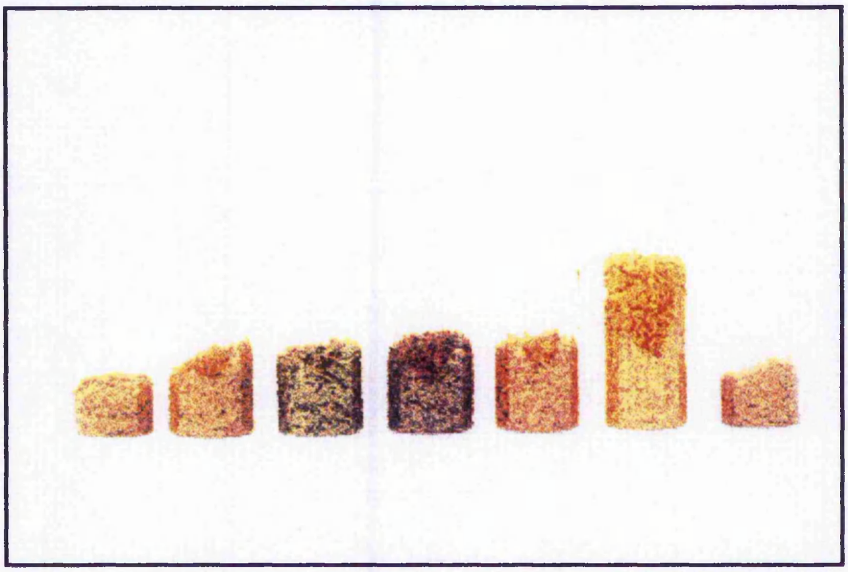


Figure 4.16 Bleached mordanted chitosan flake dyed with gardenia extract.

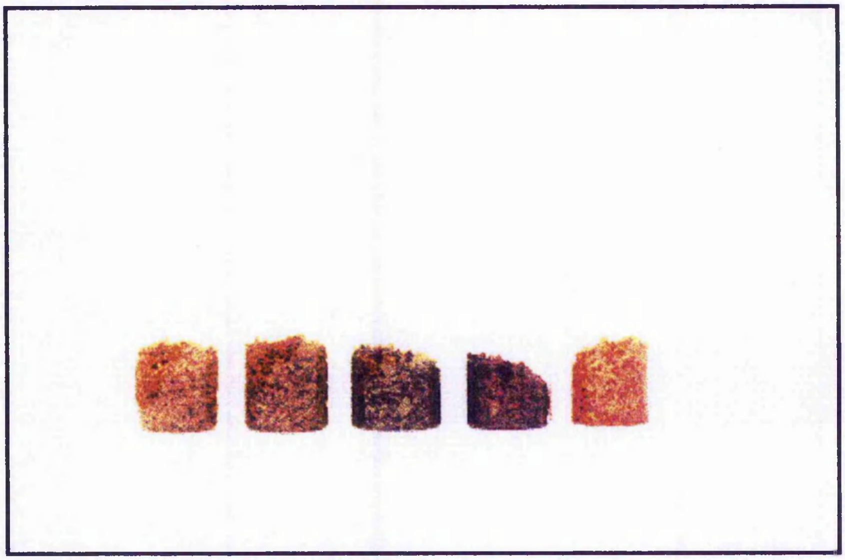


Figure 4.17 Unbleached mordanted chitosan flake dyed with gardenia extract.

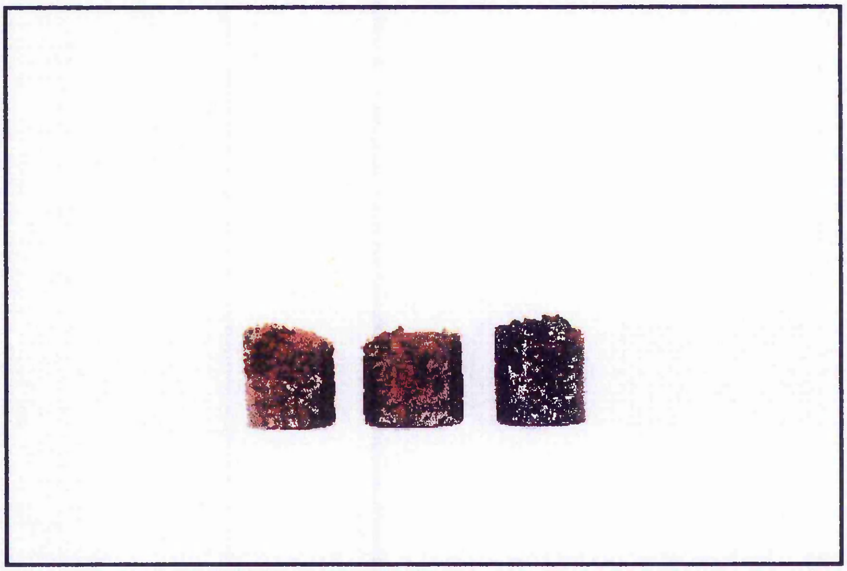


Figure 4.18 Unbleached mordanted chitosan flake dyed with green tea extract.

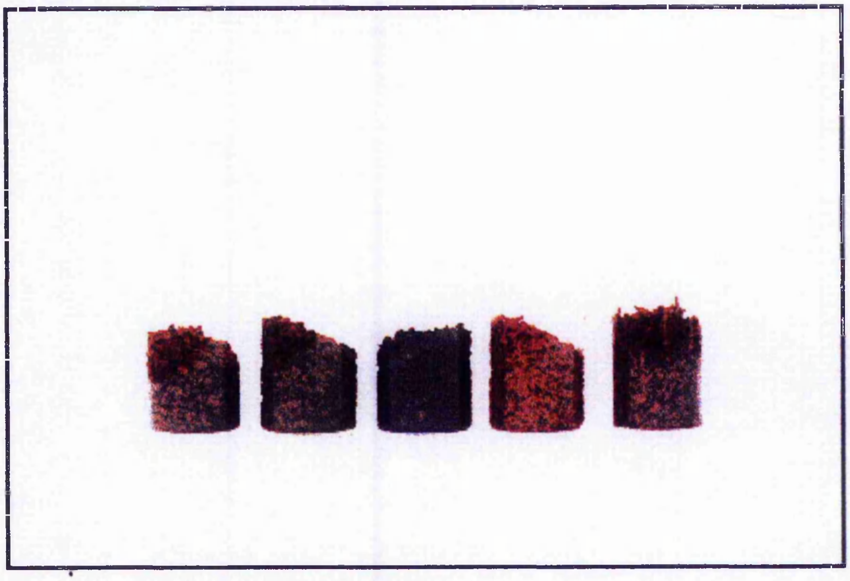


Figure 4.19 Unbleached mordanted chitosan flake dyed with onion skin extract.

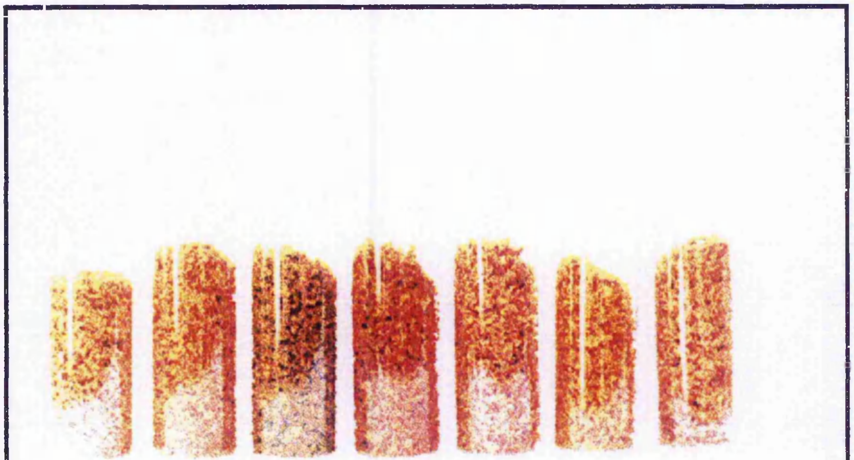


Figure 4.20 Unbleached mordanted chitosan flake dyed with turmeric extract.

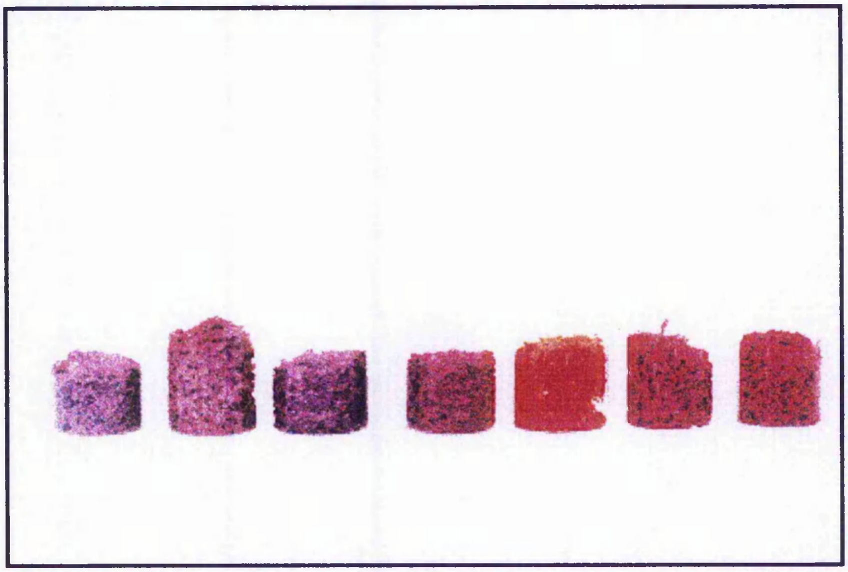


Figure 4.21 Unbleached mordanted chitosan flake dyed with alizarin (madder) extract.

Table 4.43 Colours of unbleached mordanted chitosan flake dyed with natural dyes

Mordants & Dyes	No mordant	Alum	Copper sulphate	Ferrous sulphate	Dichro-mate	Stannous chloride	Calcium acetate
Gardenia *	greenish yellow	yellow brown	green	green brown	yellow brown	bright yellow	brown
Gardenia	yellowish brown	greenish brown	brownish green	dark brown	-	orange yellow	-
Green tea	dark brown	dark brown	-	black brown	-	-	-
Alizarin (Madder)	bluish purple	pinkish purple	purple	-	reddish purple	brown red	reddish orange **
Onion skin	reddish brown	red brown	brownish black	-	-	orange brown	reddish brown
Turmeric	light brown	brown	green	brown	brownish orange	light brown	light brown

* These samples were dyed on bleached chitosan.

** If mordanted with alum then calcium acetate, a purple red was obtained.

4.7.4.2 Production of films from dyed chitosan flake

A sample of unbleached chitosan flake mordanted with ferrous sulphate and dyed with gardenia was dissolved in 0.1 M acetic acid and films cast from the solution. These had a uniform yellow-brown colour except for the presence of a number of undyed particles. The films produced similarly but using bleached chitosan flake and a range of mordants also contained undissolved particles but in these cases these particles were dyed. These particles are the insoluble fraction present in most commercial samples of chitosan and result from the heterogeneous nature of the deacetylation process[85].

4.7.4.3 Dyeing chitosan in film form

Studies were then carried out on dyeing chitosan film with natural dyes, both with and without prior mordanting. A range of shades was obtained but the films were unevenly dyed, principally because of the way the films curled up during the mordanting and dyeing processes. Furthermore, in the case of the three mordants alum, stannous chloride and potassium dichromate, all of the films broke when mordanted using 5 % o.w.f. of the mordant. This damage could be avoided by reducing the quantities of mordant applied and, in the case of dichromate, adding tartaric acid as an oxidisable substrate to prevent oxidative damage to the chitosan, or by replacing the dichromate with chromium sulphate in which the chromium is present as Cr^{+3}. No damage was sustained by the chitosan when mordanting was carried out using copper sulphate, ferrous sulphate or calcium acetate, even at high concentrations.

To overcome the problem of curling of films, the feasibility of dyeing the chitosan films while still adhering to glass plates was examined. However it was recognised that carrying out mordanting and dyeing under these conditions would require the use of an extremely large liquor ratio of the order of 1000:1 and so would not be representative of normal dyeing processes.

The technique showed considerable improvement in terms of the levelness of uptake of the dyes on the films. Typical results are shown for gardenia, which gave shades ranging from yellow to yellow-brown, greenish-yellow and green (Figure 4.22) and green tea, which gave shades ranging from dark brown to greenish-brown and reddish-brown (Figure 4.23). In the case of the alum and chromium sulphate mordants the pH was raised to 6-6.5 by addition of sodium acetate before mordanting was carried out (see Section 4.7.6). In all cases the films, after drying, could be peeled off the glass plates to give flat, easily handled, dyed films.

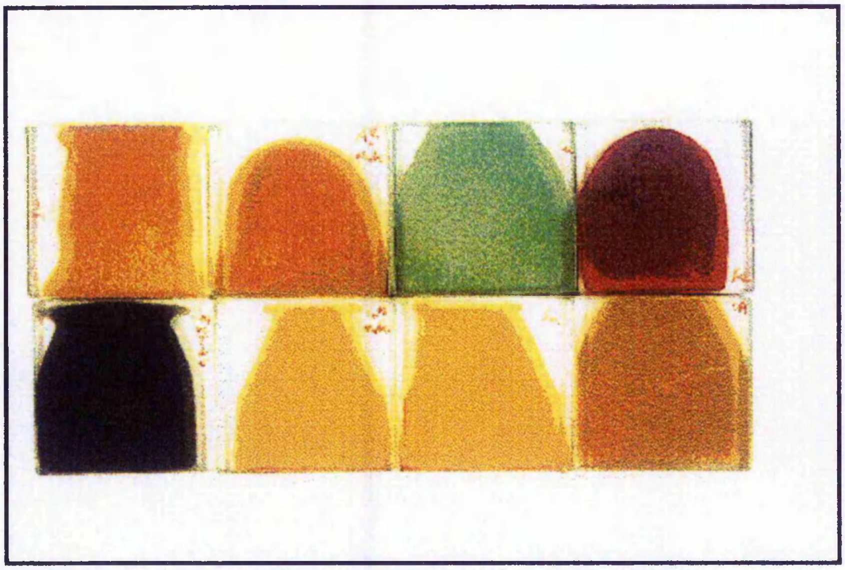


Figure 4.22 Unbleached mordanted chitosan films dyed with gardenia extract. Top row from left to right: no mordant; alum; copper sulphate; and ferrous sulphate. Bottom row from left to right: potassium dichromate; chromium sulphate; stannous chloride; and calcium acetate.

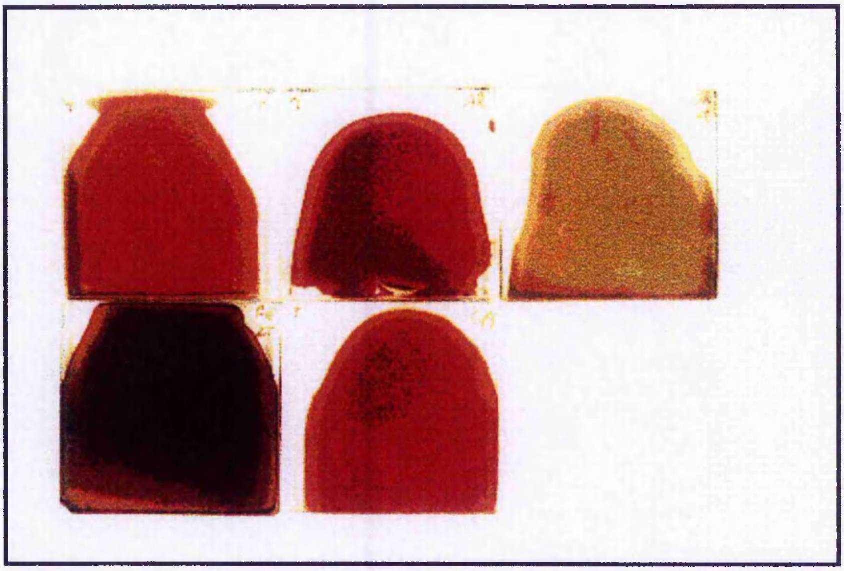


Figure 4.23 Unbleached mordanted chitosan films dyed with green tea extract. Top row from left to right: no mordant; alum; and copper sulphate. Bottom row from left to right: ferrous sulphate; and calcium acetate.

4.7.5 Reflectance measurements of chitosan films dyed with natural dyes

Reflectance curves for chitosan films dyed with gardenia and green tea on a range of mordants are shown in Figures 4.24 and 4.25. In the case of green tea all the dyeings, with the exception of that on the copper sulphate mordant, had similar shaped reflectance curves, as would be anticipated in view of the limited range of shades obtained with green tea. However, the reflectance curves obtained with gardenia were more varied, with those for dyeings on copper sulphate, potassium dichromate and ferrous sulphate being noticeably different from the others.

Figure 4.24 The reflectance curves of chitosan films dyed with gardenia using different mordants

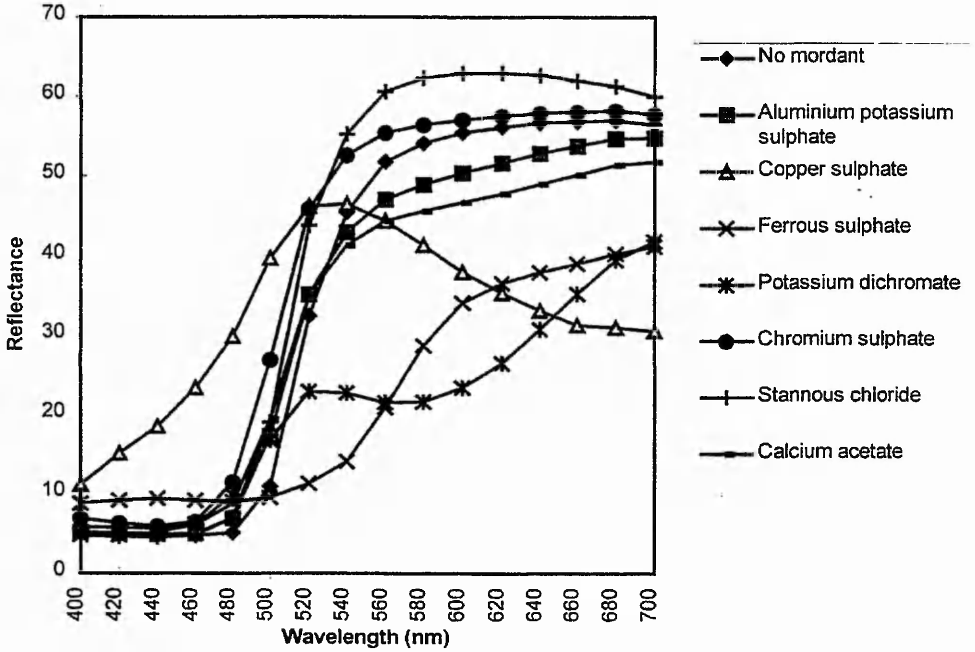
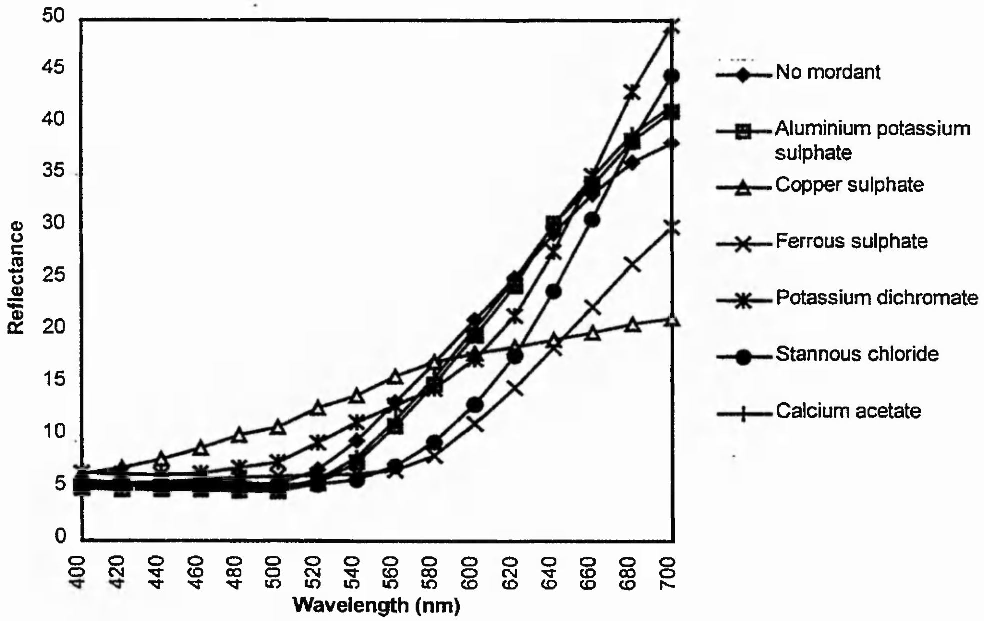


Figure 2.25 The reflectance curves of chitosan films dyed with green tea using different mordants



4.7.6 Resist effect of some mordanting treatments

Mordants are used in dyeing to increase the substantivity of a dye for the substrate and the fastness properties of the subsequent dyeing. However in the current study it was observed that two mordants, alum and chromium sulphate, produced a resist effect with gardenia when applied to chitosan films that were mordanted and dyed while still adhering to glass plates (Figure 4.26). A similar resist effect was found with the other natural dyes following mordanting with alum or chromium sulphate. Solutions of both these mordants have lower pH values (3.73 and 3.51 respectively) than the others and it was found that the resist effect was eliminated by raising the pH to around 6.5 by addition of sodium acetate prior to the mordanting step, enabling uniform deep shades to be produced (see Figure 4.26). It was also found that peeling the film from the glass plate following mordanting with either mordant, but prior to dyeing, enabled deep shades to be obtained (Figure 4.27). This suggested that these mordanting processes were producing a barrier to dye adsorption at the surface in contact with air during film formation (the "A-surface") and with the aqueous solution during the mordanting step, but not at the surface in contact with glass (the "G-surface") during both film formation and mordanting. Thus peeling the film from the glass plate prior to dyeing allows dye to penetrate the film from the G-surface despite the presence of the barrier layer at the A-surface.

As the difference in colour between gardenia on mordanted chitosan and unmordanted chitosan is very slight it was not possible to tell, from the colour of the mordanted/peeled/ dyed film, whether or not the film had been mordanted throughout or just at the A-surface. Attention was therefore turned to using a synthetic mordant dye - C.I. Mordant Blue 1 - which undergoes a considerable colour change from red to blue on complexing with metal ions such as chromium and other transition metal ions.

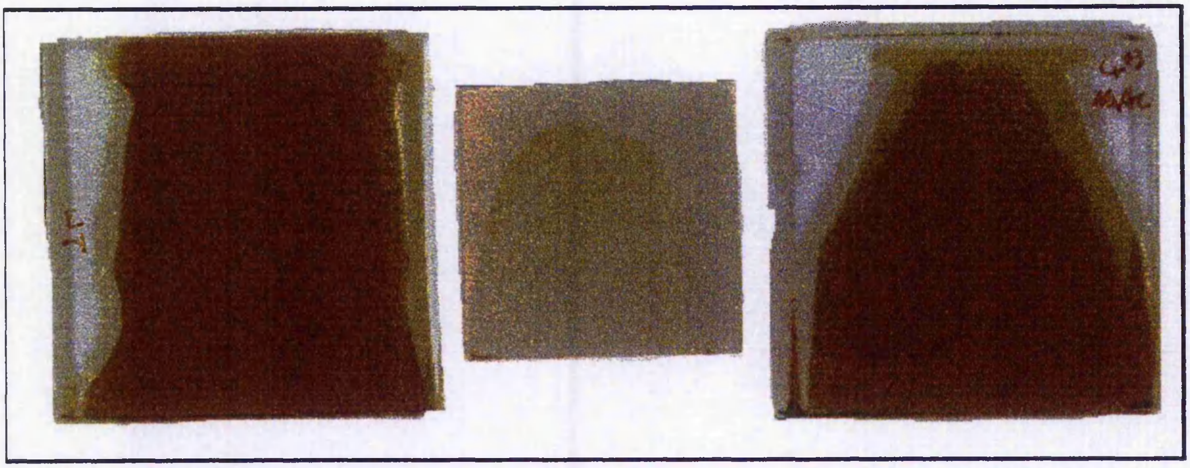


Figure 4.26 Chitosan films dyed with gardenia. From left to right: no mordant; chromium sulphate (pH 3.51); chromium sulphate (pH 6.5).

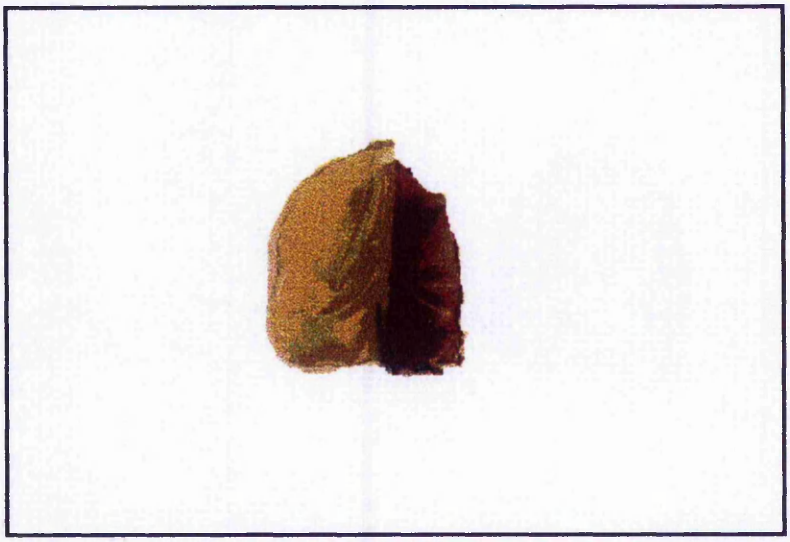


Figure 4.27 Chitosan film mordanted then dyed with gardenia, then half peeled off and the whole redyed with gardenia.

Preliminary experiments with C.I. Mordant Blue 1 (MB1) gave similar results to those obtained using gardenia. Films mordanted and dyed on the glass plate were mainly resistant to dye uptake but gave a deep blue shade if dyed after peeling off from the glass plate (Figure 4.28). The fact that the shade was blue, while that obtained on dyeing under acid conditions but without prior mordanting was red, shows clearly that the mordant penetrated through the film despite formation of a layer at the A-surface capable of acting as a barrier to dye penetration. A similar deep blue shade was obtained by dyeing first, under acid conditions, and mordanting the dyed film (Figure 4.29). It was of interest to note that dyeing on unmordanted chitosan film with MB1 under neutral conditions resulted in a very limited uptake of dye giving a very pale blue colour to the film. Obviously the dye molecules had complexed with transition metal ions present as impurities in the chitosan, suggesting that this could be developed, at least qualitatively, as a diagnostic test for the presence of trace amounts of such heavy metal ions.

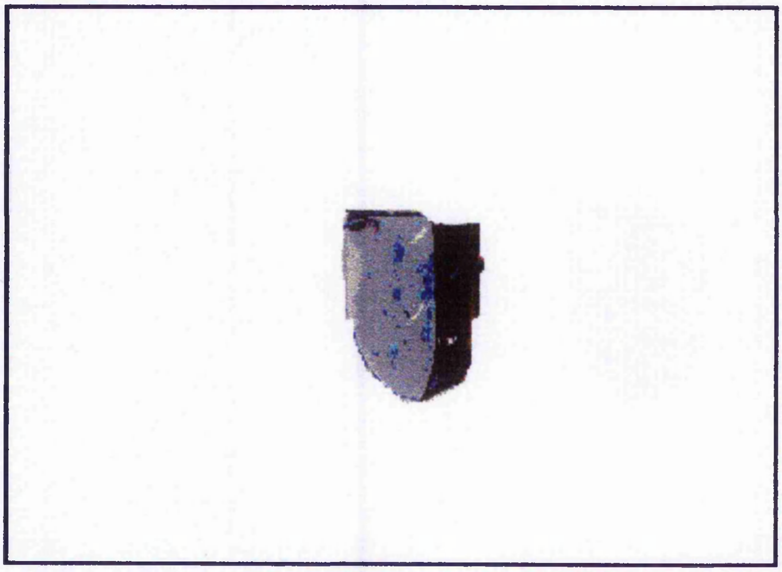


Figure 4.28 Chitosan film mordanted then dyed with MB1, then half peeled off and the whole redyed with MB1.

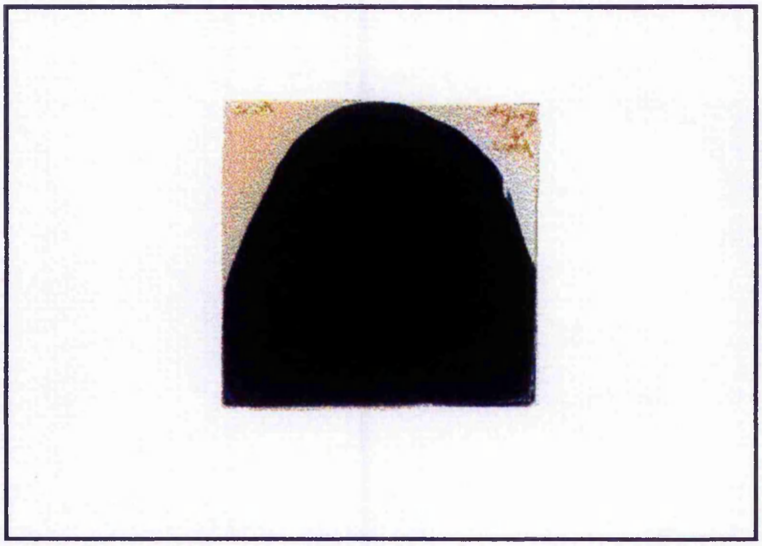


Figure 4.29 Chitosan film dyed first with MB1 and then mordanted with chromium sulphate. During the mordanting process the dyed film was converted from red to blue.

Chitosan films were mordanted on glass plates then peeled off and used to form two series of bilayers; one with the two A-surfaces in contact and one with the two G-surfaces in contact. One of each type was then dyed in gardenia extract and a second pair dyed in a solution of MB1. In both cases the bilayers which had the G-surfaces in contact with the dye solution - that is with the two A-surfaces in contact with each other - were dyed much more deeply than the bilayers which had the A-surfaces in contact with the dye solutions (Figures 4.30 and 4.31). A third pair of bilayers were used in an attempt to quantify this difference in dye uptake by measuring the change in solution concentrations on dyeing. The volumes of the dye solutions used were adjusted to take the differing weights of the bilayers into account and the dyeings were carried out in sealed flasks for 16 hours at 60°C. The colour strengths of the exhausted dye solutions were then measured using the ICS Micromatch in transmission mode and the original (blank) dye solutions as standard. The results for MB1 were very clear, the colour strength of the dye liquor which had been in contact with the G-surfaces being 0.12 while that for the dye liquor which had been in contact with the A-surfaces was 0.81. This demonstrates that considerably more dye was adsorbed by the former bilayer due to the much greater ease of penetration of the G-surfaces by the dye molecule.

It was not possible to make a similar assessment in the case of gardenia since the solutions became cloudy and a precipitate formed. This introduced errors into the measurements, indeed the measured colour strengths indicated an increase in dye concentration in the solutions despite dye uptake by the bilayers. However Figure 4.31 shows very clearly that the bilayer in which the G-surfaces were in contact with the dye solution has dyed much more deeply than the bilayer in which the A-surfaces were in contact with dye solution.

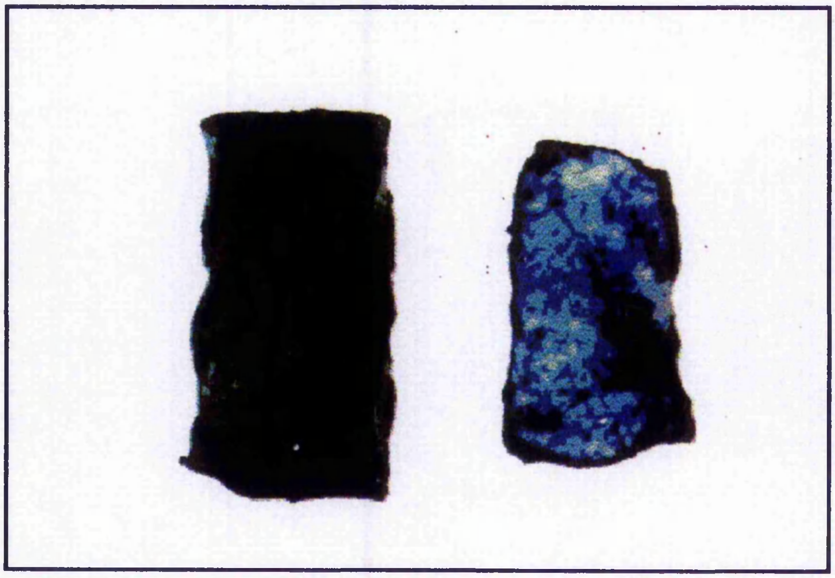


Figure 4.30 Bilayer chitosan films mordanted with chromium sulphate and dyed with C. I. Mordant Blue 1: (left) “glass” surfaces (uncrosslinked) exposed; (right) “air” surfaces (crosslinked) exposed.

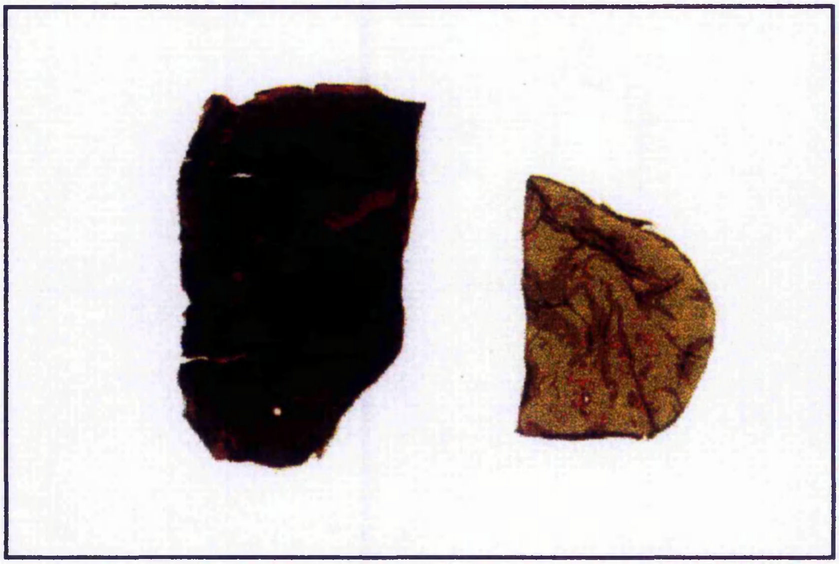


Figure 4.31 Bilayer chitosan films mordanted with chromium sulphate and dyed with gardenia: (left) "glass" surfaces (uncrosslinked) exposed; (right) "air" surfaces (crosslinked) exposed.

The most obvious explanation for the dye resist effect is that individual metal ions bind to two or more amine groups, so forming interchain crosslinks, despite the results of Ogawa *et al.*[86] which showed that under normal conditions the amine groups on two adjacent chains are too far apart to form a N-M-N link. However the barrier effect is only observed when mordanting has been carried out at relatively acid pH values and under these conditions the surface layer of the chitosan film could form a gel in which the chain segments would have considerable mobility, so allowing two or more amine groups on different chain segments to come close enough together to act as ligands for the same metal ion, thereby forming an interchain crosslink. Once sufficient crosslinks had formed in the surface layer this would act as a barrier to uptake of the relatively large dye molecules.

There are three possible explanations for the ability of dye molecules to penetrate the mordanted film once it has been peeled off the glass plate:

- there is insufficient water present at the chitosan-glass interface to allow gel formation - this could also explain why crosslinking appears to occur only at the surface layer and not within the body of the film
- the chain segments at the chitosan-glass interface adhere very strongly to the glass surface, hence have insufficient mobility to allow N-M-N linkages to be formed
- the physical characteristics of the A- and G-surfaces of the chitosan films are different

The A- and G-surfaces of mordanted and unmordanted chitosan films were examined by SEM (Figures 4.32 - 4.35). The photomicrographs show clearly that the A-surfaces are much smoother than G-surfaces, the latter showing a large number of small holes which would give dye solution access into the film. These holes are presumably produced during peeling off the film when small amounts of chitosan will adhere tenaciously to the surface of the glass plate and be pulled out of the surface.

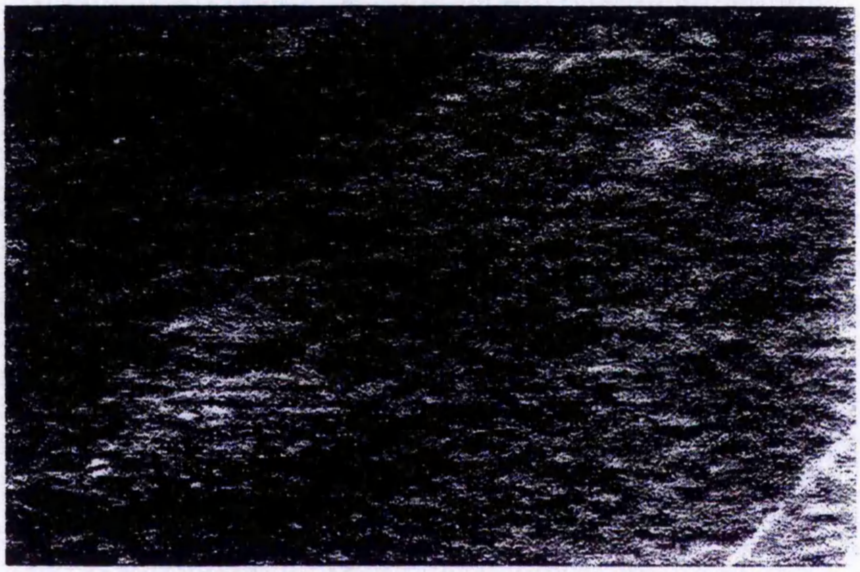


Figure 4.32 SEM photograph of "air" surface of unmordanted chitosan film.

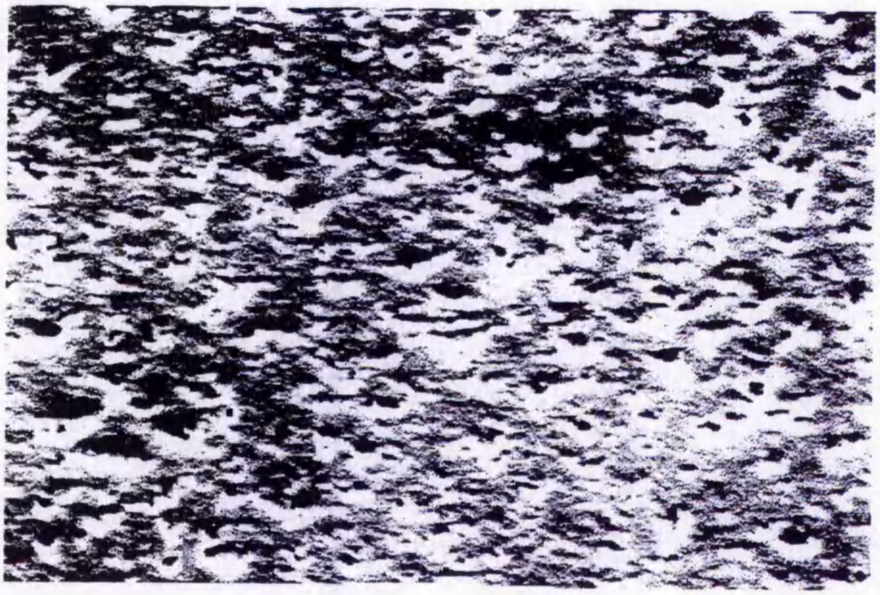


Figure 4.33 SEM photograph of "glass" surface of unmordanted chitosan film.

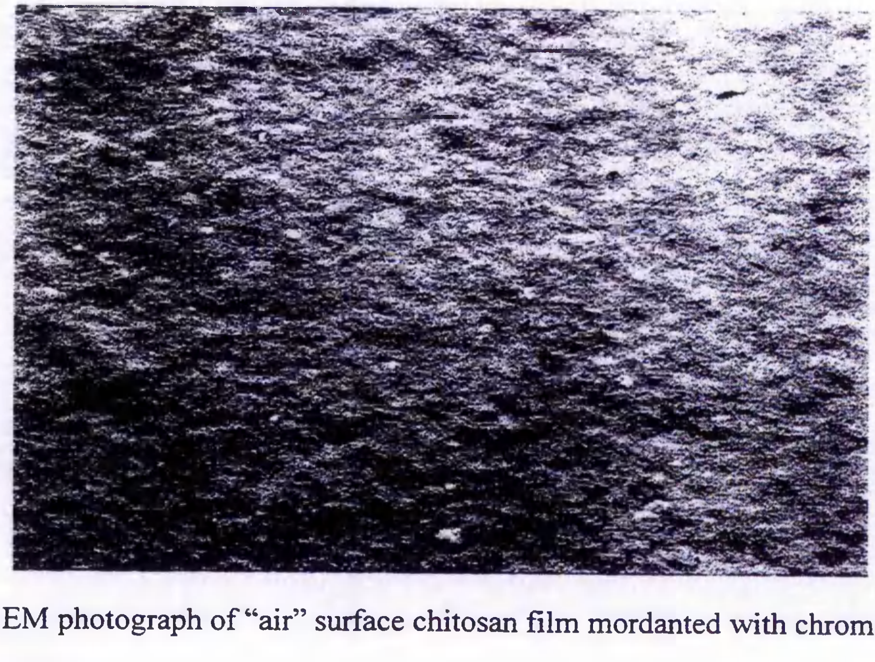


Figure 4.34 SEM photograph of "air" surface chitosan film mordanted with chromium sulphate.

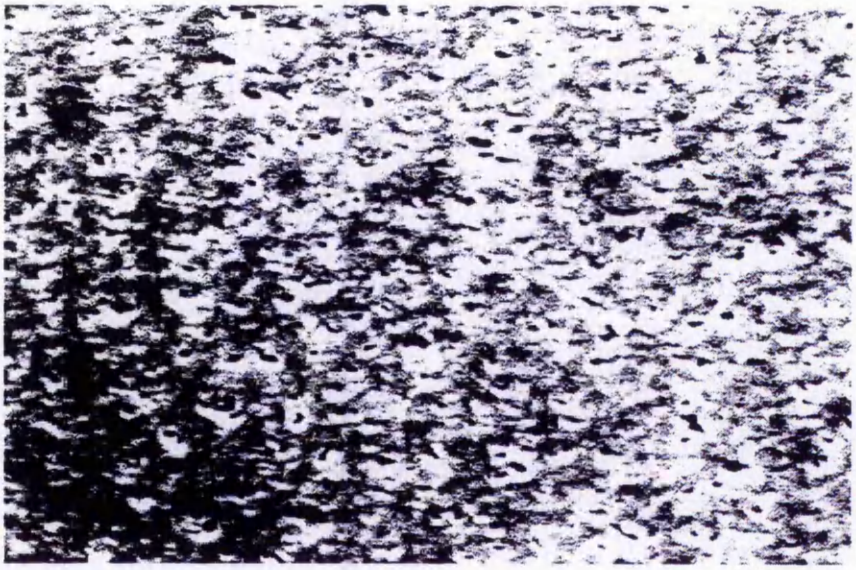


Figure 4.35 SEM photograph of "glass" surface chitosan film mordanted with chromium sulphate.

The importance of the differences in the physical structures of the two surfaces was demonstrated by the fact that a chitosan film peeled off the plate prior to mordanting was readily dyed even when mordanting had been carried out using either chromium sulphate or alum. The film shrank during the mordanting process but the structural differences between the A- and G-surfaces remained, or even increased. While the A-surface wrinkled it remained smooth overall, whereas the G-surface became even more pitted and irregular (Figure 4.36). The presence of the surface irregularities on the G-surface must prevent the formation of a crosslinked layer over the whole G-surface so that dye is still able to penetrate the film easily even after mordanting has been carried out on the free film. It may be assumed that surface irregularities on chitosan flakes also prevent complete crosslinking of the surface layer since these can be dyed to a deep shade even after mordanting with alum.

This resist effect may have potential for the production of design effects on either chitosan fibres or, more likely, chitosan-coated fibres such as cotton or polyester.

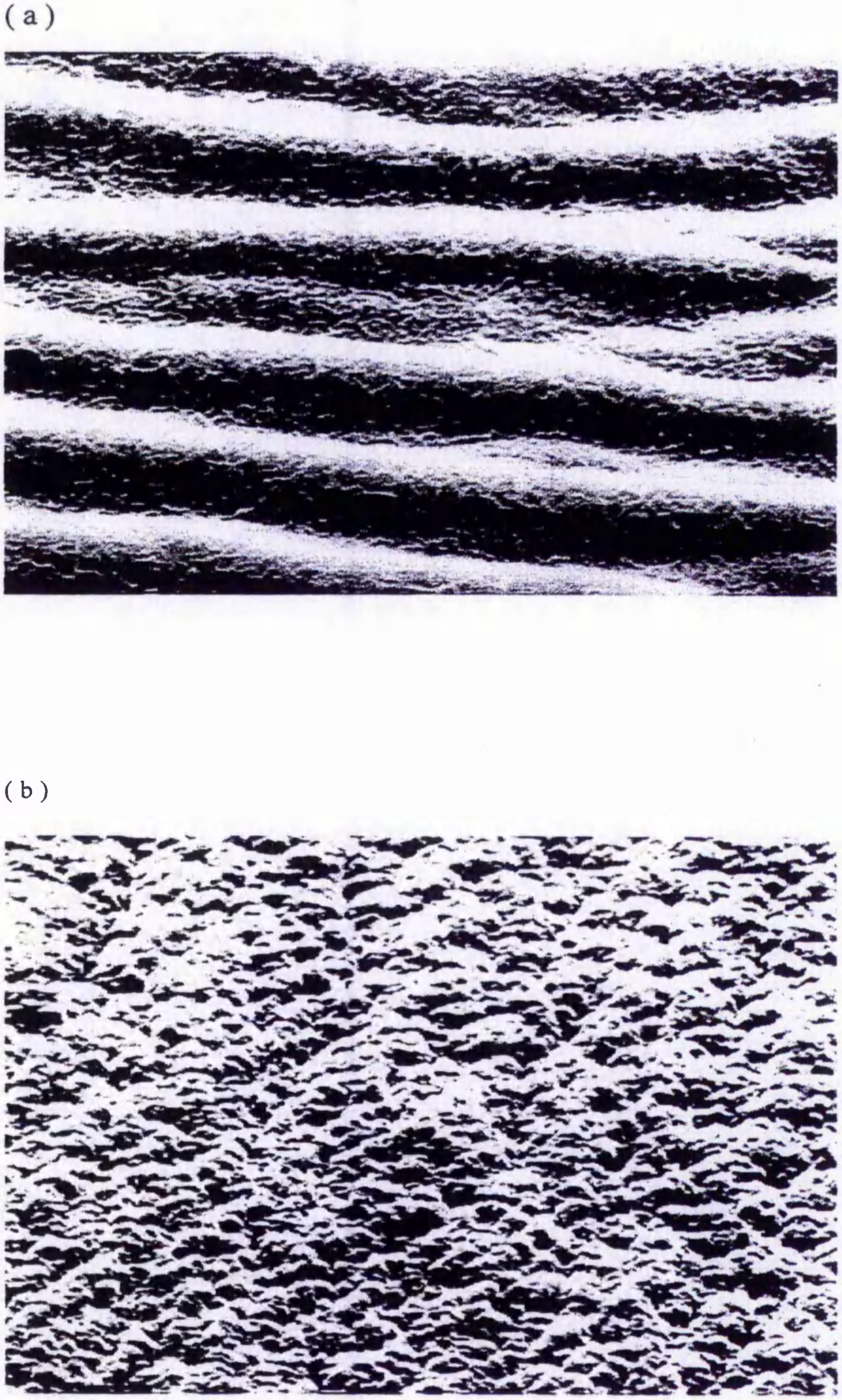


Figure 4.36 (a) SEM of A-surface after mordanting the free chitosan film with chromium sulphate; (b) SEM of G-surface after mordanting the free chitosan film with chromium sulphate.

CHAPTER 5 CONCLUSIONS

A. Microwave irradiation

1. Microwave irradiation does not damage cotton and silk fabrics. No effect has been found on either the tensile strength or the % elongation of any of the samples of these materials on irradiation for up to 30 minutes at full power.

2. Microwave irradiation does not affect the colour strength of dyed cotton and silk fabrics. No significant colour change of any cotton samples and almost of the samples of silk on irradiation for up to 20 minutes at full power.

3. Microwave irradiaton is an efficient technique for destroying fungal spores. Times as short as 2 minutes are sufficient to destroy all fungal spores examined.

4. It may be concluded that microwave irradiation would be a suitable disinfection technique for textiles particularly for sterilising Miao textiles. Sterilisation may be carried out without damaging the fabric strength or the colour of the dyed materials.

B. Dyeing chitosan with natural dyes

1. Chitosan in either flake or film form can be dyed with a range of natural dyes. A wide range of shades may be obtained with the natural dye/mordant combinations examined.

2. The reflectance curves of chitosan films and silk fabrics dyed with gardenia and green tea extracts using different mordants are similar.

3. Under certain conditions the use of alum and chromium sulphate mordants produces a resist effect on chitosan films. The resist effect is found on only one side of the film and may be eliminated by raising the pH of the mordant solution to about 6.5 prior to mordanting.

4. An explanation for the resist effect has been proposed. This involves formation of interchain crosslinks involving a metal ion and two amine groups, their formation being aided by high chain segment mobility in a gel-like layer produced at the surface of the film by the low pH values of normal solutions of alum and chromium sulphate.

5. The dyeability of chitosan, together with this resist effect, may have potential for the production of design effects on either chitosan fibres or chitosan-coated fibres and fabrics such as cotton or polyester.

REFERENCES

1. F. Flieder, M. Rakotonirainy, M. Leroy, and F. Fohrer, Disinfection Paper Using Gamma Rays, Electron Beams and Microwaves, *The 3rd International Conference on Biodeterioration of Cultural Property*, 1995, 174-82.

2. Fu Jen Catholic University Textile and Clothing Graduate Institute : Textiles and Clothing Culture Centre, *Miao Textile Design*, Fu Jen Catholic University Press Ltd, Taiwan 1993, p.16.

3. C. L. Chen, Introduction of Miao Textiles, *National Geograpical*, (Chinese Ed.) **132** 1993, 18-27.

4. Jaw Hong (craftsman), *China Miao Costume 'Legend of Miao People '*, Beijing Press, China 1985, 8-9.

5. Fu Jen Catholic University Textile and Clothing Graduate Institute, Ref. 2, pp.34-295.

6. Graduate Institute of Textiles and Clothing, *Introduction to the Chinese Textiles and Clothing Culture Centre*, Fu Jen Catholic University, Taiwan 1994.

7. Fu Jen Catholic University Textile and Clothing Graduate Institute, Ref. 2, 32.

8. M. L. Ryder, The Conservation of Textiles, *Textiles Magazine*, 1996, **3**, 15-20.

9. K. Bachmann (editor), L. A. Commoner, *Conservation Concerns--Warning Signs: When Textiles Needs conservation*, Cooper-Hewitt, National Museum of design, Smithsonian Institute, New York 1992.

10. M. Gilberg, Inert Atmosphere Fumigation of Museum Objects, *Studies in Conservation*, 1989, **34,** 80-84.

11. R. E. Child and D. B. Pinniger, Insect Trapping in Museums and Historic Houses, *International Institute for Conservation,* Preprints of Contributions to the Ottowa Congress, 1994, 129-31.

12. T. Strang, Museum Pest Management, A Systematic Approach to the Conservation (Care) of Museum Collections, *Canadian Conservation Institute*, 1992.

13. M. Gilberg and A. Roach, The Use of a Commercial Pheromone Trap for Monitoring Lasioderma Serricorne (F) Infestations in Museum Collections, *Studies in Conservation*, 1991, **36,** 243-47.

14. E.A. Back and R. T. Cotton, The Use of Vacuum for Insect Control, *Agriculture Research,* 1926, **31,** 1035-41.

15. J. E. Bergh, H. Mourier and K. P. Poulsen, Lethal Effects of Low Pressure ('Vacuum') on some Museum Pest Insects, *11th International Council of Museums Committee for Conservation*, 1996, 3-7.

16. T. J. K. Strang, The Effect of Thermal Methods of Pest Control on Museum Collections, *The 3rd International Conference on Biodeterioration of Cultural Property*, 1995, 199-212.

17. T. J. K. Strang, A Review of Published Temperatures for the Control of Pest Insects in Museums, *Collection Forum*, 1992, **8,** 41-67.

18. M. E. Florian, Conidial Fungi (Mould) activity on Artifact Materials--A New Look at Prevention, Control, and Eradication, *10th International Council of Museums Committee for Conservation*, 1993, 868-74.

19. M. Gilberg, The Effect of Low Oxygen Atmospheres on Museum Pests, *Studies in Conservation*, 1991, **36,** 93-98.

20. M. Gilberg and D. Grattan, Oxygen-Free Storage Using Ageless Oxygen Absorber, Preprints of Contributions to the Ottowa Congress, *International Institute for Conservation*, 1994,177-80.

21. N. Valentin, M. Lidstrom and F. Preusser, Microbial Control by Low Oxygen and Low Relative Humidity Enviroment, *Studies in Conservation*, 1990, **35**, 222-30.

22. U. Rosenberg and W. Bögl, Microwave Pasteurization, Sterilisation, Bleaching, and Pest Control in the Food Industry, *Food Technology*,1987, 92-99.

23. T. Ishitani, T. Kojo, and S. Yanai, Effect of Microwave Irradiation on the Spores of Molds Grown on Confectionaries, *Rept. Natl. Food Res. Inst.* 1981, **38**, 102-105.

24. C. M. Olsen, C. L. Drake, and S. L. Bunch, Some Biological of Microwave Energy, *The Journal of Microwave Power*, 1966, **1** (2), 45-56.

25. R. L. Kirkpatrick, The Use of Infrared and Microwave Radiation for Control of Stored-Product Insects, *Proceeding of the 1st International Conference of Stored-Product Entomology.* Savannah, October 1974, 431-38.

26. D. D. Reyer and G. Chauvin, Microwave Heating to Control Insect Infestation in Museum Textiles: Investigation on the Webbing Clothing Moth, Tineola Bisselliella, *The 2nd International Conference on Biodeterioration of Cultural Property*, 1992, 35-37.

27. S. F. Cleary, Considerations in the Evaluation of the Biological Effects of Exposure to Microwave Radiation, *American Industrial Hygiene Association Journal,* 1970, 52-59.

28. S. Baranski and P. Czerski, *Biological Effects of Microwaves*, Dowden, Hutchinson & Ross, Inc., U.S.A. 1976.

29. H. Fleming, Effects of High-Frequency Fields on Micro-Organisms, *Electrical Engineering*, 1944, 18-21.

30. V. Daniel, *The Non-toxic Methods of Pest Control on Museum Collections*, A speech for The National Palace Museum, Taiwan, 1996.

31. S. F. Yen, Personal Report of The Conference of Pest Control on Museum Collections, The National Palace Museum, Taiwan, 1996.

32. B. M. Reagan, J. H. Chiao-Cheng, and N. J. Streit, Effects of Microwave Radiation on the Webbing Clothes Moth, Tineola Bisselliella (Humm.) and Textiles, *Journal of Food Protection*, 1980, **43**, 658-63.

33. M. Dever, P. Hanson, R. E. Bry, and J. Aleong, Effects of Microwave Irradiation on Attagenus Unicolor (Brahm) (Coleoptera: Dermestidae) and the Physical and Chemical Properties of Wool, *Textile Research Journal*, 1990, 754-58.

34. L. A. Belyakowa, Gamma radiation as a disinfecting agent for books infected with mould spores. *Mikrobiologiya*, 1960, **29** (3), 762-765.

35. S. C. Pavon-Flores, Gamma radiation as fungicide and its effect on paper. *Journal of the American Institute for Conservation*, 1976, **16** (1), 15-44.

36. P. Justa, Gamma radiation as an Alternative Means for Disinfection of Archives, *10th International Council of Museums Committee for Conservation*, 1993, 51-54.

37. H. J. Plenderleith and A. E. A. Werner, *The Conservation of Antiquities and Works of Art, Treatment, Repair, and Restoration,* 2nd Ed. Oxford University Press, 1971.

38. C. H. Collins and J. M. Grange, *The Microbiological Hazards of Occupations*, H & H Scientific Consultants Ltd., Leeds, U.K. 1990, 6-20.

39. M. Florian, The Effect on Artifact Materials of the Fumigant ethylene Oxide and Freezing Used in Insect Control, *8th International Council of Museums Committee for Conservation*, 1987, 199-208.

40. G. Scott, Moisture, Ventilation and Mould Growth, Preprints of Contributions to the Ottowa Congress, *International Institute for Conservation*, 1994, 149-53.

41. G. Scott, Mould Growth in Tropical Environments: A discussion, *11th International Council of Museums Committee for Conservation*, 1996, 91-6.

42. F. J. Upsher, Fungal Colonization of Some Materials in A Hot-Wet Tropical Enviroment, *International Biodeterioration*, 1984, **20,** 73-78.

43. P. E. Hamrick and B. T. Butler, Exposure of Bacteria to 2450 MHz Microwave Radiation, *Journal of Microwave Power*, 1973, **8** (3), 227-233.

44. J. I. Pitt and A. D. Hocking, *Fungi and Food Spoilage*, Academic Press, Sydney 1985.

45. J. I. Pitt, E. B. Duckworth (ed), *Xerophilic Fungi and the Spoilage of Foods of Plant Origin in Water Relations of Foods*, Academic Press, London 1975.

46. K. Sakamoto, N. Kurozumi and T. Kenjo, A Simple Method for Temporary conservation of Art Objects. Effect of air Flow for Preventing Fungal Growth, *The 3rd International Conference on Biodeterioration of Cultural Property*, 1995, 183-9.

47. S. M. Robertson, *Dyes from Plants*, Van Nostrand Reinhold Co., New York 1973.

48. G. W. Taylor, Natural Dyes in Textile Applications, *Review of Progress in Coloration*, 1986, **16**, 53-61.

49. D. G. Duff and R. S. Sinclair, *Giles's Laboratory course in dyeing*, 4th ed, The Society of Dyers and Colourists, Bradford, UK 1990

50. K. G. Ponting, *A Dictionary of Dyes and Dyeing*, Mills & Boon Ltd, London 1980,104-117.

51. D. J. Hill, Is there a future for natural dyes? *Rev. Prog. Colouration*, 1997 **27**, 18-25.

52. E. Knecht, C. Rawson, and R. Loewenthal, *A Manual of Dyeing*, Chareles Griffin & Company, Ltd., London 1893.

53. R. L. M. Allen, *Colour Chemistry*, Thomas Nelson and Sons Ltd., London, 1971.

54. R. Buchanan, *A Weaver's Garden*, Interweave Press, Colorado 1987.

55. S. M. Robertson, Ref. 47, pp.75-78.

56. P. Weigle, *Natural Plant Dyeing*, A Handbook of Brooklyn Botanic Garden Record Plants and Gardens. 1973 **29** (2), 4-6.

57. C. H. Giles, A. S. A. Hassan and R. V. R. Subramanian, Adsorption at Organic Surfaces IV-Adsorption of Sulphonated Azo Dyes by Chitin from Aqueous Solution. *Journal of the Society of Dyers and Colourists*, 1958 **74**, 682-93.

58. C. H. Giles and A. S. A. Hassan, Adsorption at Organic Surfaces V-A Study of the Adsorption of Dyes and Other Organic Solutes by Cellulose and Chitin. *Journal of the Society of Dyers and Colourists*, 1958 **74**, 846-57.

59. J. A. Rippon, Improving the Dye Coverage of Immature Cotton Fibres by Treatment with Chitosan. *Journal of the Society of Dyers and Colourists*, 1984 **100**, 298-303.

60. R. S. Davidson and Y. Xue, Improving the Dyeability of Wool by Treatment with Chitosan. *Journal of the Society of Dyers and Colourists*, 1994 **110**, 24-29.

61. Y. Shimizu, The Dyeing Properties of Chitin/Cellulose Mixed Fibres. *Proceeding of the 7th International Conference on Chitin, Chitosan, and Euchis'97. Advances in Chitin Science*, Vol. II, Lyon 1997, 785-90.

62. G. A. F. Roberts, *Chitin Chemistry*, The Macmillan Press Ltd., U. K. 1992, 229-238.

63. Ref. 62, pp.206-11.

64. Ref. 62, pp.211-234.

65. S. V. Vaeck, Chemical and Mechanical Wear of Cotton Fabric in Laundering, *Journal of the Society of dyers and Colourists*, 1966, **82**, 374-79.

66. V. G. Munshi, A. V. Ukidve, (kum.) C. R. Raje, P. Bhaskar and (Smt.) S. D. Pai, Effect of Laundering on Mechanical Properties of Apparel Fabrics, *Colourage*, 1993, 11-14.

67. D. Phillips, M. Duncan, E. Jenkins, G. Bevan, J. Lloyd and J. Hoffmeister, Development of a Test to Predict Colour Fading of Cotton Fabrics After Multi-Cycle Laundering with a Bleach-Containing Domestic Detergent, *Journal of the Society of dyers and Colourists*, 1996, **112**, 287-93.

68. G. M. Venkatesh, N. E. Deweltz, G. L. Madan, and R. H. Alurkar, A Study of the Soiling of Textiles and Development of Anti-Soiling and Soil Release Finishes: A Review, *Textile Research Journal*,1974, **44**, 352-62.

69. K. Finch and G. Putnam, *The Care & Preservation of Textiles*, B. T. Batsford Ltd, London 1985.

70. W. Voegelin, W. A. Vetterli, and S. Napier, Editors, *CIBA Review 1964/1*, CIBA Ltd, Switzerland 1964, 2-25.

71. M. A. Taylor, *Technology of Textile Properties*. 3rd ed, Forbes Publications, London 1990.

72. AATCC Test Method 132 : Colourfastness to drycleaning, An American National Standard, 1993.

73. Ref. 62, pp.257-261.

74. G. G. Allan and M. Peyron, *The Kinetic of the Depolymerization of Chitosan by Nitrous Acid*, in Chitin and Chitosan, G. Skjåk-Braek, T. Anthonsen and P. Sandford (eds), Elsevier, London 1989, 443-66.

75. G. A. F. Roberts, *Determination of the Degree of N-acetylation of Chitin and Chitosan*, in Chitin Handbook, R. A. A. Muzzarelli and M. G. Peter (eds), European Chitin Society 1997, 127-32.

76. Annual book ASTM Standards, Test Method D 1682-64, Standard Test Methods for Breaking Load and Elongation of Textile Fabrics, 1991.

77. BS 2576: British Standard Method for Determination of Breaking Strength and elongation (Strip Method) of Woven Fabrics, 1986.

78. W. Garner, Rapid Fluidity Method in *Textile Laboratory Manual,* Heywood Books, London, 3rd edition, 1967, 6, 164.

79. C. Earland and D. J. Raven, *Experiments in Textile and Fiber Chemistry-Absorption of Methylene Blue by Cellulose*, Norwich Co., London 1971.

80. C. Aranyanak, Microscopical Study of Fungal Growth on Paper and Textiles, *The 3rd International Conference on Biodeterioration of Cultural Property*, 1995, 42-55.

81. BS 1006-D 01: British Standard Method for Colour Fastness to Dry Cleaning, 1978.

82. Marks & Spencer Test Method for Colour Fastness to Dry Cleaning, The Nottingham Trent University Commercial Laboratory, 1997.

83. BS 1006: British Standard Method for Colour Fastness to Domestic and Commercial Laundering, 1990.

84. A. J. Hall, *Standard Handbook of Textiles*, 6th ed., Temple Press Books Ltd., London 1965, 94-5.

85. Ref. 62, pp.116, 64-79.

86. K. Ogawa, K. Oka, T. Miyanishi and S. Hirano, in *Chitin, Chitosan and Related Enzymes*, J. P. Zikakis (ed.), Academic Press, New York, 1984, p. 327.

APPENDIX I

The British Standard Method BS 1006-D01 for dry cleaning as modified by Marks & Spencer p.l.c..

Apparatus

1. Rotadyer, consisting of a oil bath containing a rotatable shaft.
2. Fume cabinet
3. 200 ml steel cylinders (35 ± 5 mm diameter × 199 ± 5 mm high)
4. Multifibre adjacent fabric
5. Non-rusting mesh drying tray
6. Chemical balance accurate to at least ± 0.01g

Reagent

Tetrachloroethylene

Sample

1. Using a ruler and a pair of scissors, and without marking the fabric, cut a sample 100 mm × 40 mm.
2. Cut a piece of multifibre strip 100 mm × 40 mm.

Method

1. Ensure the Rotadyer cylinders are thoroughly dry.
2. Heat the rotadyer to 40° C. Do not heat the cylinders.
3. Sew the specimen and multifibre strip together along one short side using white cotton thread.
4. Weigh the composite sample and calculate the volume of tetrachloroethylene required to give a 50:1 liquor ratio.
5. Working in the fume cabinet, place the composite sample in the Rotadyer with the calculated volume of tetrachloroethylene and seal the pot.
6. Place the pot in the Rotadyer and run the machine for 30 minutes at 40° C.
7. Remove the composite sample and squeeze to remove the excess tetrachloroethylene. With the sample and multifibre fabric in contact only at the line of stitching, place the fabrics on the mesh drying tray, and leave to dry inside the fume cabinet.

Mounting and assessment

1. The solvent remaining in the cylinder is filtered through filter paper. The colour of filtered solvent is compared with that of unused solvent in 2.5 cm diameter glass tubes using a spectrophotometer.

2. Mount the specimen and multifibre strip on white paper. Assess the extent of staining and change in colour using the grey scales in the darkroom.

3. Assess the extent of staining and change in colour, colour strength and ΔE, using a colorimeter.

APPENDIX II

Reflectance values for silk dyed with a range of natural dye/mordant combinations.

Table II-1 The reflectance values of silk fabric dyed with gardenia

Wavelength	*No mordant*	*Alum*	*Copper sulphate*	*Ferrous sulphate*	*Dichromate*	*Stannous chloride*	*Calcium acetate*
400	9.05	14.62	13.17	8.60	13.56	10.61	16.45
420	5.93	10.46	11.00	7.33	9.81	8.65	11.82
440	4.89	8.64	9.92	6.69	8.15	7.43	9.74
460	5.20	9.13	10.72	7.25	8.63	7.87	10.22
480	6.84	11.73	13.51	9.16	10.88	10.05	13.03
500	15.17	21.95	21.91	16.04	20.45	19.34	23.61
520	32.30	37.90	32.36	26.27	35.76	35.53	39.06
540	41.05	44.19	36.51	31.13	42.02	42.81	45.03
560	45.06	47.01	38.76	34.30	45.02	46.24	47.46
580	46.63	48.15	40.21	36.17	46.34	47.63	48.49
600	47.54	48.91	41.23	37.62	47.32	48.49	49.15
620	48.54	49.90	42.29	38.92	48.45	49.41	49.82
640	49.99	51.37	43.61	40.56	50.01	50.77	51.01
660	51.68	52.96	45.10	42.35	51.73	52.43	52.44
680	54.07	55.32	47.21	44.75	54.08	54.78	54.70
700	56.55	57.65	49.47	47.33	56.39	57.18	57.08

Table II-2 The reflectance values of silk fabric dyed with green tea

Wavelength	*No mordant*	*Alum*	*Copper sulphate*	*Ferrous sulphate*	*Dichromate*	*Stannous chloride*	*Calcium acetate*
400	20.71	20.42	9.59	8.00	19.91	23.47	22.25
420	23.47	23.77	10.76	8.74	22.43	28.28	25.87
440	25.22	26.05	11.68	9.34	24.54	29.70	27.92
460	26.49	27.72	12.73	9.68	26.61	30.59	29.17
480	27.83	29.61	14.23	9.76	28.83	32.77	30.52
500	29.19	31.59	15.68	9.99	30.51	35.42	31.81
520	31.54	34.77	18.01	10.29	32.88	39.56	34.40
540	33.63	37.11	20.23	10.60	34.70	41.92	36.35
560	35.72	39.16	22.61	10.87	36.50	43.55	38.28
580	37.47	40.75	24.59	11.23	37.99	44.90	39.75
600	39.32	42.39	26.70	11.75	39.57	46.38	41.24
620	41.37	44.22	28.96	12.54	41.35	48.05	43.08
640	43.66	46.32	31.55	13.59	43.56	50.05	45.29
660	46.04	48.34	34.23	14.90	45.89	52.09	47.53
680	49.16	51.28	37.24	16.60	48.73	54.66	50.55
700	52.14	54.26	40.07	18.52	51.48	57.28	53.43

Table II-3 The reflectance values of silk fabric dyed with thistle

Wavelength	*No mordant*	*Alum*	*Copper sulphate*	*Ferrous sulphate*	*Dichro-mate*	*Stannous chloride*	*Calcium acetate*
400	30.15	26.38	15.51	12.96	23.82	21.26	33.33
420	33.99	29.69	17.59	15.36	26.27	25.97	36.36
440	36.52	32.24	20.10	18.24	28.90	29.76	38.43
460	38.75	34.69	22.73	20.99	31.54	33.11	40.24
480	40.52	36.98	25.30	23.30	34.05	36.15	41.71
500	41.85	38.42	26.96	25.25	35.63	37.98	42.78
520	42.81	39.75	28.58	28.15	37.01	39.73	43.46
540	43.39	40.64	29.72	30.41	37.87	41.00	43.94
560	44.20	41.57	30.90	32.77	38.77	42.37	44.49
580	44.81	42.31	31.81	34.44	39.56	43.51	44.95
600	45.30	43.07	32.77	35.83	40.36	44.60	45.37
620	46.05	43.94	33.76	37.09	41.28	45.68	45.98
640	47.27	45.30	35.07	38.66	42.67	47.16	47.14
660	48.77	46.96	36.83	40.47	44.43	48.92	48.62
680	51.21	49.56	39.36	42.94	46.96	51.45	50.99
700	53.68	52.16	41.82	45.52	49.57	54.03	53.46

Table II-4 The reflectance values of silk fabric dyed with silver birch

Wavelength	*No mordant*	*Alum*	*Copper sulphate*	*Ferrous sulphate*	*Dichro-mate*	*Stannous chloride*	*Calcium acetate*
400	17.43	16.70	9.35	5.68	11.78	8.75	16.20
420	25.41	22.62	9.96	7.43	15.79	14.83	24.87
440	29.71	26.86	11.23	9.17	18.49	22.98	29.32
460	32.27	30.69	13.65	10.90	21.43	30.61	31.71
480	34.12	34.14	17.27	12.31	25.10	36.14	33.53
500	35.82	36.08	19.88	13.13	27.92	38.83	35.31
520	37.74	38.42	22.75	14.02	30.68	41.26	37.45
540	39.54	40.32	25.47	14.69	33.15	42.84	39.28
560	41.48	42.20	28.53	15.41	36.24	44.33	41.29
580	42.85	43.44	30.92	16.04	38.84	45.41	42.70
600	44.07	44.59	32.98	16.86	41.07	46.47	44.06
620	45.33	45.78	34.77	17.80	42.95	47.66	45.41
640	47.02	47.39	36.64	19.05	45.11	49.28	47.19
660	48.87	49.18	38.74	20.51	47.28	51.08	49.08
680	51.56	51.90	41.47	22.48	50.06	53.66	51.74
700	54.23	54.57	44.22	24.55	52.70	56.17	54.41

Table II-5 The reflectance values of silk fabric dyed with turmeric

Wavelength	*No mordant*	*Alum*	*Copper sulphate*	*Ferrous sulphate*	*Dichromate*	*Stannous chloride*	*Calcium acetate*
400	14.51	15.54	9.67	8.78	15.20	10.85	16.98
420	13.27	13.87	9.38	8.57	14.11	9.51	15.81
440	13.81	14.17	9.99	9.37	14.68	9.87	16.33
460	17.67	17.84	12.10	12.18	18.18	13.24	20.15
480	31.20	30.94	24.06	20.60	27.75	26.33	32.96
500	44.38	44.70	35.24	29.26	37.94	42.00	44.95
520	51.93	52.78	41.83	36.64	45.75	53.03	51.41
540	51.94	52.79	43.67	40.03	47.15	53.79	51.52
560	52.14	52.64	44.69	43.31	47.73	54.27	51.70
580	50.55	50.77	45.08	44.47	47.26	51.97	50.58
600	49.80	49.89	45.38	45.46	47.16	50.65	50.04
620	49.83	49.82	45.81	46.54	47.58	50.45	50.30
640	50.60	50.57	46.77	47.90	48.61	51.01	51.22
660	51.75	51.82	48.06	49.45	50.03	52.03	52.42
680	53.77	53.87	50.16	51.83	52.26	54.03	54.46
700	55.96	56.17	52.40	54.28	54.69	56.22	56.65

Table II-6 The reflectance values of silk fabric dyed with alizarin (madder)

Wavelength	*No mordant*	*Alum*	*Copper sulphate*	*Ferrous sulphate*	*Dichromate*	*Stannous chloride*	*Calcium acetate*	*Alum→ Calcium*
400	38.95	29.45	23.41	13.67	36.94	25.54	41.55	32.59
420	39.21	26.81	23.33	15.18	36.24	22.43	41.20	29.89
440	37.43	23.26	22.95	16.18	34.11	20.22	39.30	26.05
460	34.16	19.97	22.01	16.45	31.19	19.49	36.26	22.48
480	29.91	17.72	20.07	16.20	28.00	20.85	32.64	20.18
500	27.70	17.65	18.57	15.91	26.44	23.89	30.74	20.17
520	25.89	19.75	17.45	15.76	25.95	30.06	29.60	22.61
540	25.92	23.47	17.51	15.98	27.27	36.37	30.12	26.75
560	27.36	30.24	19.00	16.93	30.53	42.46	32.36	33.59
580	30.04	37.98	21.86	18.52	34.97	46.14	35.40	40.89
600	34.09	44.62	26.85	21.58	40.05	48.44	39.82	46.60
620	39.27	48.12	32.42	25.79	43.84	49.81	44.58	49.13
640	45.04	50.40	37.77	30.85	46.68	51.29	48.53	50.79
660	49.48	52.24	41.63	35.57	48.80	52.78	51.17	52.28
680	53.02	54.55	44.81	40.27	51.31	54.95	53.86	54.50
700	55.87	57.05	47.22	44.44	53.92	57.30	56.43	56.82

Table II-7 The reflectance values of silk fabric dyed with onion skin

Wavelength	*No mordant*	*Alum*	*Copper sulphate*	*Ferrous sulphate*	*Dichro-mate*	*Stannous chloride*	*Calcium acetate*
400	9.00	5.19	5.20	4.64	6.87	3.90	4.84
420	14.39	5.20	4.75	5.22	8.86	4.25	7.45
440	18.08	5.99	5.15	6.05	10.10	4.94	9.91
460	21.80	8.83	6.98	7.51	12.06	5.66	13.82
480	25.06	13.83	10.65	9.04	15.62	7.51	18.59
500	26.27	17.00	12.32	9.86	17.99	11.21	20.74
520	28.38	20.80	13.52	10.86	20.10	18.94	23.19
540	31.67	24.79	14.96	11.78	22.17	25.66	26.53
560	35.66	29.71	17.48	12.95	25.09	31.68	30.75
580	38.78	34.44	20.52	14.06	28.22	36.11	34.47
600	41.70	38.97	25.04	15.41	32.55	40.07	37.98
620	44.07	42.18	29.79	16.92	37.06	43.10	40.88
640	46.56	45.00	34.30	18.79	41.31	46.06	43.69
660	48.88	47.52	37.94	20.97	44.74	48.66	46.25
680	51.70	50.47	41.31	23.56	48.23	51.70	49.30
700	54.39	53.29	44.21	26.16	51.27	54.65	52.21

Table II-8 The reflectance values of silk fabric dyed with nettle

Wavelength	*No mordant*	*Alum*	*Copper sulphate*	*Ferrous sulphate*	*Dichro-mate*	*Stannous chloride*	*Calcium acetate*
400	35.44	24.71	23.98	11.74	32.49	22.33	35.32
420	36.49	26.33	26.08	13.84	33.90	24.64	36.63
440	37.90	28.56	28.20	16.40	35.68	27.12	38.20
460	39.41	31.03	30.39	18.78	37.61	29.64	39.81
480	40.86	33.57	32.61	20.70	39.54	31.93	41.49
500	41.85	35.26	34.04	22.28	40.83	33.36	42.60
520	42.41	36.48	35.38	24.16	41.76	34.52	43.32
540	42.70	37.28	36.21	25.66	42.26	35.51	43.75
560	42.99	38.22	36.90	27.26	42.89	36.72	44.21
580	43.33	39.10	37.51	28.60	43.41	38.06	44.61
600	43.71	40.11	38.24	30.04	44.03	39.51	45.08
620	44.30	41.31	39.02	31.66	44.86	40.98	45.73
640	45.57	42.99	40.36	33.69	46.25	42.80	47.00
660	47.17	44.90	42.09	35.97	47.90	44.82	48.50
680	49.64	47.67	44.66	39.06	50.44	47.58	50.84
700	52.30	50.47	47.46	42.23	53.04	50.43	53.40

Table II-9 The reflectance values of silk fabric dyed with plantain

Wavelength	*No mordant*	*Alum*	*Copper sulphate*	*Ferrous sulphate*	*Dichromate*	*Stannous chloride*	*Calcium acetate*
400	36.94	32.92	22.21	11.46	31.25	16.08	34.55
420	39.13	35.63	25.32	14.47	34.37	26.01	37.80
440	40.91	37.97	28.66	17.67	37.54	33.76	39.93
460	42.81	40.32	31.79	20.56	40.50	38.18	42.33
480	44.73	42.45	34.64	22.89	43.18	41.04	44.67
500	45.69	43.81	36.50	24.54	44.63	42.51	46.00
520	46.30	44.47	37.91	26.47	45.63	43.41	46.83
540	46.56	44.93	38.68	27.89	46.12	43.95	47.28
560	46.94	45.46	39.24	29.30	46.89	44.61	47.73
580	47.23	45.91	39.63	30.34	47.37	45.08	48.14
600	47.49	46.28	40.09	31.30	47.86	45.59	48.52
620	48.01	46.90	40.74	32.46	48.54	46.19	49.09
640	49.11	47.99	41.75	33.97	49.70	47.39	50.19
660	50.50	49.35	43.57	35.78	51.12	48.84	51.59
680	52.89	51.84	46.58	38.47	53.47	51.33	54.00
700	55.35	54.38	49.57	41.19	55.86	53.90	56.50

Table II-10 The reflectance values of silk fabric dyed with indigo

Wavelength	*Reflectance data*
400	14.45
420	17.70
440	16.79
460	14.75
480	12.60
500	11.23
520	9.04
540	7.26
560	5.99
580	5.03
600	4.28
620	3.88
640	3.68
660	3.89
680	5.48
700	12.69

APPENDIX III

Reflectance values for chitosan films dyed with a range of natural dye/mordant combinations.

Table III-1 The reflectance values of chitosan films dyed with gardenia on different mordants

Wave-length	*No mordant*	*Alum*	*Copper sulphate*	*Ferrous sulphate*	*Dichro-mate*	*Chromic sulphate*	*Stannous chloride*	*Calcium acetate*
400	5.20	5.26	11.19	8.76	4.86	6.91	4.78	5.80
420	4.95	5.05	15.09	9.21	4.80	6.35	4.66	5.75
440	4.83	4.92	18.50	9.40	5.10	5.92	4.55	5.65
460	4.82	5.02	23.36	9.20	6.20	6.48	4.79	6.06
480	5.13	6.96	29.87	9.06	9.82	11.50	7.01	8.81
500	10.99	17.27	39.75	9.57	16.79	26.95	19.09	19.47
520	32.50	35.22	46.20	11.31	22.90	45.94	43.85	35.18
540	45.48	42.96	46.50	14.15	22.73	52.60	55.26	41.38
560	51.82	47.04	44.37	20.89	21.51	55.41	60.62	44.39
580	54.08	48.90	41.36	28.72	21.59	56.40	62.30	45.58
600	55.40	50.36	37.99	34.13	23.41	57.02	62.87	46.71
620	56.14	51.66	35.35	35.56	26.50	57.48	62.93	47.80
640	56.65	52.89	33.18	38.00	30.82	57.88	62.68	49.04
660	56.79	53.82	31.37	39.07	35.27	58.06	61.97	50.16
680	56.98	54.73	31.00	40.32	39.50	58.22	61.28	51.39
700	56.40	54.80	30.60	41.24	41.86	57.73	59.97	51.81

Table III-2 The reflectance values of chitosan films dyed with green tea on different mordants

Wavelength	*No mordant*	*Alum*	*Copper sulphate*	*Ferrous Sulphate*	*Dichro-mate*	*Stannous chloride*	*Calcium acetate*
400	5.28	5.02	6.37	5.06	6.46	5.70	5.13
420	5.46	4.90	6.97	5.32	6.34	5.56	5.24
440	5.61	4.87	7.78	5.58	6.31	5.46	5.21
460	5.68	4.87	8.82	5.80	6.44	5.41	5.18
480	5.52	4.78	10.16	6.02	6.93	5.35	5.08
500	5.38	4.69	10.85	6.16	7.48	5.35	5.03
520	6.80	5.47	12.66	6.26	9.38	5.38	5.79
540	9.53	7.48	13.88	6.37	11.33	5.84	7.94
560	13.22	10.96	15.66	6.73	12.90	7.14	11.49
580	16.95	14.91	17.06	8.16	14.52	9.41	15.53
600	21.12	19.63	17.88	11.19	17.35	13.01	20.28
620	25.20	24.39	18.50	14.63	21.51	17.71	25.10
640	29.44	30.42	19.22	18.43	27.70	23.92	30.25
660	33.18	34.04	19.94	22.39	35.03	30.81	34.86
680	36.29	38.33	20.74	26.51	43.08	38.24	38.99
700	38.16	41.19	21.29	30.10	49.54	44.69	41.69

APPENDIX IV

Paper presented: Dyeing chitosan with natural dyes

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Dyeing Chitosan with Natural Dyes

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Abstract

A study of dyeing chitosan with natural dyes has been carried out using chitosan in film form and two natural dyes, extracts of gardenia and green tea. Films were cast and neutralised on glass plates and, for ease of handling, dyeings were mainly carried out with the films still adhering to the plates.

The colours obtained with gardenia and different mordants ranged from yellow to yellow-brown, greenish yellow and green while dark brown, greenish-brown and reddish-brown were obtained using green tea. The reflectance curves were measured and compared with those of silk fabric dyed by the same processes; in most cases similar reflectance curves were obtained. The exceptions were dyeings obtained using copper sulphate and potassium dichromate mordants.

In the case of two mordants, aluminium potassium sulphate (alum) and chromic sulphate, dyeing on the plate following mordanting was not possible, although the films could be dyed if stripped from the plate after mordanting and then treated with the dye solution. The explanation for this behaviour is that the low pH of these mordanting solutions causes gelation of the surface layer of the film, thereby allowing increased chain segment mobility, and this allows cross-linking of the chains in the surface layer. This cross-linked layer resists penetration by the dye molecules so that dyeing does not occur unless the film is removed from the plate, thereby exposing the uncross-linked surface to the dye solution. The structures - smooth and rough with holes - of the air surface and glass surface respectively has been confirmed by SEM since the effect of mordanting could not be recognized by SEM measurement.

The results demonstrate that chitosan and silk dyed with gardenia are of similar shade, depth and brightness but that silk dyed with green tea is lighter in depth than is chitosan. This may be attributed to the greater number of "dye sites" available in chitosan compared to silk and suggests that in some cases an improved product could be obtained by pre-treating silk fabric with chitosan.

Introduction

Natural dyes and chitosan

Silk and wool are amine-containing protein fibres that may be dyed with natural dyes. Although the full colour gamut may be produced using synthetic dyes, which normally have better all-round fastness properties than natural dyes, there is a small but expanding niche market for textile fabrics dyed with natural dyes. Chitosan is an amine-containing polysaccharide which is currently being proposed both as an agent for coating fibres and fabrics, and for the production of fibres, either alone or in blends with cellulose, and it was of interest to investigate whether or not chitosan may be dyed with natural dyes.

The first study of uptake of dyes on chitin was carried out by Giles and Hassan in 1958.[1,2] Since then some researchers have studied the dye coverage, dyeability, and dyeing behaviour of natural fibres treated with chitosan and of chitin/cellulose mixed fibres.[3,4,5] Synthetic dyes, including vat, direct, acid, and reactive dyes, were used in these studies which showed that chitin and chitosan show good adsorption properties for many dyes. However, no work has been devoted to its dyeing behaviour with natural dyes.

Many natural dyes consist of a number of coloured components and the final shade obtained is to some extent dependent on the proportion of these components. A large proportion of natural dyes are mordant dyes; these require the presence of additional substances, frequently metal ions, to impart affinity for the fibre and/or to develop the true colour. Before synthetic dyes were produced, all fibres were dyed by natural dyes, but the use of natural dyes decreased dramatically with the advent of synthetic dyes, due to both the greater ease of application and superior all-round properties of the latter. This decrease was accentuated by the development of synthetic fibres. Of the current synthetic fibres only the polyamides (nylon 6 and nylon 6.6) would appear to have the potential to be dyed with natural dyes. However chitosan-coated synthetic fibres should be dyeable with natural dyes.

The principal mechanism of anionic dye uptake on chitosan at acid pH is ion exchange:

$$\text{Chit-N}^{+}\text{H}_3\text{X}^{-} + \text{Dye-SO}_3^{-} \Leftrightarrow \text{Chit-N}^{+}\text{H}_3\text{O}^{-}_3\text{S-Dye} + \text{X}^{-}$$

Additional dye ions may be adsorbed through other attractive forces - van der Waals' forces, hydrophobic bonding and hydrogen bonding, depending on the nature of the dye ion - so that the plateau may be in excess of that expected from an ion exchange process alone. With low molecular weight dyes, where these additional attractive forces will be also minimum, there is a 1:1 stoichiometry between the $-N^{+}H_3$ groups in the chitin/ chitosan substrate and the $-SO^{-}_3$ groups of the adsorbed dye when the system is allowed to reach equilibrium in the presence of an excess of dye.[6]

Mordants

Mordants can be described as metallic salts with an affinity for both fibers and dyestuffs, which improve the dye uptake and colour fastness.[7,8] The material to be used may be mordanted prior to dyeing or the mordant may be added to the dyebath. The pre-mordant method is historically the more important. In the current research, a wide range of mordants were used:

1. Aluminium potassium sulphate ('alum', $AlK(SO_4)_2.12H_2O$), which is usually combined with cream of tartar (potassium hydrogen tartrate) in a ratio of 3 parts of alum to 1 part of cream of tartar. It is used for mordanting light, pure colours.
2. Cupric sulphate ('blue vitriol', copper sulphate, $CuSO_4.5H_2O$), which is often used to help make colours in the green range as it itself imparts a bluish-green colour to the fibre.
3. Ferrous sulphate ($FeSO_4.7H_2O$). In the natural dye field iron is called a "saddening" agent because it makes a colour darker or duller.
4. Potassium dichromate ('chrome', $K_2Cr_2O_7$) or chromic sulphate ($Cr_2(SO_4)_3.15H_2O$) used to deepen the colours achieved and to make them more lasting.

5. Stannous chloride ($SnCl_2$), often used as a brightening agent to make a colour sharper or lighter.
6. Calcium acetate ($Ca(CH_3COO)_2$), often used as a brightening agent to make a colour brighter.

Materials and Methods

Preparation of chitosan films for dyeing

The 5% unbleached chitosan solution was spread on a small glass plate (6 cm × 6 cm) using a coating blade. The films were dried on an level table overnight at room temperature and, while still on the glass plate, neutralised in 2.5% ammonia solution for 1 hr then rinsed with distilled water and dried in the air at room temperature.

Mordanting

For ease of handling the mordanting and dyeing of the chitosan films were carried out with the films still adhering to the plates. Films were mordanted in 300 ml distilled water with 0.2g copper sulphate or calcium acetate, following the mordanting procedure in the literature.[9, 10] In the case of ferrous sulphate the concentration of ferrous sulphate used for mordanting was reduced from 0.2g to 0.1g to avoid formation of a precipitate on the surface of the film.. Also the amounts of alum, stannous chloride and potassium dichromate were also reduced to 0.1 g/300 ml because higher concentrations damaged the film during mordanting at the boil. Although potassium dichromate was mixed with tartaric acid for mordanting, the colour of film is uneven or the film broke on the glass plate after drying. Potassium dichromate was later replaced by chromic sulphate as it was thought that the film would be damaged by oxidation during reduction of the Cr(VI) to Cr(III). 0.04g alum, stannous chloride, and chromate were used for mordanting. The pH of alum and chromate solution was measured at 3.73 and 3.51, and raised the pH to 6.50 with sodium acetate prior to mordanting. The solutions were stirred regularly during the mordant process which consisted treatment at the boil for 30 min.

Dyeing

The mordanted film, still adhering to the glass plate, was dyed with natural dyes using extracts of gardenia and green tea. A 150 ml portion of the extract was mixed with 150 ml distilled water to prepare a bath for dyeing. After dyeing the chitosan glass plate combination was cooled and rinsed with distilled water then dried in the air.

SEM Measurement

Films were mounted on a SEM specimen holder then coated with gold-palladium. The surface morphology of the films was observed with a Cambridge Stereoscan 600 Instrument at an accelerating voltage of 20 kv.

Results and Discussion

Dyeing of chitosan flakes

The initial studies involved dyeing chitosan flakes with the natural dyes after mordanting. The products obtained were deeply coloured, with gardenia giving mainly yellow hues and green tea giving mainly greens. In view of the difficulties in assessing the colours of the products other than visually, because of the particulate nature of the chitosan, attention was turned to the use of chitosan films.

Dyeing of chitosan films

The colours obtained with gardenia and the different mordants ranged from yellow to yellow-brown, greenish yellow and green. A yellow colour was obtained in the absence of any mordant, and related shades were obtained with calcium acetate, stannous chloride, alum and chromic sulphate. The similarity in shade of the dyeing obtained in the absence of mordant and those produced using calcium acetate, stannous chloride, alum and chromic sulphate is shown by the similarity in their reflectance curves (Figure 1). Shades ranging from green to brown were obtained with copper sulphate, potassium dichromate and ferrous sulphate. Using potassium dichromate to mordant the films caused considerable damage to them due to reduction of the Cr(VI) to Cr(III) during the mordanting process bringing about oxidative degradation of the chitosan through attack on the amine groups. An attempt was made to overcome this by adding tartaric acid as a preferential reducing agent but the film was still extensively damaged. Also it was found necessary to raise the pH of two of the mordant solutions, aluminium potassium sulphate and chromium sulphate, from 3.73 and 3.51 respectively to 6.5 by addition of sodium acetate in order to obtain dyeings (see below).

Use of green tea extract gave a much narrower shade range - dark brown, greenish-brown and reddish-brown - as can be seen from the reflectance spectra (Figure 2). All the curves, with the exception of that for the copper sulphate mordant, have very similar shapes.

Comparison of dyed chitosan and silk fabric

The colours of silk dyed with gardenia or green tea and treated with a range of mordants are similar except for samples mordanted with copper sulphate and ferrous sulphate. Figures 1-4 demonstrate that chitosan and silk dyed with gardenia are of similar shade, depth and brightness but that silk dyed with green tea is lighter in depth than is chitosan. This may be attributed to the greater number of "dye sites" available in chitosan compared to silk and suggests that in some cases an improved product could be obtained by pre-treating silk fabric with chitosan.

Cross-linked surface of film

In the case of two mordants, potassium aluminium sulphate and chromic sulphate, dyeing of the chitosan film on the plate following mordanting was not possible unless the pH of the mordanting solution was raised from about 3.5 to 6.5 by addition of sodium acetate (see above). The pH values of the other mordants were close to neutral. It was first assumed that the low pH of the alum and chromic sulphate solutions caused protonation of the $-NH_2$ groups of the chitosan, thereby preventing them acting as ligands for binding the metal ions. However, if the mordanted film was peeled off the glass and then treated in the gardenia extract, dyeing took place. This suggested that these two mordanting processes form a barrier at the surface of the film in contact with the mordant solution and that this barrier prevents dye uptake.

Because of the similarity in shade produced on chitosan by gardenia itself and gardenia on either a potassium aluminium sulphate or chromic sulphate mordant, it was not possible to tell whether it was the unmordanted colour or the mordanted colour that was obtained on dyeing a film that had been peeled from the glass plate after mordanting with chromic sulphate. To investigate this use was made of the synthetic dye C. I. Mordant Blue 1 (MB 1) which is red in the uncomplexed state and blue when complexed with Cr(III) ions. The mordanted film did not dye with MB 1 while still adhering to the plate but when peeled from the plate it dyed a deep blue, indicating that the metal:dye complex was formed throughout the film and not just at the surface that had been in contact with the mordant solution, demonstrating that the Cr(III) ions had penetrated through the film.

In a further experiment four films were mordanted on glass plates then rinsed, dried and peeled off the plates. The films were them stuck together in pairs, pair (I) having the two faces previously in contact with the air joined together and the two surfaces previously in contact with the glass exposed, and pair (II) having the two faces previously in contact with the air exposed. On dyeing in a C. I. Mordant Blue 1 dyebath pair (I), having the 'glass' faces in contact with the dye solution, gave a dark blue shade whereas pair (II), having the 'air' faces in contact with the dye solution, gave overall a pale blue shade (Figure 5). Repeating this experiment with fresh films and using gardenia extract as the dye gave similar results with pair (II) dyeing to a much paler shade (Figure 6).

A possible explanation for this behaviour is that interchain crosslinks are formed at the 'air' surface of the film by the metal ions binding to two amine groups from different chains. Ogawa *et al.*[11] have conclusively shown that in the solid state chitosan/metal ion complexes contain only one $-NH_2$ group, but the low pH of these two mordanting solutions could cause gelation of the surface layer of the film. The chains at the surface would be in a quasi-solution state so that the chain segments would have increased mobility, thereby allowing two amine groups from different chains to come close enough together to form $-NH_2 \rightarrow M^{+3} \leftarrow H_2N-$ cross-links between the chains in this surface layer. This cross-linked layer would then resist penetration by the relatively large dye molecules so that dyeing did not occur. The fact that peeling the film from the plate enables dyeing to take place may be due to several factors. The first is that the chitosan chains in contact with the glass are firmly held in position through their adhesion to the glass surface, so restricting chain segment mobility and preventing the required close approach of two amine groups. The second is that there is insufficient water at the chitosan/glass interface to allow gelation. The third is that peeling the film from the plate disrupts the film surface. Figures 7-10 are SEM photographs of the 'air' and 'glass' surfaces for both unmordanted and mordanted chitosan films. These show clear differences in appearance with 'air' surface being much smoother than the 'glass' surface which has a large number of small holes. It is likely that these holes, which would provide entry to dye molecules, are formed during the peeling process through the loss of small portions of chitosan which adhere tenaciously to the glass surface.

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Figure 1 The reflectance curves of chitosan films dyed with gardenia using different mordants

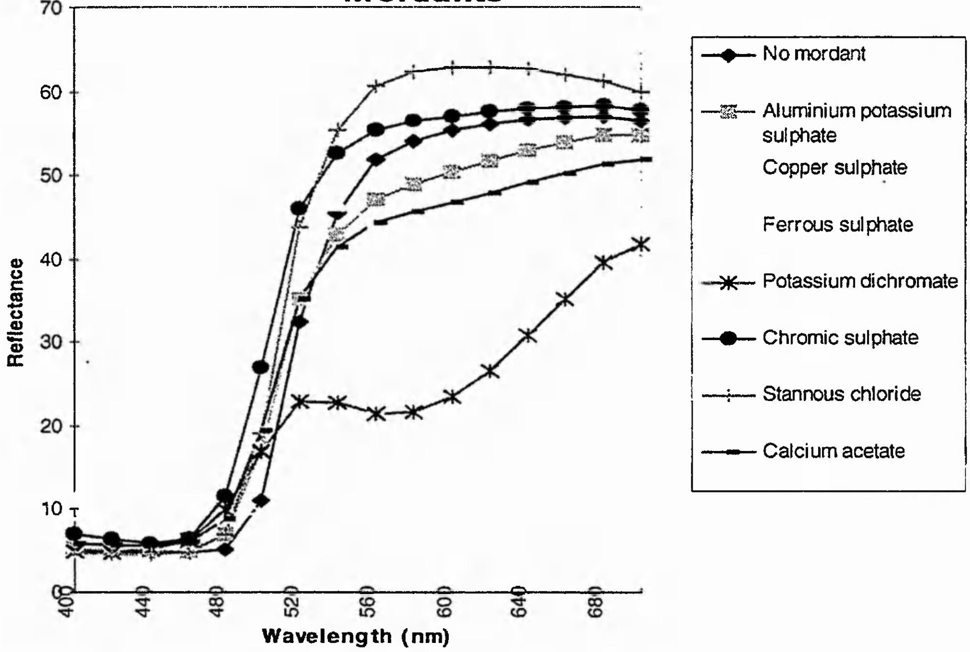


Figure 2 The reflectance curves of chitosan films dyed with green tea using different mordants

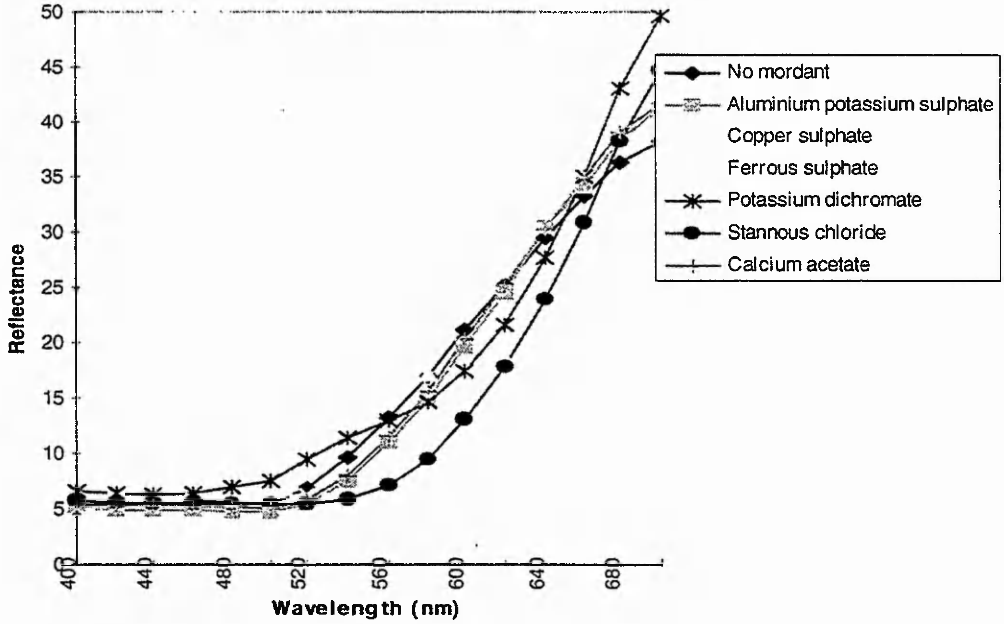


Figure 3 The reflectance curves of silk fabric dyed with gardenia using different mordants

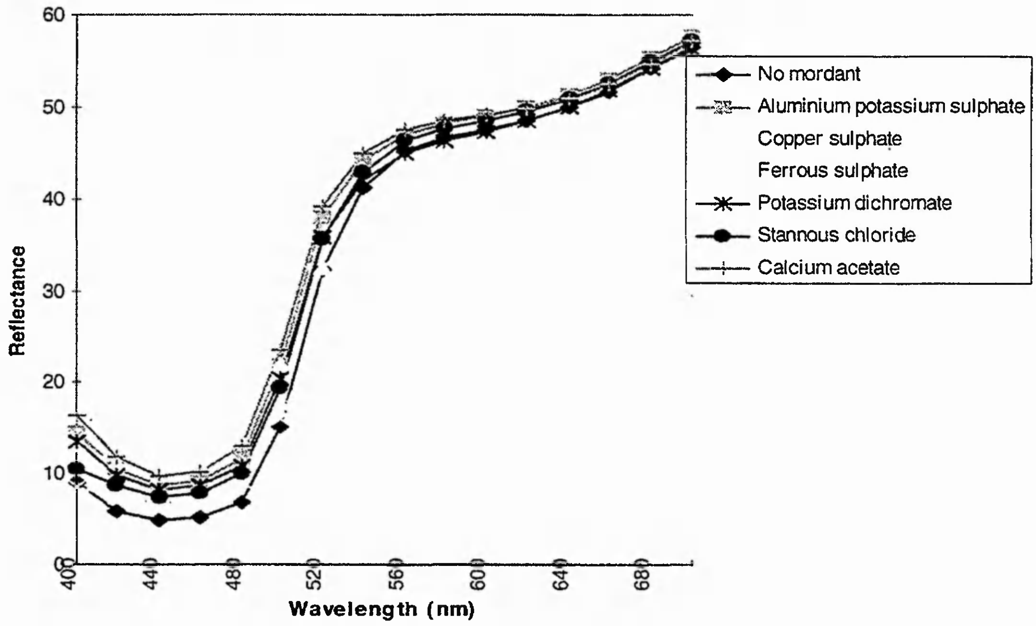
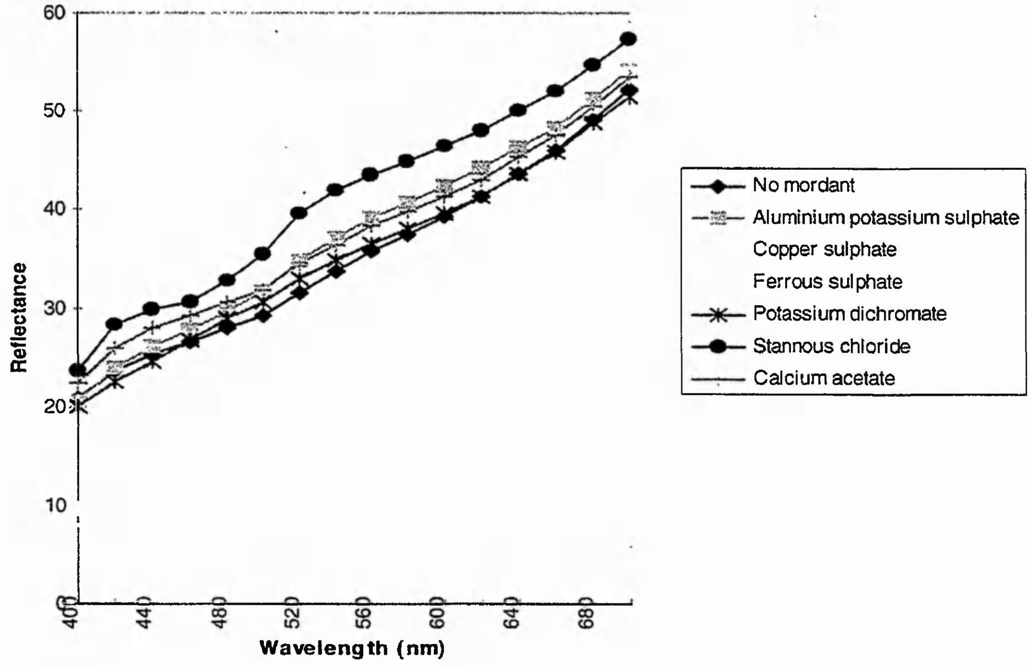


Figure 4 The reflectance curves of silk fabric dyed with green tea using different mordants



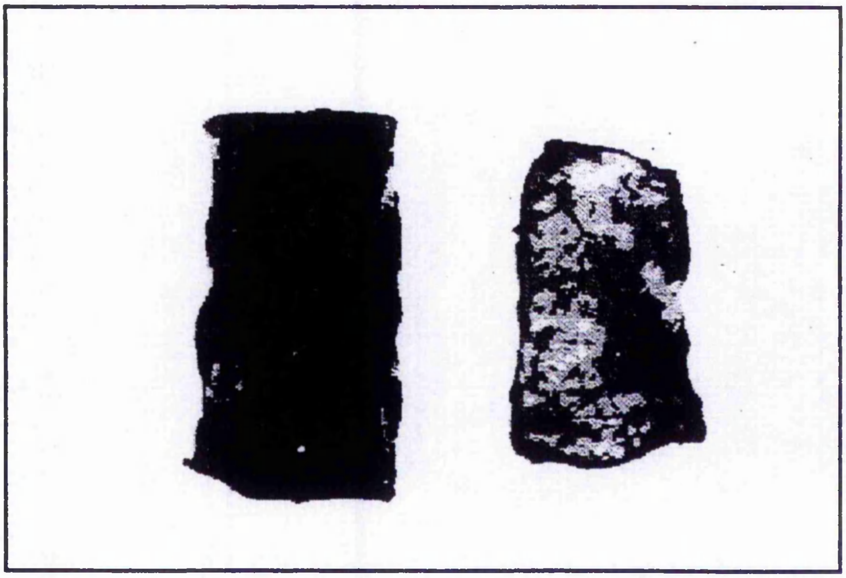


Figure 5 Bilayer chitosan films mordanted with chromic sulphate and dyed with C. I. Mordant Blue 1: (left) "glass" surfaces (uncrosslinked) exposed; (right) "air" surfaces (crosslinked) exposed.

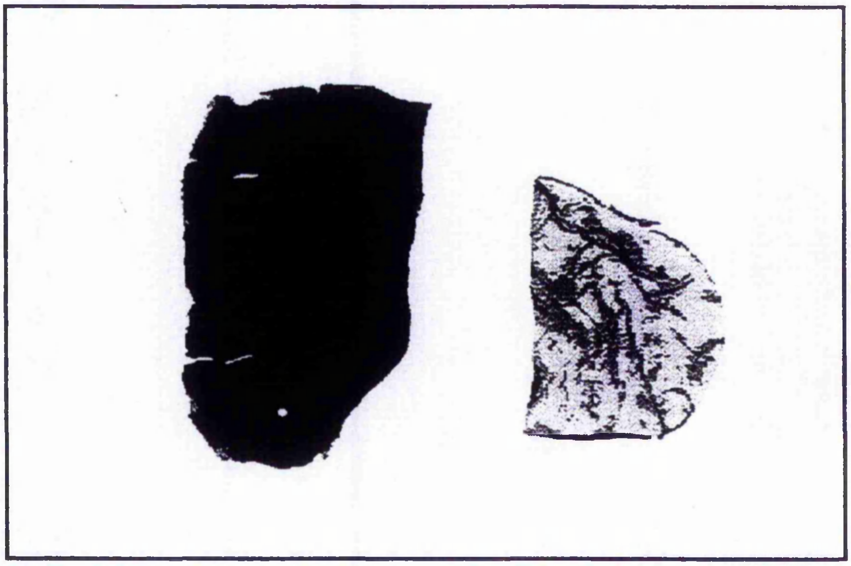


Figure 6 Bilayer chitosan films mordanted with chromic sulphate and dyed with gardenia: (left) "glass" surfaces (uncrosslinked) exposed; (right) "air" surfaces (crosslinked) exposed.

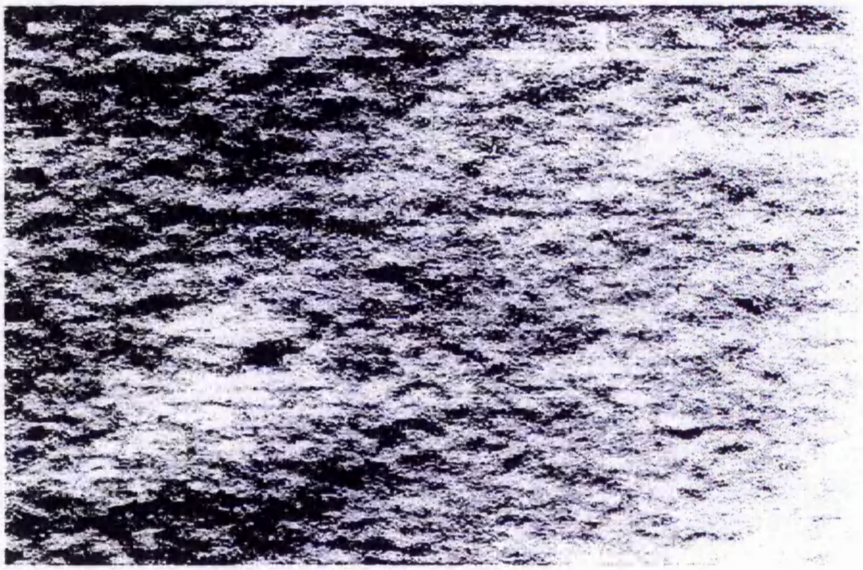


Figure 7 SEM photograph of “air” surface of unmordanted chitosan film.

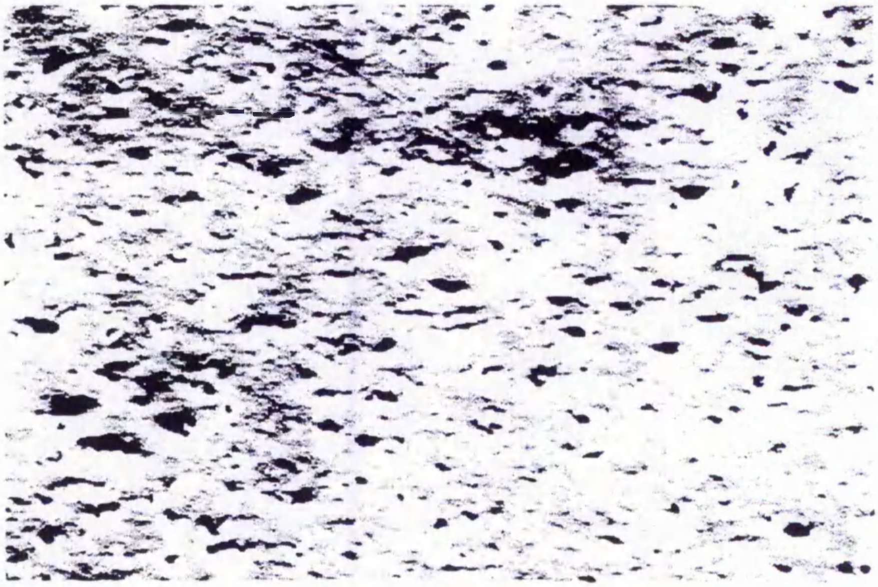


Figure 8 SEM photograph of “glass” surface of unmordanted chitosan film.

Figure 9 SEM photograph of "air" surface chitosan film mordanted with chromic sulphate.

Figure 10 SEM photograph of "glass" surface chitosan film mordanted with chromic sulphate.

Reference

1. C. H. Giles, A. S. A. Hassan and R. V. R. Subramanian, Adsorption at Organic Surfaces IV-Adsorption of Sulphonated Azo Dyes by Chitin from Aqueous Solution. *Journal of the Society of Dyers and Colourists*, 1958 **74**, 682-93.

2. C. H. Giles and A. S. A. Hassan, Adsorption at Organic Surfaces V-A Study of the Adsorption of Dyes and Other Organic Solutes by Cellulose and Chitin. *Journal of the Society of Dyers and Colourists*, 1958 **74**, 846-57.

3. J. A. Rippon, Improving the Dye Coverage of Immature Cotton Fibres by Treatment with Chitosan. *Journal of the Society of Dyers and Colourists*, 1984 **100**, 298-303.

4. R. S. Davidson and Y. Xue, Improving the Dyeability of Wool by Treatment with Chitosan. *Journal of the Society of Dyers and Colourists*, 1994 **110**, 24-29.

5. Y. Shimizu, The Dyeing Properties of Chitin/Cellulose Mixed Fibres. *Proceeding of the 7th International Conference on Chitin, Chitosan, and Euchis'97. Advances in Chitin Science*, Vol. II, Lyon 1997, 785-90.

6. M. S. Masri, V. G. Randall and A. G. Pitman, Use of Crosslinked Chitosan in the Finishing Treatment of Wool Fabric for Laundering-Shrinkage Control, *Proceeding of the 1st International Conference on Chitin and Chitosan*. Boston 1977, 306-14.

7. S. M. Robertson, *Dyes from Plants*, Van Nostrand Reinhold Co., New York 1973.

8. P. Weigle, *Natural Plant Dyeing*, A Handbook of Brooklyn Botanic Garden Record Plants and Gardens. 1973 **29** (2), 4-6.

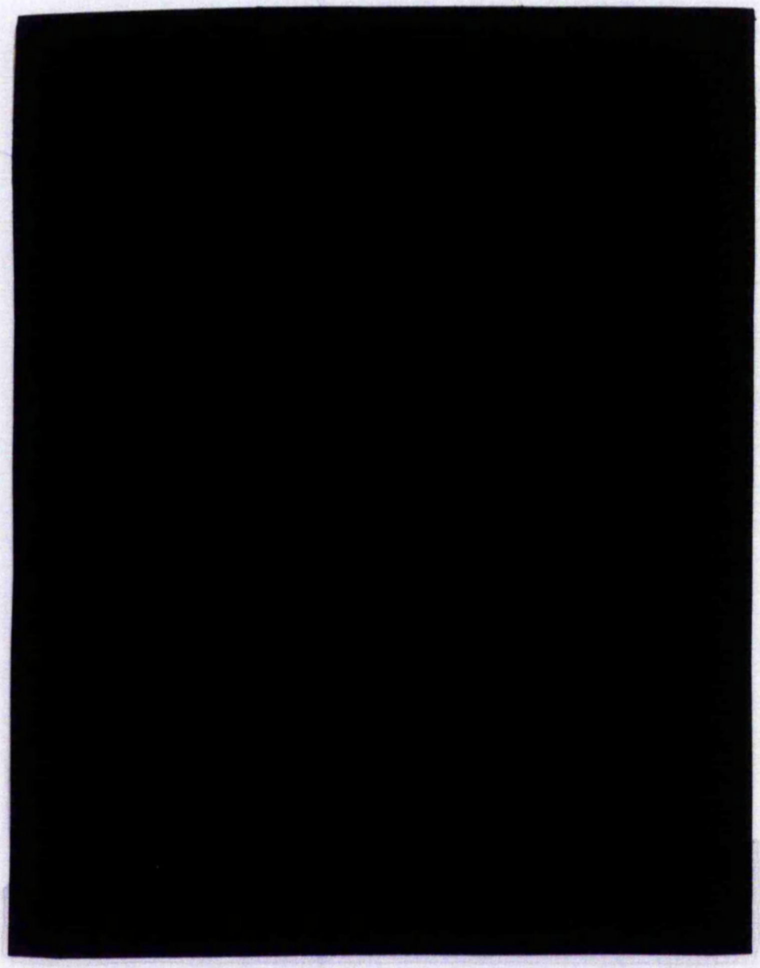
9. K. G. Ponting, *A Dictionary of Dyes and Dyeing*, Mills & Boon Ltd, London 1980, 104-117.

10. R. Buchanan, *A Weaver's Garden*, Interweave Press, Colorado 1987.

11. K. Ogawa, K. Oka, T. Miyanishi and S. Hirano, in *Chitin, Chitosan and Related Enzymes*, J. P. Zikakis (ed.), Academic Press, New York, 1984, p. 327.

APPENDIX V

Sample of indigo-dyed, ox-gel coated cotton fabric produced by the Miao people.



Sample of indigo-dyed ox-gel coated cotton fabric produced by the Miao people.