THE INFLUENCE OF POWER ULTRASOUND ON LEATHER PROCESSING

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The candidate confirms that the work submitted is her own and that appropriate credit has been given where reference has been made to the work of others

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ABSTRACT

The effects of ultrasound (38 kHz, 1.3 W cm^{-2}) on the dyeing, fatliquoring and tanning of leather have been investigated and the mechanisms whereby ultrasound influences these processes were elucidated.

Compared with a conventional process, ultrasonic dyeing can either shorten the dyeing time by 40-70% or facilitate low temperature dyeing. This remarkable enhancing effect has been attributed mainly to an increased diffusion coefficient (D) of dyestuff in the presence of ultrasound. It was found that sonication is more effective in the initial phases than in the late phases of the dyeing process.

Application of ultrasound during the fatliquoring process or simply in the preparation of fatliquors resulted in an increase of leather fat contents (up to 40%), especially in the inner corium layer, indicating an improved penetration. This can be partly attributed to a reduction of particle size by 20-30%. In contrast to dyeing, ultrasound was found to be more effective later rather than earlier in the fatliquoring process.

Chromium and aldehyde tanning processes were accelerated only marginally (~10%) but the mimosa tanning process was speeded up significantly (by up to 100%) by using ultrasound. Leathers tanned in the presence of ultrasound had shrinkage temperatures 3-5°C higher than conventionally processed controls. A more even chromium distribution and less chromium leaching were obtained after using ultrasound. The results showed that ultrasound can increase the dispersion rate and the available tannin content (by 7%) of mimosa, as well as reducing its particle size by 50%. It was also found that ultrasonic treatment can prevent mould from growing on mimosa tanned leathers.

It is concluded that ultrasound is more effective in a process which involves a colloidal rather than a true solution system. The prevailing effects of ultrasound on the former processes are to increase the diffusion coefficient and reduce the aggregation. This is due to cavitation.

(approximately 30,000 words)

CONTENTS

ABBREVIATIONS

ULT	Ultrasound
GA	Glutaraldehyde
BLC	British Leather Confederation
BSLT	British School of Leather Technology
DSC	Differential Scanning Calorimetry
DTA	Differential thermal analysis
SEM	Scanning Electron Microscopy
AA	Atomic Absorption spectrometry
GN	Grain layer
OC	Outer corium
IC	Inner corium
SD	Standard deviation
I. P.	Isoelectric point
COD	Chemical oxygen demand
EAD	Electro-Acoustic Dewatering

CHAPTER 1

INTRODUCTION AND LITERATURE SURVEY

1.1 General Introduction

The conversion of raw hide or skin into leather relies on many wet processes such as liming, unhairing, degreasing, tanning, fatliquoring and dyeing. All these processes use a large amount of water and electrical and thermal energy. In addition, most of these processes involve the use of various chemicals to assist and accelerate the process. They are normally carried out at an elevated temperature in order to transfer active chemicals from the processing liquid medium to the leather in a reasonable period of time. Due to the world-wide shortage of energy and concern for the environment, scientists and engineers in the leather industry have been seeking various techniques to shorten the process time, lower the process temperature, reduce the usage of chemicals and hence save energy and minimise the discharge of effluent. These techniques have included the application of pressure, vacuum, microwave and ultrasound energy [Luckhaus, 1933; Visser, 1992 and Ernst, 1950]. Amongst them, ultrasound has shown the greatest potential due to its recent rapid development and ease of application to the industrial situation. It has been successfully used in many textile wet processes, e.g., textile dyeing and finishing [Smith, 1988; Shimizu, 1989 and Thakore, 1988, 1990]. Investigation of the application of ultrasound to leather making dates back to the early 1950s and some encouraging results were obtained at that time. However, because of the technical problems relating to ultrasound production and the high costs of early equipment,

this technology has been neglected for more than 30 years except for one isolated piece of research work [Herfeld, 1978].

In recent times, ultrasound technology has matured so that it is within the reach of commercial application. Compared with many other modern technologies the application of ultrasound is inexpensive and, even more importantly, it has greater general applicability across a breadth of scientific research and industrial application [Mason, 1991].

Based on the operating power, the use of ultrasound can be divided into two main groups, high power applications and low power applications [Bremner, 1991]. High power ultrasound (energy intensity one to several thousands Wcm^{-2}) may cause a permanent chemical or physical change within a material. Table 1.1 shows a list of applications of high power ultrasound. Low-power ultrasound, with frequencies generally in the MHz range and power levels of milliwatts or below has been used in many different areas as well, especially as a non-destructive, non-invasive testing technique for diagnosis, foetal scanning, weld inspection and thickness measurement [Bremner, 1991].

It is clear that ultrasound is now finding many promising new applications and it is therefore timely to re-initiate research concerning the application of power ultrasound in leather making from both an academic and a commercial point of view. In the following sections, some successful applications of ultrasound will be reviewed.

In the first section, ultrasound and cavitation effects will be briefly described. In addition, the general spectrum of ultrasound applications will be given. In

sections 2 and 3, applications of ultrasound in the textile industry and in leather making will be extensively reviewed.

Table 1.1 Application of high power ultrasound [Bremner, 1991]

Area	Application
Biology	Homogenisation, cell disruption, sterilisation, extraction from plants
Engineering	Cleaning metals, soldering, welding, abrasion, fatigue testing, metal-grain refinement, drilling
Geology	Location of mineral and oil deposits, echo ranging, depth finding
Industrial	Filtration, crystallisation, air scrubbing, dispersion of solids, drying, crystal growth, degassing, treatment of mineral slurries, flow enhancement, powder production, defoaming, degreasing, emulsification
Medicine	Inhalers, sterilisation, imaging, physiotherapy, dental descaling and drilling
Physics	Cavitation, wave phenomena, acoustics, speed of ultrasound
Polymers	Polymerisation, depolymerization, molecular weight degradation, graft copolymerization

Ultrasound is a high frequency sound wave which can be transmitted through any elastic medium. In a liquid medium the oscillation of the molecules induced by the sound wave generates cavitation bubbles throughout the system. The collapse of these bubbles in an acoustic field generates a highly localised region of extremely high temperature, pressure and shear force [Mason, 1991 and 1993]. This can cause remarkable chemical and mechanical effects within the system. It might therefore be hypothesised that the application of power ultrasound within the leather industry will accelerate most of the wet processes by enhancing the diffusion and penetration of chemicals into the leather, and by increasing the interaction between chemicals and leather fibres. These effects could possibly lead to a reduction in processing time, temperature and the required concentration of chemicals, thus increasing the working efficiency and improving product quality. The application of ultrasound may also reduce the environmental pollution resulting from leather production, a factor which is becoming more and more important.

1.2 Introduction to Ultrasound

The establishment of the concept of ultrasound dates back to 1880 with the discovery of the piezoelectric effect by Curie, followed by the invention of the ultrasonic whistle by Galton in 1893. The first application of ultrasound was conducted in 1917 by Paul Langevin who is thought of as the father of ultrasound [Mason, 1976] due to his echo-sounding technique. Langevin's discovery resulted in a method of detecting icebergs so as to avoid any repetition of the Titanic disaster [Lorimer and Mason, 1987]. The first practical use of ultrasound was in the detection

of submarines during World War I. Up until World War II, Rochelle salt piezoelectric crystals, along with magnetostrictive transducers, were the main sources of ultrasound. During and after World War II, a series of breakthroughs occurred in the search for new materials which could act as ultrasound sources, such as ammonium dihydrogen phosphate (ADP) and especially the ferroelectric ceramics. These have become the most widely employed electromechanical transducers and their introduction resulted in an upsurge in the number of applications of ultrasound [Bremner, 1991].

During the 1950s and 1960s some significant progress was made in the understanding of the phenomenon of cavitation and other effects of ultrasound. Thus there was a rapid expansion in the application of ultrasound to various chemical processes. The last decade (1980s) saw an ever wider application across the whole breadth of chemistry from polymer science to chemical physics, which is expected to lead to more commercial application.

1.2.1. Nature of ultrasound

Ultrasound is a longitudinal wave with frequency above 17 kHz, beyond the audible range of human beings [Shoh, 1988]. Being a sound wave, ultrasound is transmitted through any medium, solid, liquid or gas, which possesses elastic properties. The ultrasonic wave velocity (c) in a fluid can be expressed as follows:

$$c = \sqrt{\frac{B}{\rho}} \qquad (1\text{-}1)$$

where B is the adiabatic bulk modulus and ρ is the density of the fluid. In water the velocity of propagation is about 1500 m/s at 20°C and atmospheric pressure. If the

frequency is 20 kHz, which is the highest limit of audible sound, the wavelength will be 75 mm. As the wave propagates through the medium the ultrasonic energy (sound intensity, *I*), which is mathematically described as the energy transmitted per second per cm^2 area, will be given by:

$$I = \frac{P_A^2}{2\rho c} \qquad (1\text{-}2)$$

where P_A is the maximum pressure amplitude of the wave [Lorimer and Mason, 1987]. The energy propagation is basically responsible for the chemical or physical effects of ultrasound on the medium. These effects, which result from ultrasound application, are extremely complicated and have not been fully understood. However, cavitation is believed to be one of the most important effects [Bremner, 1991 and Mason,1991]. Cavitation is a typical phenomenon in a liquid medium through which ultrasound is transmitted. In a liquid medium ultrasonic waves alternately compress and stretch the liquid (Fig. 1.1) [Suslick, 1990], with the result that a series of compression waves are formed, separated by rarefaction waves [Lorimer and Mason, 1987]. When the negative pressure (i.e., acoustic pressure on rarefaction, $P_c \approx 2\sigma/R$, where σ is surface tension and R is the critical distance) reaches such a level that the distance between the molecules of the medium exceeds the critical molecular distance (R) necessary to hold the liquid intact, the liquid will break down and voids or cavitation bubbles will be created. In water the critical distance is assumed to be 10^{-8} cm. The oscillations make these bubbles grow and contract. At a certain size, the bubbles can be driven into an implosive collapse (Fig. 1.1) [Suslick, 1990] with the release of large amounts of energy in and around these microbubbles. The 'hot-spot' theory suggests that temperatures of up to 5000 K and

pressures of several thousand atmospheres are produced during this collapse [Suslick, 1989]. Obviously such a localised high temperature and pressure will have a great effect on the medium. So cavitation is generally considered to be responsible for most of the interfacial and chemical effects which are observed in solid/liquid or liquid/liquid systems when ultrasound is applied [Senapati, 1991].

The occurrence of cavitation depends upon both the ultrasound source and the propagating medium. The frequency is one of the most important factors. The higher the frequency the higher the power which is required if the same cavitation effects are to be maintained: e.g. ten times more power is required to make water cavitate at 400 kHz than at 10 kHz [Mason, 1991]. When the ultrasound frequency is increased to the megahertz region the cavitation in liquid decreases significantly because the rarefaction cycle becomes too short to permit the molecules to be pulled apart sufficiently to generate a bubble [Lorimer and Mason, 1987]. Therefore, frequencies between 20-50 kHz are normally used in cleaning baths and this range has also been found suitable for sonochemistry [Mason, 1991].

In addition to frequency, there are also many other factors which affect the generation of cavitation, such as solvent viscosity, temperature, external pressure, ultrasound intensity and surface tension. It is difficulty to produce cavitation in a highly viscous solvent because the formation of microbubbles in this case requires a very high negative pressure. Temperature is another important factor affecting cavitation. Increasing the temperature will raise the vapour pressure of the medium and so lead to easier cavitation but less violent collapse [Mason, 1991]. Rosenburg [1960] observed that the number of pits in aluminium increased as the temperature increased from 10 to 50°C and decreased from 50 to 90°C with ultrasound of 8 kHz

frequency. Increasing the external pressure will lead to both an increase in the cavitation threshold and the intensity of cavity collapse. Cum [1988] found that, at a certain frequency, there is a particular external pressure which will provide an optimum sonochemical reaction. Therefore it is very important to create suitable experimental conditions in order to obtain a maximum effect of ultrasound in a system.

1.2.2 Effects of Cavitation in liquid and liquid/solid systems

As described above, acoustic cavitation develops in three stages: nucleation, bubble growth and violent implosion. In a pure liquid system, the structure of a cavitation bubble is illustrated in Fig. 1.2. When the cavitation bubbles collapse, the vapour is subjected to an enormous increase in both temperature and pressure which may generate many reactive species, e.g., free radicals [Riesz *et al.*, 1990]. These reactive species may enter the bulk medium through the interface to react with the chemicals in the medium [Kruus, 1990]. Very few significant investigations have been done to understand the impact of effects in the wet processes of leather making. However, it may be surmised that the physically induced changes in the chemical structure of the processing medium caused by the collapse of bubbles may indeed have a significant effect on the wet process of leather making. In the liquid immediately surrounding the bubble an intense shock wave will be produced as liquid rapidly rushes into the volume previously occupied by the bubble. This will create enormous shear forces which may also be expected to have a significant effect on the system.

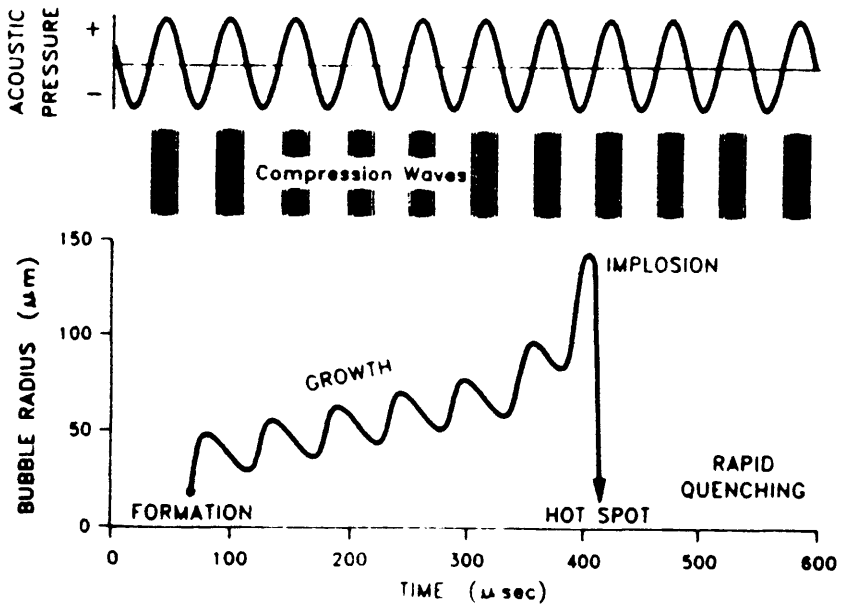


Fig. 1.1 Idealized representation of bubble growth and collapse during transient cavitation [Suslick, 1990]

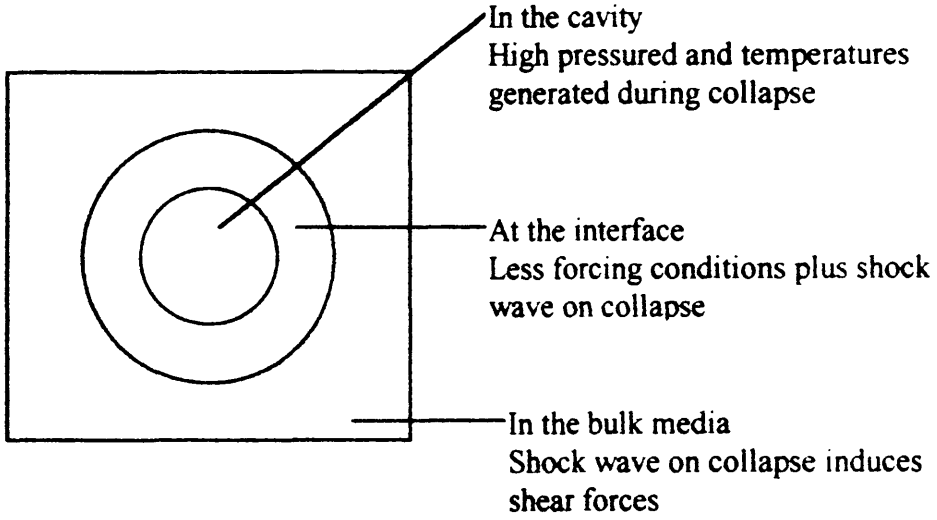


Fig. 1.2 Cavitation effect in a homogeneous liquid [Mason, 1991]

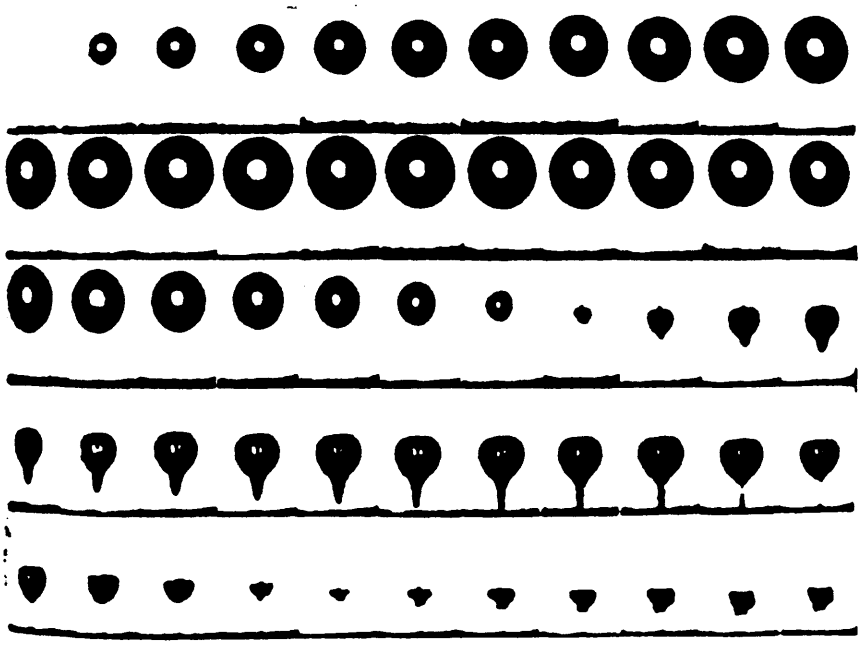


Fig. 1.3 The asymmetrical collapse of a detached air bubble near a solid boundary [Boudjouk, 1991]

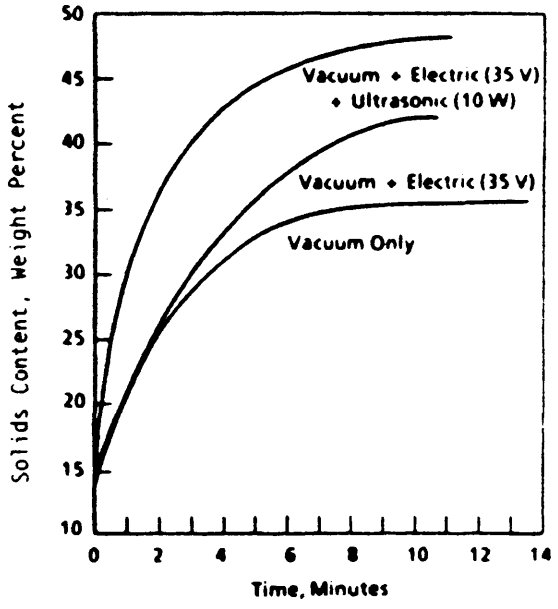


Fig. 1.4 Effect of combining an electric field (35 V) and an ultrasound field (10 W) during vacuum dewatering of corn gluten [Senapati, 1991].

The wet processes of leather production basically involve heterogeneous systems of solid and liquid. When cavitation is generated in a solid/liquid system, the nature of bubble collapse differs substantially from that in a liquid only system. The presence of the solid distorts the pressure profile arising from the sound field, and this will affect the cavitation collapse near the surface. This kind of cavitation generates a moving jet of liquid directed at the surface. The speed of the jet is greater than 100 m/s, as has been shown by the high speed microcinematography of W. Lauterborn (Fig. 1.3). Such a high speed jet is very likely to increase the mass migration and penetration from the liquid medium to the solid phase, especially when the solid phase is a porous material, such as leather.

Surface cavitation could enhance the chemical reactivity of solids in many ways. Some important effects might be the removal of a passivating surface coating and the generation of short-lived high temperatures and pressures at the surface [Suslick, 1990]. In addition, local turbulent flow ought to improve the movement of chemical intermediates and mass transport between the liquid phase and the solid surface, thus enhancing the reaction rates.

1.3 Applications of Ultrasound in Industry and Scientific Research

As described in Section 1.1, ultrasound has been widely used both commercially and academically. An ultrasound unit can be seen in nearly every chemical or physical laboratory. Reduced cost of the facility makes industrial scale application a real possibility and currently there are pilot scale trials of some industrial wet processes, e.g., textiles and leather making. The future potential is believed to be encouraging.

1.3.1. General application of ultrasound

Although the general applications of ultrasound are numerous and cover a broad range, the review in the following sections concentrates mainly on those most successful applications which take advantage of cavitation and other physical or chemical effects produced by ultrasound. Due to the specific relevance of textile dyeing/finishing to leather making, they are reviewed in separate sections.

1.3.1.1 Commercial applications of ultrasound

1. *Cleaning and atomisation*

Ultrasonic cleaning has already been established in commercial practice. It has been successfully used in applications ranging from delicate electronic parts to large scale industrial moulds. Typical examples include hospital glassware and surgical instruments, photographic lenses, filters, electronic printed circuit boards, semiconductors and ball bearing engine parts. Ultrasound cleaning works better on those sound-reflecting materials such as metal, glass, and plastic. Besides saving time, it is especially efficient for those parts which it is impossible to clean by other methods, such as parts with a complex geometry or with tiny blind holes. A wide range of ultrasound cleaners of different sizes and capacities are readily available in the market throughout the world.

Ultrasonic atomisation of liquids is another successful application in various areas, such as medical inhalation therapy, air humidification, atomisation of fuel oil, paints, molten metals, food and pharmaceuticals. Ultrasound atomisation has many advantages over conventional techniques [Senapati, 1991]. First of all the operation pressure is much lower, especially for viscous liquids. Secondly, droplet size

distribution can be controlled within narrow ranges with typical mean diameters between 1 and 500μm. Finally orifice cleaning can be minimised or eliminated because ultrasound energy has a self-cleaning action. For fuels, improved spray stability, combustion efficiency and some other benefits have been reported [Senapati, 1991]

Medical nebulizers used in inhalation therapy were the first significant commercial uses. Nebulizers operate at frequencies of 1-3 MHz and produce droplet sizes of 1-5 μm. In recent years, inexpensive ultrasonic humidifiers for home use have appeared on the market [Shoh, 1988].

2. *Degassing and Dewatering*

Degassing and dewatering are routine processes in the chemical industry and ultrasound has been successfully applied to them. For degassing, the effect is particularly rapid in aqueous systems and can be used to remove any dissolved gas down to a very low level [Mason, 1993]. The process has been used in the degassing of carbonated drinks, beer, photographic solutions and other liquids [Brown, 1965]. In the dewatering process, the advantages of using ultrasound lie in its high efficiency and its suitability for use with a high concentration of solids without the need for thermal drying [Senapati, 1991]. This is of course particularly important in the dewatering of heat-sensitive materials. A novel patented process called Electro-Acoustic Dewatering (EAD) is being developed by collaboration among several companies in North America and Europe. Fig. 1.4 shows the results of dewatering of corn gluten with about 13% solids in the slurry. In this case, EAD enhanced the solid content in the field cake to about 47% compared with 35% obtained by conventional vacuum filtration process. It is well known that continuous drying of fabric is a

common operation in textile processing and normally fabrics are squeezed by mechanical rollers to remove the excess water and then dried to evaporate the rest of water by heating. It has been shown that a high-intensity ultrasonic horn in direct contact with fabric can remove a greater amount of water than mechanical rollers, thus reducing the energy requirements of the final drying [Shoh, 1988].

3. *Homogenisation*

Another important application of ultrasound is homogenisation, which is a very critical procedure in the food, drugs and cosmetic industries. These industries involve a variety of emulsions and ultrasound can be used to efficiently produce very stable and high quality emulsions. Today, nearly every food-processing plant uses an ultrasonic homogeniser at one or more stages of production [Boudjouk, 1988]. For instance, ultrasound has been used in the production of baby foods, condensed milk, fruit juices and ice cream [Cracknell, 1980].

Some other industries also rely on ultrasound to prepare high quality emulsions. At the U.S. Bureau of Mines, crude oil and brine were treated by an ultrasound unit (20 kHz) to produce stable emulsions of 5% oil in brine. In the presence of only 1% of an emulsifying agent, a 1:1 emulsion could be stabilised. The reason for this was the reduction of the particle size of the emulsion prepared by ultrasonic irradiation. Typically the particle size was around 8-10 μm in the presence of ultrasound compared to a size of >20 μm without ultrasound [Boudjouk, 1988].

1.3.1.2. Applications in research

1. *Chemical Reactions*

Besides the physical effects described above, ultrasound also has many significant effects on chemical reactions. Sonochemistry has become a very important branch of modern chemistry and chemical engineering. The research work includes studies of organic, inorganic and organometallic chemistry, polymerisation and polymer degradation, together with some work on catalysis chemistry. Most of the results obtained show that reaction rates have been accelerated by the introduction of power ultrasound. The benefits of using ultrasound are listed in Table 1.2

Table 1.2 Beneficial Effects of Sonication on Chemical Reactivity [Lindley]

1. Accelerate a reaction
2. Permit the use of less extreme conditions
3. Make a process more economical by facilitating the use of cruder reagents
4. Reduce the number of steps required, (favouring "one-pot" syntheses)
5. Reduce any induction period involved
6. Enhance radical reactions and catalyst efficiency

2. *Miscellaneous applications*

Apart from the above major applications, ultrasound has also been used in many other different areas. In the metallurgical industry, power ultrasound has been used to improve the grain refinement of metals, to remove gas from metals, to

relieve stress in welds, to work harden surfaces and to improve extrusion processes.

Ultrasound has also been used in cutting and drilling metals, plastics and other materials. Typical examples are the ultrasonic drill and saw [Cracknell, 1980]. This might be a direct use of ultrasound vibration. One of the interesting features of ultrasonic drilling is that it can be used to drill square or other non-circular holes in hard and brittle materials. In plastics, other applications include property modification, improved moulding, surface treatment and activation, curing and even the potential for recycling.

Power ultrasound with low intensities can be used to accelerate biochemical reactions in living cells [Sinisterra, 1991]. High power ultrasound alone is known to disrupt biological cell walls and thereby destroy bacteria [Mason, 1993]. Destruction of bacteria by ultrasound has been studied for the pasteurisation of milk and as an alternative or supplement to traditional sterilisation methods [Jacobs, 1954 and Uko, 1974]. It has also been found that the sterilisation can be finished in a shorter time and at a lower temperature by the application of ultrasound.

1.3.2 Ultrasound in textile processes

The wet processes used in the textile industries, such as dyeing and finishing, are very similar to those in leather making in many aspects. The application of ultrasound in the textile industries probably can be dated back to 1941 when Sokolov [1941] used ultrasound to improve a textile dyeing process. After that ultrasound was intensively investigated in many different processes, such as sizing, desizing, finishing and other areas [Goltman, 1962; Elgal, 1979; Thakore, 1990; and Cronshow *et al.*, 1956]. The use of ultrasound in textile processes shows many

advantages such as saving process time, energy and the amount of the chemicals used, as well as improving the product quality.

1.3.2.1. Emulsification and homogenisation

In the textile industry, many processes need either homogeneous solutions or emulsions or dispersions, e.g., sizing and finishing agents, dye dispersion. The application of ultrasound in these fields has led to great benefits as have been reported by previous researchers [Goltman, 1962; Aplavin, 1964; Anon, 1956; Lifshits, 1960 and 1963; U.S patent 3,147,954]. In the preparation of starch sizing agents for instance, the operation time could be shortened and the temperature could be lowered by using ultrasound. The performance of the sized yarns were superior to those prepared by either conventionally prepared starch or modified starch.

Ultrasonic homogenisation is a useful tool to prepare emulsions and solutions as fibre lubricants. Ramaszeder [1968] found that an oil/water emulsion prepared using ultrasound sonication remained stable for more than 212 hours while those prepared by conventional mechanical stirring were stable for only 12 hours. The reason for this huge difference was that a very fine particle emulsion was obtained after using ultrasound. A paraffin/stearine emulsion prepared by Lifshits [1960] using ultrasound had an average particle size of 1 μm whereas its counterparts prepared by conventional methods had an average particle size at least 3 times larger.

Fridman obtained a very fine dispersion of phthalocyanine pigments in distilled water using a 30 kHz frequency ultrasound unit. The stability of the dispersion was much better than that prepared by conventional stirring. The effect of

ultrasound on the quality of dispersions was also studied by Simanovich [1962]. He prepared dispersions of vat and disperse dyes at 50°C using a 9.4 kHz frequency audible sound unit for 20 minutes and determined the particle size of the dispersion by microscopy. He found that about 93% of the particles were less than 1μm as compared to only 50% when a conventional method was used. Kubilyus [1962] studied the change in the solubility of direct dyes in cool water. He noticed a considerable increase in the solubility of two direct dyes, Blue M and Brown MX, when ultrasound was used. Somewhat similar observations were obtained by Smirnova and Tynvin [1963] in their investigations. They concluded that the effectiveness of ultrasound treatment depends upon the nature of the dyes and their physicochemical properties, in particular, their solubility in water.

In the case of water soluble dyes ultrasound mainly constitutes an effective means of mechanical agitation [Gupta, 1968], whereas in case of pigments it provides a means of pigment dispersion and penetration which is not provided by conventional methods.

From all these results, it is clear that ultrasound is a very powerful tool in the preparation of homogeneous solutions, emulsions and dispersions for wet textile processes.

1.3.2.2. Sizing and desizing

Sizing and desizing are always one of the largest thermal energy consuming processes in the textile industry and ultrasound can be used to accelerate these processes. Thus it was found that the use of ultrasound in such processes could lead to a considerable energy saving compared to the conventional sizing and desizing

techniques [Hall, 1986 and Valu, 1963]. Starch granules do not all gelatinise at the same temperature. The old method of size preparation normally takes up to two hours. This preparation time could be significantly reduced when ultrasound was applied because the gelatinization temperature of the starch granules was reduced due to the agitation of ultrasonic vibration. Consequently starch consumption could be reduced by 10% although no explanation was given for this. In addition, the results showed that a natural starch homogenised by ultrasound could have a superior performance to that of some chemically modified starches [Goodman, 1963]. Ironically it was found that ultrasonic homogenisation was not desirable for jute sizing, as this could allow the size to penetrate the fibres, while the purpose of sizing for jute is to form a uniform film on the fibre surface but not penetrate into the fibres [Goodman, 1963].

Trauter *et al.*[1994] studied the effect of ultrasound on the affinity of the sizing agents for cotton, polyester and cotton/polyester blend warp yarns. The results indicated that there was a considerable potential for increasing the affinity of the size for the fibre and thus increasing the efficiency of the sizing process. The consumption of sizing agent is also lower when using conventional techniques [Trauter, 1994].

In contrast to above researcher's work, Valu *et al.* [1963] studied the effect of ultrasound on the desizing of woven cotton fabric. The investigations were carried out using an ultrasound transducer with a power output of 2-4 kW. Their results showed that a significant reduction in chemicals and energy could be achieved while the whiteness and wettability of the resulting fabrics were the same as those obtained without ultrasound. Elgal [1979] also studied the desizing process with ultrasound.

Similarly he found that the size agents can be much more easily removed from the fabric by using ultrasound.

1.3.2.3. Dyeing

Among the wet processes of the textile industry, one of the most active areas where the use of ultrasound has been closely examined is dyeing. Numerous investigations have been conducted in which ultrasound is used to prepare dyeing solutions or dispersions and to speed up the dyeing process. Both low and high frequency ultrasound transducers have been used in studies of the effect of ultrasound on the solubility of dyestuffs and their uptake by different fibres and fabrics [Brauer, 1951; Rath *et al.*, 1952; Alexander, 1953; Androsov, 1960; Wisniewska, 1972 and 1975; Thakore, 1988 and 1990]. In most cases ultrasound was found to enhance the dyeing rates and reduce the processing time.

Sokolov and Tumansky [1941] were the first to use sound waves in a textile dyeing process. An audible sound device with a frequency of 9.5 kHz was used. They found that the rate of dyeing increased 2-3 fold when substantive dyes were applied to cotton fabric. Ten years after their studies had been published, Brauer [1951] successfully applied this technique to the dyeing of cellulose fabric by vat dyes and observed a 25% reduction of the dyeing time; two different frequencies of ultrasound (22 and 175 kHz) were used in his experiment. The depth of the shade on fabric obtained with 175 kHz was found to be much darker than that obtained with 22 kHz.

Similar results were obtained by Alexander and Meek [1953]. They employed an ultrasound device with a frequency of 17.3 kHz to dye cotton with a

direct dye, wool with an acid dye, and nylon and acetate with disperse dyes. In the dyeing of cotton and wool they obtained a 2.7 fold increase in the rate of dye absorption which was similar to that obtained from conventional agitation. On the other hand a significant increase in rate of dyeing was obtained with disperse dyes on nylon and acetate fibres in comparison with the effects of mechanical stirring.

Chuz and Demoroslov [1962] obtained quality dyeings with water soluble systems on a pilot scale. They produced about 400 dyeings with vat dyes on cotton cloth and claimed a 50% reduction in dyeing time, a 10% reduction in the consumption of water and steam, and a 2% reduction in chemical used. The increase in dye uptake and acceleration in dyeing were believed to be due to an increase of dye diffusion into the fabrics.

In contrast to the above researchers, Valu *et al.* [1963] looked at the effect of audible frequency sound waves (0.6~3.5 kHz) on the dyeing process. They found that direct dyeing of cotton at 30°C was accelerated by the application of the sound wave at this range of frequency. In addition the amount of dye on the surface decreased. This could be attributed to the better penetration of dye into the fibres when sonic energy was applied. Fredman [1956] expanded his study to a wider range of frequencies (from sonic to ultrasonic). He also used a variety of dyestuffs and fibre materials, e.g. viscose, cotton, wool and silk. Similarly, positive results were also obtained with the dyestuffs, pigments and fibres used.

Since the 1970s, research in this area has been mainly theoretical and contributed to a deeper understanding of the mechanisms underlying ultrasonic effects. Wisniewska [1972 and 1974] studied the kinetics of polyamide fabric dyeing in acid and disperse dyes at 50, 70 and 90°C with and without ultrasound (0.6 and

2.0 MHz frequency). The results showed that the dyeing rate reached a maximum at 50°C. He attributed this result to the deterioration in the orientation of crystallites in the insonated fibres so that more sites were accessible to the dye molecules. By comparing the results with and without ultrasound, he also concluded that the process temperature and dye concentration could be reduced while still achieving the same amount of dye exhaustion when ultrasound was used. Since 1987, Thakore has published a series of papers on the modification of the dyeing process using ultrasound [Thakore, 1990(a, b, c, d) and Thakore, 1988(a, b)]. An ultrasound unit with a frequency 40 kHz and varied input power was employed in his investigations. He dyed cotton fabric with two different direct dyestuffs at 45, 60 and 80°C.

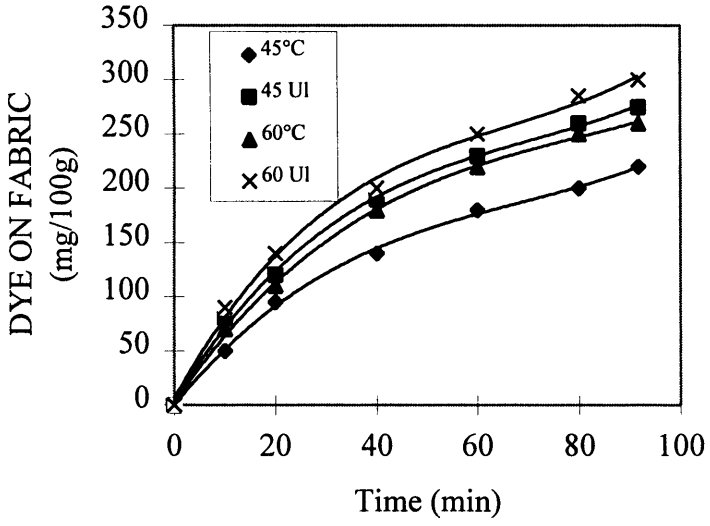


Fig. 1.5 Effect of ultrasound on rate of dyeing of C.I. Direct Yellow 12 at different temperature [Thakore, 1988 a]

Fig. 1.5 shows the dye uptake of a cotton fabric dyed with C.I. Direct Yellow 12 at 45 and 60°C with and without ultrasound. A significant increase of dye uptake

after using ultrasound is evident. The kinetics of dyeing and diffusing were studied in this work, and results confirmed that ultrasound cavitation accelerated the rate of dyeing and the amount of dye uptake. The effect was more obvious in a thicker fabric. As in the previous studies, the same amount of dye uptake could be obtained even at lower dye concentration, or dyeing temperature, or shorter dyeing time. Higher diffusion coefficient values were obtained using a cellophane film diffusion apparatus. A faster diffusion of dye from the fibre surface to the interior was associated with the presence of ultrasound. Based on these results, Thakore summarised the influence of ultrasonic cavitation on the dyeing process as follows:

(1) Greater impact of dye molecules onto the fibre surface.

(2) Reduced restraining forces between dye and fibre.

(3) Increased rate of movement of dye inside the fibre with an accelerated dye diffusion process.

At about the same time, Smith *et al.*[1988] studied the dyeing of cotton yarn and various fabrics with a number of direct dyes from the viewpoint of dye equilibrium. An ultrasound unit with a 20 kHz frequency and 180 watts power was used in this study. They observed an increase in the apparent standard affinity of all dyes after treatment with ultrasound for up to four hours. Ultrasound accelerated the dye exhaustion, increased the colour yield and improved the quality of the resulting fabric. They also studied the effects of ultrasonic energy on the above properties. It was found that the higher the energy the better the improvement of these properties.

In addition to the natural fibres or fabric mentioned above, the effect of ultrasound on some synthetic fibre dyeing processes has been intensively studied.

Shimizu, *et al.* [1989] studied the dyeing of nylon 6 film. Amorphous and unoriented nylon 6 film samples were dyed at 20, 40 and 60°C under ultrasonic radiation with a frequency of 27 kHz. The dye uptake of all dyes used was increased and the activation energies were decreased when ultrasound was used. The decrease in activation energy (E_a) varied among different dyes. Disperse dyes had the greatest decrease in E_a whilst the reactive dyes had the least.

With the rapid development of ultrasound technology, ultrasound units, such as the cleaning bath, have become routine pieces of equipment in most chemical laboratories in industrial and academic institutions. As a result, more and more significant work has been done in this area especially since 1990 [Thakore, 1990; Saligram, 1993; Carrion, 1995; Oner, 1995 and Shukla *et al.*, 1995]. Saligram *et al.* [1993] focused on the ultrasound-aided dyeing of polyester with disperse dyes and silk with basic and acid dyes at low temperature. Low temperature dyeing of silk with ultrasound was also studied by Shukla *et al.* [1995]. Cationic, acid and metal-complex dyes were used in the experiment. Besides the encouraging results such as shorter dyeing time, lower dyeing temperature and energy consumption, some explanations were also presented. It was implied that the higher the relative molecular mass of the dye molecule, the more effective was the ultrasound in increasing the dye uptake. For those dyes with a tendency to aggregate, ultrasound could disaggregate dye particles at lower temperatures. This would obviously facilitate an increase in dye uptake.

In contrast to much previous work, Ahmad [1996] recently reported that little advantage was gained by using ultrasound compared with conventional dyeing methods in the dyeing of polyester.

Although the effects of ultrasound on the dyeing process is obviously complicated and far from being fully understood, a number of points are widely shared by many researchers [Junger, 1957; Goodman, 1963; Wisniewska, 1972, 1974; Thakore, 1988, 1990 and Smith 1988]. Thus it is believed that ultrasound aids dyeing by influencing the following:

(1) dispersion: breaking up of micelles and large aggregates into uniform dispersions in the dye bath.

(2) degassing: expulsion of dissolved or entrapped gas or air molecules from both fibre capillaries and interstices at the fibre crossover points of a fabric into the surrounding liquid and subsequent removal of the bubble by cavitation, thus facilitating dye-fibre contact.

(3) diffusion: accelerating the rate of diffusion of dye inside the fibre by piercing the insulating layer covering the fibre and accelerating the interaction or chemical reaction, if any, between dye and fibre.

Based on the above review, it is clear that with the continued development of ultrasound technology and the reduction in the cost of such facilities, ultrasound-aided dyeing would seem to have promising commercial prospects.

1.3.2.4. Finishing

Finishing is another major application of ultrasound in textile fabrication. Many research publications may be identified especially since the 1970s [Yushkin, 1975; Ionescu, 1978; Antonescu, 1979; US patent 4431684, 1984]. Scinkovich *et al.* [1975] treated a cotton fabric with 8 to 18 kHz audible sound and ultrasound in a urea-formaldehyde resin and determined the change in physical properties before

and after 60 washing cycles. The crease recovery angle, even after 60 washings, was much higher than without ultrasound, and there was only very slight reduction in the tensile strength. A US issued patent (US Pat. 4302485, 1981) described a method and apparatus for treating military fabrics with a liquid repellent finish in the presence of a high frequency ultrasound waves. An increase in finish add-on was observed and the durability of repellence to laundering and wearing was measured to determine the effect of the ultrasound treatment. Safonov [1984] bleached cotton fabrics using peroxide in the presence of ultrasound at 20 kHz. An increase of the bleaching rate and reduction of the bleaching time were observed. Similar results were obtained by Poulakis *et al.* [1991]. They said treatment of cotton fabrics with peracetic acid assisted by ultrasound at low temperatures produced bleaching effects comparable to bleaching with hydrogen peroxide. There was less fibre damage with an optimum removal/decolorization of seed husks, as well as less effluent. Ultrasound was also used to clean merino and crossbred wool by Adzhiashvili [1985]. He claimed that cleaning processes were speeded up, fibre loss was eliminated and fibre properties were improved.

Ultrasound has also been successfully used in textile bonding [Srivastava, 1995; Metcalf, 1994 and Lutzow *et al.*, 1993], spinning, coagulation of filaments [Du-Pont-de-Nemours, 1995], cleaning of textile machine parts [Cronshow, 1956 and Gollmick *et al.*, 1971] and various drying processes [Bernhardt *et al.,* 1992].

1.3.3. Ultrasound in Leather Making

It is apparent from the above discussion that ultrasound technology holds great commercial promise for the textiles industry. By implication, the same may be said for the leather industry.

As described in section 1.1, the effects of ultrasound on the wet processing of leather have been reported for over 40 years. Most of the literature in this field was published between 1950 and 1960 [Ernst, 1950; Fridman, 1953; Mieczyslaw, 1953 and Gutmann, 1955]. After that there was almost 20 years of silence in this area because of the technical limitation and high cost of ultrasound equipment. With developments in electronic engineering and in the theory and practice of ultrasound which have occurred in the last decade or so, ultrasound has been revisited and shown to have a very promising prospect for the leather industry [Bufalo, 1993; ALPA SpA, 1995; Xie, 1995 and 1996; Mantysalo, 1995 and 1996]. The application of ultrasound to leather making will be reviewed in relation to the following four aspects: (1) liming and unhairing, (2) tanning and dyeing, (3) fatliquoring, and (4) dry cleaning

1.3.3.1. Liming and unhairing

To remove the hair from the skin or hide is a major aim of the beamhouse stage of processing. This process includes removing the hair, epidermis and the keratinous materials which fill in the hair follicles. In order to remove the hair efficiently and completely, the first requirement is to soak the skin and hide in a water bath containing wetting agents such as surfactants, salts, acids or alkalis, wherein the skins or hides pick up water and swell to a desired degree [He, 1990]. In

the process the connection between the hair and the skin is loosened and the hair will be easier to remove. After soaking, the operation continues by adding chemical or biological agents to remove or degrade the hairs. The agents used include amines, oxidants, alkali and enzymes.

The alkali method is the most widely used method because of its simplicity and suitability for commercial production. When $Ca(OH)_2$ together with a small amount of Na_2S are used, the process takes a long time (over 48 hours) [He, 1990]. Besides being a lengthy process another problem lies in the production of sulphur in the discharged effluent [Bienkiewicz, 1983]. Enzyme methods avoid this problem and simplify the process but they are difficult to control with a consequent risk of collagen destruction due to combine of enzyme attack [Bienkiewicz, 1983]. Other unhairing methods, such as thermal and oxidative unhairing, have also been of much interest to both academic institutions and industry but they have some serious disadvantages, such as the generation of SO_2 which is toxic to human beings and detrimental to environment. For these reasons they have never been used practically [He, 1990].

The application of ultrasound to unhairing promises solutions to these problems and a speeding up of the process. In the early 1950s, Fridman and his colleagues [1953] first explored the use of ultrasound in an unhairing process. In their experiments, a transducer with a frequency 1200 kHz and a power of 8-10 W/cm^2 was equipped with a cooling system in reaction vessel. From the experimental results, they found that after 6 hours ultrasound treatment at 30°C the hair and epidermis came off easily and the grain surface was smooth. This is much quicker than the standard alkali method.

After Fridman's pioneering work, many other researchers joined this area. A French company, Realisations Ultrasoniques, patented a technique in 1958 [British Patent, 837521, 1956]. They claimed that ultrasound can be successfully used to remove hairs. In their experiment, a dry skin was soaked for at least 50 hours in a water bath containing an antiseptic and a wetting agent. The skin was then dried slightly before being dipped into a water tank and treated by ultrasound with a frequency of 10-100 kHz. They claimed that a three minutes treatment was usually sufficient to cause the ligaments holding the hair bulb to become effectively separated. Thereafter, the removal of the hair from the skin pre-treated in this manner was more readily effected using normal procedures. They also claimed that the hair and skin did not suffer from any damage or degradation and that the treated skins were very easy to tan.

At the same time, Mieczyslaw [1958] studied the effect of ultrasound on unhairing and tanning processes. Ultrasound with frequencies from 300 kHz to 3 MHz was used in his experiments with calfskin. He found that soaking time was reduced to one hour and liming time was reduced to one and half hours (cf. 18-20 hours for the standard process).

After the above initial work, research activity in this area declined until 1978 when Herfeld [1978] re-examined the use of this technique in the wet processes of leather making. However, his conclusion was quite different from previous researchers. He found that although the hair of ultrasonically soaked pelts was considerably cleaner, and that there was a slight improvement in the diffusion rate of the liming chemical, there was no shortening of the time needed for hair loosening to

occur when 20 and 40 kHz ultrasound was used. He also concluded that this high cost technique was not worthwhile for leather making.

More recently ALPA SpA [1993] in Italy successfully applied ultrasound to liming and unhairing on a commercial scale. They produced 100 hides using a newly developed piece of equipment and obtained a series of encouraging results. The process was fully patented. They claimed that ultrasound enabled a rapid penetration of a minimum amount of sulphide directly to the hair root after immunisation of the hair shaft with lime. This allowed complete hair removal after ultrasound treatment for 3 hours followed by overnight draining and washing. They also reported that the chemical oxygen demand (COD) levels were reduced compared with a conventional hair saving process. The typical COD from a conventional process at similar float levels is between 36,000-65,000 mg/L but the COD from their ultrasound process was very considerably reduced. The results are summarised in Table 1.3 :

Table 1.3 The COD value after using ultrasound

Raw material	COD mg/L
Calf	23,700
Kips	19,300
Cow hide (25/30 Kg)	17,350
Butts (12 Kg)	17,210
Buffalo (40-45 Kg)	18,400

1.3.3.2. Tanning

Over 85% of the world's leather is tanned using a tannage based on chromium (III) [Luck, 1986 and Thomson, 1985]. Other tannages include vegetable, aldehyde, oil, syntan and organic tannage *etc*.. Tanning is one of the most time consuming processes in leather making, especially vegetable tanning for heavy leathers which requires about two weeks [He, 1990]. Therefore a considerable number of new techniques have been studied which offer to speed up the process without impairing the quality of the finished product. In 1950 Ernst *et al.* first suggested the employment of ultrasound as a novel technique for assisting the tanning process. They used this technique in the tanning of calf skin by chrome, vegetable and synthetic tannages. The ultrasound they used had a frequency of 760 kHz with a power output of 15.5-25 W. After three and half hours vegetable tanning with ultrasound treatment, inspection of the pelts indicated that there was considerable speeding-up of the tanning process with ultrasound and the pelt was already showing a leather-like appearance. Viewing of the cross-section of the tanned leather showed it deeply penetrated by the tanning agents. The control sample (no ultrasound) showed very little trace of either leather like appearance or penetration of the tanning agent. Results for syntan were even more positive than for the vegetable tannage. However they did not find any rate increase for chrome tanning although the tanning agent appeared to be much more uniformly deposited on the skin surface with a dark colour than that in the control sample. Although the reason for a lack of improvement in chrome tannage was not fully understood, they proposed the following hypothesis. The width of channels separating adjacent polypeptide chains in collagen is in the order of 15 Å while the complex chromium

ions, even if hydrated, are comparatively small. The radius of the unhydrated chromium ion is only 1.62 Å. It therefore should not be difficult for the chrome complex to pass through these channels. As a result, there is not much scope for ultrasound to speed up the process of penetration.

In contrast to chrome tanning, the vegetable tanning processes were more favourably influenced by ultrasound. The large and highly polymerised vegetable tanning materials have a complicated coiled-up and chain-like structure [Gutmann, 1955]. Mark [1945] had shown that even relatively strong bonds can be disrupted by ultrasound. It was surmised by Gutmann that the depolymerising action of the ultrasound greatly increases the penetration of the tanning agent into the pelt. It was further hypothesised that the large shear force produced by the ultrasound will tend to break up any absorbable clusters of tanning agent which otherwise could clog the pelt openings and slow down the diffusion progress. It was also suggested that ultrasound tends to open the residual linkage between opposing side-chains of the collagen molecules thereby increasing the number of reaction sites available for tanning.

Another pioneering research worker in this field is Zapf [1949]. He investigated the influence of ultrasound on soaking, liming, bating, tanning, dyeing and fatliquoring. Zapf's technique was patented in 1949. About the same time, Witke [1952] published a paper discussing the possibility of the application of ultrasound to the extraction of tanning material. He reported that with ultrasound the tanning material can be extracted at lower temperatures. In addition, he claimed that ultrasound was beneficial in chrome tanning and that chemical reactions, such as hydrolysis, was accelerated.

In 1960 Akselband [1961] reported a novel application of ultrasound in chrome tanning and fatliquoring. He simplified the traditional tanning and fatliquoring into a single process using ultrasound. The oil emulsion containing 1.8% Cr_2O_3 (based on wet pelt) was pre-treated by ultrasound for 15 minutes followed by the normal tanning. After tanning it was found that the Cr_2O_3 content in the goatskin leather was 4.8% as compared to 3.5% for normal tanning with the same amount of Cr_2O_3.

Another important tannage used in leather making is based on vegetable tannin materials and here again there are several reports of the use of ultrasound. As described earlier, Ernst successfully applied ultrasound to vegetable tannage in 1953. Subsequently, Miezcyslaw [1958], in investigating the use of ultrasound in vegetable tanning, found that quebracho extract subjected to ultrasound (200 kHz - 3 MHz) showed a rise of 7% in tannin content, which was interpreted as a depolymerization of phlobaphenes. The rate of tannage appeared to be greatly accelerated under the influence of ultrasound. For instance, sulfited quebracho and Tanigan Extra A (Syntan materials) completely penetrated a calfskin of 7 mm thickness in 8 hours with ultrasound but ordinary quebracho took 12 hours to penetrate only half the thickness. In an oil tannage the oil was emulsified, oxidised and then reacted faster under irradiation with ultrasound.

In contrast to the above studies, Simoncini [1953] tried to apply a very low frequency of 50 Hz, well outside the ultrasonic range, in vegetable tanning. In the case of chestnut extract tanning, he reported that the sound wave could accelerate the tannage. In a 96 hours tanning process (with 23 hours of irradiation) the degree of tannage was 64%. In a 144 hours tanning (with 33 hours of irradiation) the degree of

tannage increased to 82%. In the same year, Fridman *et al.* [1953] used a much higher frequency ultrasound during the tanning process (1.2 MHz and a power of 8-10 W/cm^2); they found that at 30°C the tanning process was completed in 18 hours while without ultrasound the process required 114 hours under the same conditions. In addition, they concluded that the ultrasound made the tanned leather fuller.

Based on results for these various laboratory or bench scale studies, many attempts have been made to apply this technique in tannery. Masner [1960] reported that the vegetable tanning process could be shortened to 20-48 hours by using ultrasound. He also reported that the chrome tanning process could be considerably shortened. Another example of the application of ultrasound in a tannery is the work by Wenzinger [1959]. He tried to develop an automation line which involved the use of a moving belt to convey the hide from one vat to another. This could only be feasible if existing tanning processes were to be speeded up. He claimed that such a speeding up could be accomplished by the use of ultrasound and reported that a hide of 3 mm thickness was completely penetrated by quebracho in 30 minutes under ultrasound treatment while a control hide sample showed practically no penetration for the same period of time. The reason for this might be that the aggregation of tanning materials was reduced by ultrasound, while the high speed of the moving wave may also help the tannin penetrate inside the leather.

In spite of Masnor and Wenzinger's encouraging results, ultrasound was not applied commercially in the tannery probably because of the immaturity of the technology for generating ultrasound and the high costs of such facilities at that time. The ultrasound transducer was primarily sufficient only for laboratory work. The capability to scale up a process which works well in a 250 mL laboratory

glassware, to a 250 gallon vat was not available at that time.

Besides the application of ultrasound in the tannery, another successful use of ultrasound was in the extraction of vegetable tannins. Thus Karpman *et al* [1962] treated a liquid suspension of willow bark extract at 50°C with an ultrasound unit (300 kHz, 400W). In comparison with the control sample, the tannin content in the extracts was increased from 49.6% to 51.4% after 90 minute ultrasound treatment and the insoluble fraction dropped from 2.6% to 1.3% after 120 minutes treatment. Surprisingly this insoluble fraction was then found to rise again to 1.6% after 180 minutes treatment. More interestingly, the viscosity of the tannin solution decreased from 171.6 to 133.4 cp. when it might have been expected to increase due to the higher tannin concentration. Similar results were obtained by Alexa *et al.* [1964]. They used 800 kHz ultrasound in a similar experiment and found that the tannin content in the extract obtained with ultrasound applied for 45 minutes reached a level only obtained by the normal process after 8 hours.

Another new direction for the extraction of plant tanning substances was reported by Khr [1966]. Various tanning raw materials (80g) were added to 400 ml, 0.3% $NaHSO_3$ aqueous solution and irradiated by ultrasound for 20 minutes at 20°C, followed by decantation of the extraction. The results indicated that a more rapid and complete extraction could be accomplished by using ultrasound.

1.3.3.3. Fatliquoring and Dyeing

Fatliquoring is a process whereby fat is introduced into the leather. Softness of leather results from various processes in the tannery, among which fatliquoring is one of the most important.

The use of ultrasound in the preparation of fatliquor emulsions was one of the earliest applications of ultrasound to leather making because it takes advantage of the typical effect of cavitation. One important piece of early work was by Gourlay [1959] who reported that ultrasound could be used to emulsify fatliquor efficiently. Afterwards many research papers were published in this area. Aksel'band *et al.* [1961], for example, developed an apparatus which could prepare an oil emulsion by ultrasound in 15 minutes. The emulsion containing 1.8% Cr_2O_3 (based on pelt weight at 20-22% basicity) was prepared and used in chromium tanning for goatskin. The chromium content in tanned leather achieved by this method was reported to be 10% higher than that in the control sample.

Kotlyarevskaya and his colleagues [1964] systematically studied the application of ultrasound in fatliquor preparation. An acoustic pipe of the Polman type was applied in their experiment. The emulsion was prepared at 40-45°C by 5~15 minute ultrasound treatment. The preparation of 50 litres of emulsion at 30-40°C and 3-5 atm. pressure at a distance of 2-4 mm from the resonator nozzle took only 3-5 minutes. The emulsion was stable for 5-7 days. More than 70% of the particles had a diameter of less than 1.5 μm and very few exceeded 5 μm. Senilov and Metelkin [1960] did similar work in this field and also obtained positive results.

Based on the results of previous work in this area, it is apparent that ultrasound is an ideal technique for preparing high quality dispersions of fatliquor. In addition it also appears to reduce the particle size of the fatliquor emulsion.

In contrast to the fatliquoring process, only a few publications concerning leather dyeing could be traced, among which Tielborger [1954] can be seen as pioneer. He patented a process in Germany in 1954. This patent was concerned with

the application of ultrasound to leather dyeing, tanning and degreasing processes. He claimed that dyeing and degreasing were facilitated by use of ultrasound in the frequency range 150 to 960 kHz.

1.3.3.4 Dry cleaning

The effect of ultrasound on leather dry-cleaning processes was studied by Herfeld [1978] using frequencies of 22-40 kHz. Artificially soiled pieces of leather were sonicated at 30°C in perchloroethylene or a fluorinated hydrocarbon. An 8~10 minute treatment gave the same result as that of 30 minute washing in revolving apparatus. Another advantage was that less dyestuff and fat was found in the washing liquid. As a consequence the leather remained soft and pliable.

1.4 RESEARCH AIMS AND PLAN

1.4.1 General research aims

It can be seen from the above literature survey that most of the research work on the application of ultrasound to leather making was carried out between 1950 and 1970. As described in Section 1.1, many encouraging results were achieved at that time but the research was not continued because of the technical limitations associated with ultrasound generation. Consequently, the effects of ultrasound on the leather making processes have not been clearly explained and the mechanisms by which ultrasound influences the leather processes are still unknown. With the rapid development of this technique in the past decade, some academic and industrial institutions have started to re-evaluate ultrasound technology and its commercial

significance.

Today, environmental concern has become a very important issue all over the world. The treatment of the effluent from the tannery has drawn a great deal of attention in leather industry. As described in the previous sections, apart from increasing production efficiency, ultrasound is also expected to reduce the concentration of chemicals which are often toxic to life or detrimental to the environment. It is therefore timely to re-consider its suitability as a tool in leather making. It is in the light of these observations that the present research has been initiated. The main aims are:

- To examine the potential of ultrasound for improving tanning, dyeing and fatliquoring processes in leather making.
- To gain a better understanding of the mechanisms whereby ultrasound influences these processes in leather manufacturing

1.4.2 Outline of thesis

- *Chapter 2 Methodologies*

Ultrasonic equipment unit and various experimental or analytical methods used in this work are introduced.

- *Chapter 3 Effects of Ultrasound on the Dyeing Process*

The dyeing rate and dye uptake using different dyes were studied at different temperatures with and without ultrasound treatment. The dye diffusion was studied using a diffusion membrane technique. In addition, dye penetration into leather was examined by microscopy. All the results are presented and discussed in this chapter.

- *Chapter 4 Effects of Ultrasound on the Fatliquoring Process*

In Chapter 4, the effects of ultrasound on the behaviour and performance of fatliquor emulsion are reported, including the particle size, penetration and stability of fatliquoring emulsions.

- *Chapter 5 Effects of Ultrasound on the Tanning Process*

Chrome, vegetable and aldehyde were examined under different with and without the application of ultrasound. Shrinkage temperatures (T_s) were determined by differential scanning calorimetry (DSC). The kinetics of these tanning processes were also studied.

- *Chapter 6 Concluding Remarks*

Concluding remarks are presented in this chapter, together with suggestions for future work.

CHAPTER 2

METHODOLOGIES

In this study, the investigation focused on dyeing, fatliquoring and tanning. For each process, the materials, experimental procedures and all the chemical analysis methods are detailed in the relevant individual chapter. In this chapter, the ultrasound unit and the various methodologies used are described.

2.1 EQUIPMENT UNIT

Most of the major experiments, such as those involving dyeing, fatliquoring and tanning were carried out on a laboratory scale experimental unit.

2.1.1 Ultrasonic unit and water bath

The ultrasound unit used for the present study was supplied by Kerry Ultrasonics Ltd and consisted of an ultrasound generator (A) and a submersible transducer (B). The arrangement is shown schematically in Fig. 2.1. The generator (KS375) created the appropriate electronic signals which were transmitted to the transducer (KST360), which transformed them into mechanical vibration and therefore sent out ultrasonic waves. The frequency of this ultrasound unit was fixed at 38 kHz. The transducer was mounted on one side of a 45 litre water bath (C), and leather samples (E) were placed in a reaction vessel (D). A mechanical stirrer driven by a speed-adjustable motor (F) was used in some cases with the vessel. In order to

achieve more efficient transmission of the ultrasonic energy, 1% (w/w) detergent was added to the water bath (C).

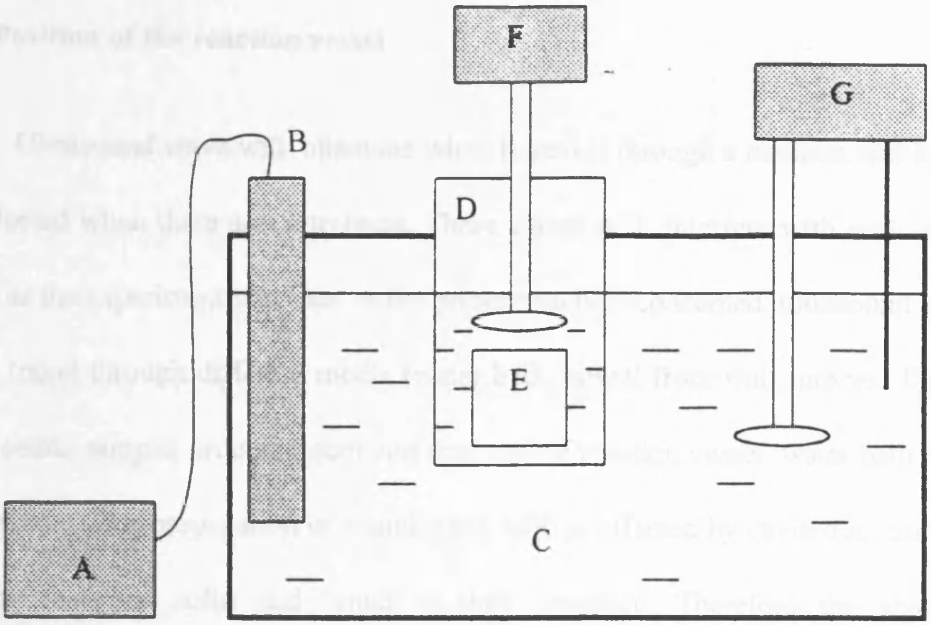
2.1.2 Reaction vessel

As shown in Fig. 2.1, the ultrasound transducer was mounted in the water bath. This bath was too big to be used directly as a reaction vessel and it was necessary to use another smaller container (D) instead. This was in order to save chemicals and protect the transducer from corrosion. In this circumstance, it is clear that the ultrasound energy has to be transmitted through the wall of the reaction vessel in order to reach the sample (E). It was therefore very important to choose the right shape and material for the reaction vessel. It has been found that the geometry and the wall thickness of the reaction vessel have a significant effect on sonochemical reactions [Senapati, 1991]. In order to generate the maximum impact of ultrasound on the reaction, a vessel with a flat surface facing the transducer would be used, which permits a higher energy transmission than a curved surface does. This was confirmed by the work of Mason [1991]. Therefore two cuboid shaped glass containers with sizes of 100×100×100 mm and 100×100×50 mm were used for the present experiments (Fig. 2.2).

The commercial processes of leather making are conducted in large drums. In order to imitate this process, two bench-scale drums were designed. One was made of metal with a size of ϕ200×100 mm and the other was made of glass with a size of ϕ250×100 mm. A schematic diagram of the vessels and drums used is shown in Fig. 2.2.

Fig. 2.1 Schematic illustration of the ultrasound apparatus
A - Ultrasonic generator (KS375) B - Submersible transducer (KST 360)
C - Water bath (containing 1% detergent)
D - Reaction vessel E - Leather sample
F - Stirrer with adjustable speed G - Temperature control unit

Fig. 2.2 Schematic illustration of reaction vessels
H - Two different sized glass containers I - Metal or glass drum



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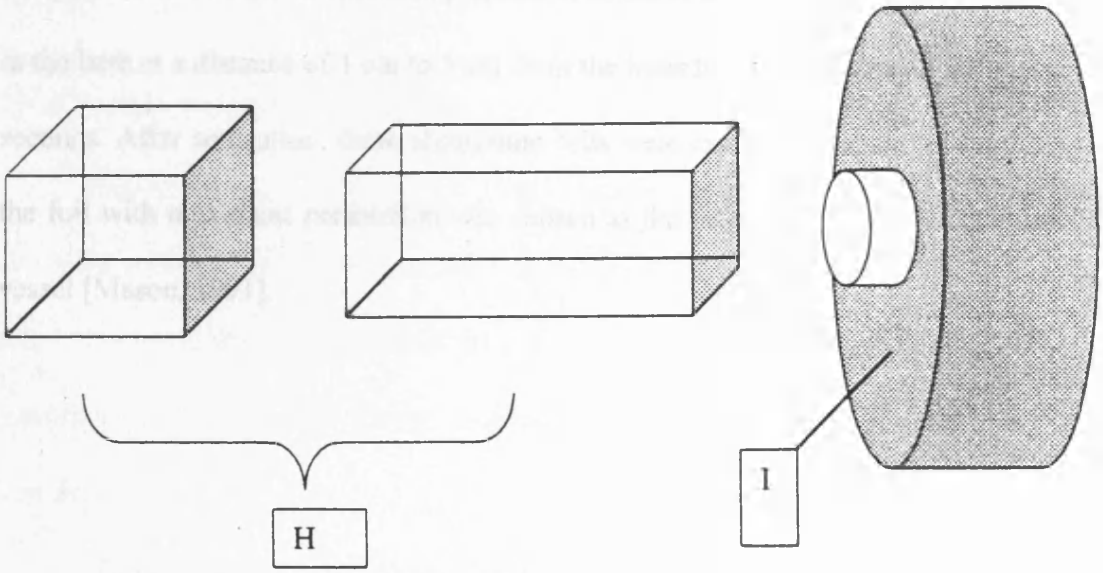


Fig. 2.2 Schematic illustration of reaction vessels
H - Two different sized glass containers I - Metal or glass drum

2.1.3 Position of the reaction vessel

Ultrasound wave will attenuate when it travels through a medium and it will be reflected when there are interfaces. These waves will interfere with each other. As far as the experiment unit used in the present study is concerned, ultrasound wave has to travel through different media (water bath, vessel front wall, process liquor, hide /leather sample, process liquor and rear wall of reaction vessel. water bath *ect.*). Furthermore , the propagation of sound wave will be affected by cavitation and the coupling between solid and liquid at their interface. Therefore the absolute ultrasound intensity in the system and its distribution are very difficult to determine theoreticlly. But the real intensity will be lower than $1.3/cm^2$ (estimated by ultrasound power(700 w) divided by the surface area of transducer (510 cm^2), which is a conventional way to estimate the intensity). Idealy, the intensity should be determined by a calibrated hydrophone placed in the reaction vessel. In the present study, in order to find an optimum position, a series of aluminium foils were placed in the bath at a distance of 1 cm to 5 cm from the transducer and sonicated for 30-60 seconds. After sonication, these aluminium foils were examined and the position of the foil with maximum perforation was chosen as the best place to put the reaction vessel [Mason, 1991].

2.2 INSTRUMENTAL METHODS

2.2.1 Ultraviolet (UV)/Visible spectrophotometry

The chromium content, tannin content and dye concentration were determined by UV/visible spectrophotometry. The principle of this method is based on Lambert-Beer law, which shows that absorbance (A) is directly proportional to concentration for a dilute solution.

Two different types of UV spectrophotometer were used in experiments. For an unknown sample, the first scan was conducted on a PYE unicam SP6-160 UV spectrophotometer with a quartz cell to obtain a full spectrum in the UV and visible ranges. Once the characteristic peak was determined, the subsequent testing and calibration of this sample were conducted on a Spectronic 501 UV spectrophotometer.

The data obtained from UV spectrophotometers was used to characterise the kinetics of tanning and dyeing.

2.2.2 Atomic absorption spectroscopy (AA)

The chromium content in the leather sample was normally determined by a chemical analysis method (the details will be presented in chapter 5). However, in order to confirm the results obtained from such a measurement, an atomic absorption spectrometer (Pye unicam atomic absorption spectrophotometer model SP-2900) was used.

When heated to a sufficiently high temperature, most compounds break apart into atoms in the gaseous phase. Such atomisation is usually accomplished with a flame or furnace in atomic spectroscopy. If the frequency of incident radiation from

the source is exactly equal to the frequency of the first resonance line of the free analyte atoms, the transitions from the ground state to the first excited state occur. Part of the energy of the incident radiation is absorbed. AA spectroscopy is based on this principle and measures the absorption of radiant energy associated with this transition [Willard, 1988]. According to the established theory [Qinhu, 1983], the absorbance (A) of atoms can be expressed as follows;

$$A = 0.4343 \frac{2\lambda^2}{\Delta\lambda_D} \sqrt{\frac{\ln 2}{\pi}} \frac{\pi e^2}{mc^2} n f_\lambda l \qquad (2\text{-}1)$$

where, m is the mass of electron, e is the charge of electron, c is the speed of light, f is the intensity of absorption line at given wavelength λ, l is a constant at given wavelength, n is the concentration of the ground state atoms and $\Delta\lambda_D$. is the difference of wavelength in Doppler state Obviously there is a linear relationship between A and n; therefore the concentration of analyte atom can be obtained easily according to the A value.

Before testing, the calibration curve was established by using chromium nitrate aqueous solution with known concentrations (5-20 ppm). Samples had to be diluted with distilled water in a volumetric flask (the concentration in the range 5-20 ppm) and directly aspirated into the atomic absorption flame. The chromium content was then measured at a wavelength of 360 nm.

2.2.3 Particle size analysis

The particle sizes of fatliquor emulsions and Mimosa liquors were measured by a sub-micro particle analyser (Coulter Model N4MD with size distribution processor analysis, located in the BLC laboratories). Multiple scattering angle detection was employed to measure the particle size of samples.

The principle of this method is based on the Brownian motion theory and photon correlation spectroscopy (PCS) [Coulter Model N4MD instruction]. When the random collision of particles occurs in solution, it causes suspended particles to diffuse through the solution and the diffusion coefficient (D) can be expressed by equation (2-2):

$$D = \frac{K_b T}{3\pi \eta d} \qquad (2\text{-}2)$$

where D is diffusion coefficient, K_b is Boltzmann's Constant, T is absolute temperature, η is viscosity of the solvent and d is the equivalent spherical hydrodynamic diameter of particles.

From the above equation, it is clear that particle size (d) can be easily determined when the diffusion coefficient (D) is known. D can be determined by the following equation [Braithwaite, 1977; Zhou, 1991]:

$$R(t) = 1 + e^{-2DK^2t} \qquad (2\text{-}3)$$

where $R(t)$ is the autocorrelation function. Therefore the diffusion coefficient (D) can be obtained from equation (2-3) when the relationship between $R(t)$ and t is experimentally determined. K is the experimental constant which is dependent on the wavelength of scattered light and the angle between incident and scattered light. This angle was fixed at 90° in the present study.

The particles undergoing Brownian motion are detected and sized by illuminating the particles with a laser beam and measuring the scattered light with a photomultiplier.

2.2.4 Differential scanning calorimetry (DSC)

Differential scanning calorimetry is a thermal analysis technique in which differences in heat flow into a sample and a reference are measured as a function of the temperature of the sample while the two are subjected to a controlled temperature programme. DSC can be used to follow phase changes or conformational transitions. Many useful characteristics of reactions can be obtained from DSC measurement. Thermodynamic parameters during the phase transition, e.g., T_g (glass transition temperature), T_m (melting temperature) and enthalpy change, can be determined from DSC. In the present study, DSC was used as one of the methods to determine the shrinkage temperature of leather samples.

The shrinkage temperature (T_s) of collagen is a characteristic property. It has been established that this hydrothermal shrinkage is the result of melting or fusion of the crystalline regions in the collagen molecule [Wohlisch, 1932; Wiederhorn 1951]. Support for this view was also provided by Astbury [1940] who observed that the characteristic X-ray diffraction pattern of crystalline collagen disappeared on shrinkage. Witnauer and Wisnewski [1964] were the first to study the thermal behaviour of collagen and leather by applying differential thermal analysis (DTA). They found that T_m from the DTA thermogram has a good correlation with T_s measured by a conventional method. Since their pioneering work, DSC has been widely used to study the thermal denaturation of hide and leather by many researchers [Privalov, 1970; Naghski, 1966; Takenochi, 1995; Covington, 1989; Komanowsky, 1991 and 1992].

The advantage of the DSC method is that both melting temperature and enthalpy change (ΔH) can be obtained in one test and only a very small amount of sample is

required. Furthermore, because the melting or shrinkage phenomenon of hide and leather is a first order phase transition [Bienkiewicz, p243], the change of Gibbs free energy (ΔG) at the transition point is equal to zero, i.e.:

$$\Delta G = \Delta H - T_m \Delta S = 0 \qquad (2\text{-}4)$$

Therefore:

$$T_m = \frac{\Delta H}{\Delta S} \qquad (2\text{-}5)$$

where ΔS is the entropy change and T_m is the melting temperature in Kelvin. Thus, the entropy change can be calculated from equation (2-5).

In the present study, a computer controlled DSC (Mettler TC 10A, located in the laboratories of the BLC Leather Technology Centre) was used to measure the shrinkage temperature of tanned leather. A 5~10 mg sample of wet leather sample was mounted into a sample pan and sealed with the lid. After sealing, the sample pan was placed in the heating chamber and heated through the appropriate temperature range (20-130°C) at a heating rate of 5°C per minute. After testing, all the samples were dried and weighed to determine the enthalpy. Fig. 2.3 is a typical DSC thermogram and several important temperatures can be defined, i.e., onset temperature, peak temperature and extrapolated onset temperature. In this work, the onset temperature (the temperature at which the slope of the thermogram first departs from the base line) was taken as the shrinkage temperature [Naghski, 1966].

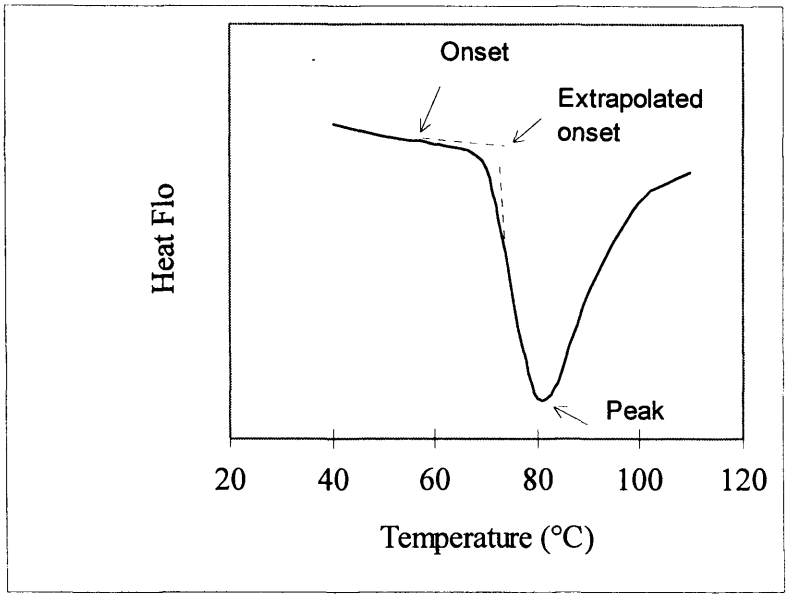


Fig. 2.3 DSC thermogram of sheepskin (tanned by aldehyde)

2.2.6 Scanning electron microscopy (SEM)

When an electron collides with the surface of a conducting material a secondary electron is emitted from the sample. This is the basic principle behind scanning electron microscopy where a fine beam of electrons is scanned across the surface of the sample. The electrons emitted after the sample has been exposed to the scanning beam are used to provide a signal which is used to modulate the intensity of an electron beam in a cathode ray tube, the beam of which is synchronous with the sample scanning beam. This produces an image of the sample [Billmeyer, 1984].

A Hitachi model S-2500 microscope was used to examine the morphologies of samples after chrome-tanning with and without ultrasound. Specimens for SEM were fixed onto an aluminium stub and sputtered with gold. All the micrographs were analysed in a computer with an ISIS software.

2.2.6 Viscosity

The viscosities of fatliquor emulsions and Mimosa liquors before and after ultrasound treatment were measured by using a Brookfield DV-III cone-on-plate rheometer, shown schematically in Fig. 2.4. The plate is stationary and the cone rotates at a certain angular velocity. The shear stress, shear rate and viscosity can be automatically calculated via the following equations. This was done with the associated software (Rheocalc):

$$Viscosity\ (cP) = \frac{Shear\ stress}{Shear\ rate} \qquad (2\text{-}6)$$

Where

$$Shear\ stress\ (dynes/cm^2) = \frac{T}{\frac{2}{3}\pi\ r^3} \qquad (2\text{-}7)$$

$$Shear\ rates\ (sec^{-1}) = \omega\ /\ sin\theta \qquad (2\text{-}8)$$

where T is full scale torque (dynes·cm), r is cone radius (cm), ω is angular velocity of cone (rad/sec) and θ is cone angle (degree).

Different concentrations of fatliquor emulsion were prepared at room temperature. Their viscosities were tested at 20, 30 and 40°C with different shear rates.

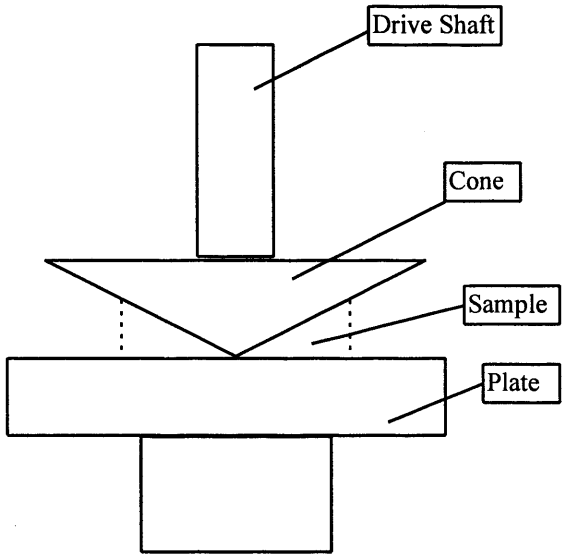


Fig. 2.4 Schematic representation of the cone-on-plate rheometer [Brookfield]

CHAPTER 3

EFFECTS OF ULTRASOUND ON THE DYEING PROCESS

3.1 INTRODUCTION

Dyeing is one of the most important processes for the final appearance of leather. The dyeing process greatly depends on the properties of hide and skin, as well as the tanning process used. Tanned leather can be dyed in various ways according to the desired characteristics of the end products. For some products, thorough dyeing is required, i.e., the dye must penetrate evenly through the leather. However for some other products, e.g., shoe uppers, a surface dyeing only may satisfy the end use. It has been found that it is almost impossible to thoroughly dye leather with a thickness over 3 mm without using high quality dyestuffs or high temperature and longer dyeing times. It has been known for some time that higher molecular mass dyestuffs could achieve a better colour fastness for leather but they normally have a poor water solubility and large particle size.

As reviewed before, ultrasound could enhance the dyeing rates and improve the dyestuff's solubility and the dye penetration in the dyeing of textile fibre or fabric [Junger, 1957; Thakore,1988-1990 and Saligram, 1993]. It was expected that the application of ultrasound in the leather dyeing process could be beneficial in all these aspects. The dyeing time might be shortened and the dyeing temperature might be reduced, so the overall energy input would be lower. In addition, the dye penetration could be improved. In this chapter the application of ultrasound in the dyeing process will be systematically discussed and the mechanism of the ultrasonic

effects on dyeing will be explained. In the present study, five different dyestuffs were employed in the dyeing of four different types of leather samples. All experiments were carried out in the apparatus shown schematically in Fig. 2.1 and 2.2. The concentrations of dye solution, the dyeing time and the temperature were selected as variable factors in a comparison of the ultrasonic and non-ultrasonic processes. This chapter includes the following sections: a brief description of the nature of leather and the properties of the dyestuffs which were used, the experimental detail and finally the experimental results and discussions.

3.1.1 Nature of the leather

Leather consists of a three-dimensional network of collagen fibres. Its structure is quite different from that of textile fabrics in terms of fibre weave. The density of fibre assembly in leather shows an increasing gradient from flesh to grain layers, resulting in a difference in dye affinity between these two sides. In addition the leather properties also vary due to differences in species, breed, living conditions of the animals. Different areas within the same hide or skin also have different properties. All these factors will affect dyeing and the quality of dyed leathers. These are the reasons why leather is one of the most difficult substrates to dye [Eitel, 1984].

3.1.2 Dyestuffs used in leather dyeing

A great number of dyestuffs have been used in leather dyeing to produce different characteristics in various products. The dyestuffs used in the leather industry include acid, direct, pre-metallised, mordant, disperse and reactive dyes. Among these dyes, acid dye is the most commonly used in leather dyeing; some

80% of leather dyes belong to this class [Knapton and Nursten, 1976]. Acid dyes normally have a good water solubility and can be used either for penetration or as a surface only dye, but they have a poor wet fastness. They have very wide suitability for different types of leather and sometimes they are applied together with direct dyes. Direct dyes are used on chrome-tanned leather for surface dyeing but they give poor yield on vegetable-tanned materials. Pre-metallised dyes are often used when high fastness is required or for special requirements. Normally they are not applied as a main component in leather dyeing because of their high cost. Mordant, disperse and reactive dyes only have limited uses in leather dyeing, but reactive dyes are developing rapidly and could offer a very good wet-fastness. Reactive dyes have been widely used in some special cases, such as washable gloving and clothing leather.

3.1.3 The mechanism of leather dyeing

In leather dyeing as in the dyeing of textile fibres, the interaction between leather fibres and dye molecules can be divided into the following categories, i.e., electrostatic attraction, van der Waals forces, hydrogen bonds and hydrophobic interaction [Rys, 1989 and Bienkiewicz, 1983, p454]. However, in comparison with textile fibre dyeing, leather dyeing has its own specific features that can be summarised as follows [Dasgupta, 1975].

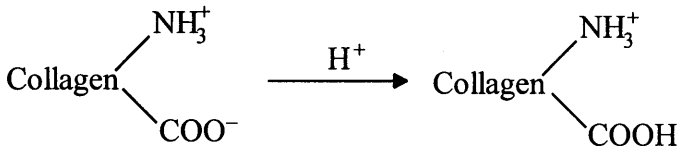
(1) Textile dyeing normally uses high temperatures to speed up the process. However, due to the susceptibility of tanned collagen fibres to denaturation at high temperature, leather is dyed at a much lower temperature, making the process more time-consuming and difficult.

(2) The tanning process normally imparts an initial colour to leather, e.g., pale blue for chrome-tanned leather. This should be taken into account in the dyeing process and at the stage of product design.

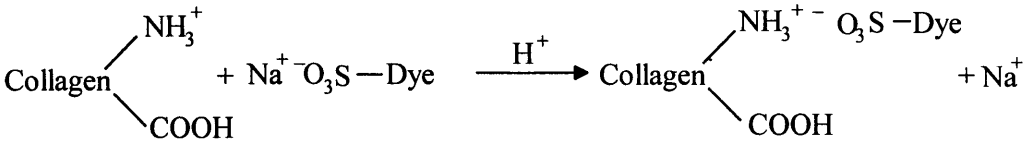
(3) Leather to be dyed contains an abundance of foreign matter (e.g., tanning agents, fats, surfactants, sugars, phenols) which may possibly react with dyestuffs. All these factors make leather dyeing unique in comparison with dyeing of other protein fibres.

As described above, leather is essentially composed of collagen fibres. Like most polypeptide fibres such as silk and wool, collagen fibres contain functional groups in the side chains, e.g., amino and carboxyl groups. These groups play a very important role in leather dyeing. They can form strong chemical and physical interactions with the dye molecules, such as a covalent bond, a hydrogen bond or an ionic bond, thus offering the dyed leather some colour fastness. On the other hand, the isoelectric point (I.P.) of collagen is another factor which has to be considered. The values of I.P. vary from one product to another depending on the properties of raw materials and tannage. The I.P. of the chrome-tanned leather is in the range of 6.0-7.0, whilst that of the vegetable tanned leather is 3.2-4.0 and that of aldehyde/oil tanned leather is 4.5 [Heidemann, 1993]. It is essential to ensure that dyestuff and leather have opposite charges in the fixation. For example, vegetable-tanned leather has negative surface charges at pH ~ 5, so the collagen fibres in the leather have a strong electrostatic attraction to cationic dyestuffs. In contrast to vegetable-tanned leather, chrome-tanned leather has a predominantly positive charge, so it hardly binds to cationic dyestuffs but readily reacts with anionic dyes instead.

When leather dyeing is carried out in an acidic medium with an acid dye, the interaction between sulfonic groups in the dye and amino groups in the collagen fibre can be simplified as follows [Han, 1990, p 224].



Scheme 3.1



Scheme 3.2

However for chrome tanned leather, the fibres have quite a high level of positive charge before dyeing because tanning is normally conducted in an acidic medium. Therefore the process shown in **Scheme 3.1** becomes unnecessary. On the contrary, chrome tanned leather is first treated with alkali rather than acid to partially neutralise the excess positive charges on the collagen fibres. The purpose of this pre-treatment is to slow down the fast reaction between dye and leather shown in **Scheme 3.2**, thus allowing dye molecules to penetrate deeply into the leather inner layer. Otherwise, in the initial stage of the dyeing process, a concentrated layer of dye will be formed on the surface of leather. This layer could be a barrier for the further penetration of dye molecules into the inner layers of the leather, so it is necessary to reduce the affinity of the dyestuff to the leather in the initial stage of the dyeing process. This is realised by a pre-neutralising treatment. Most commonly used neutralising agents include sodium bicarbonate, ammonium bicarbonate, borax,

etc. Following treatment by these salts, the pH of the leather will increase from its initial level of 3.5~4.0 to the required level of 6.0~6.5, at which the leather is ready to be dyed. When the charges on the leather and dyestuff, after dissociation, are the same, the dyestuff is bound very weakly to leather, as only the secondary forces (van der Waals forces) are participating in the bonding [Bienkiewicz, 1983], and the dye molecules may easily penetrate into the inner layers of leather. When the penetration reaches the desired level, weak acid is added to lower the pH value and this leads to the fixation of dyes firmly onto the collagen fibres.

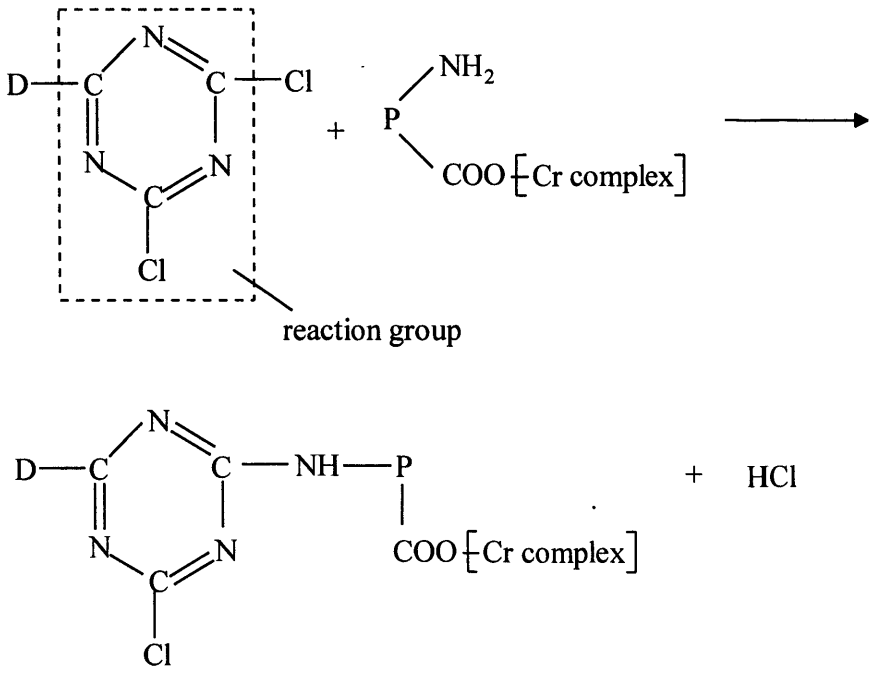
Another dye used in the present study was a reactive dye. The structure of a reactive dye molecule may be divided into two parts, i.e., a chromophore and a functional group. The reactive functional groups can form strong covalent bonds with collagen fibres and so offer an excellent wash fastness for the end products [Dasgupta, 1976]. The chromophore also contains ionic groups which help to make the dyestuff water soluble.

A typical reaction between a reactive dye and chrome-tanned leather is shown in **Scheme 3.3**.

3.2 MATERIALS

3.2.1 Leather samples

Four different leather samples were used in the dyeing process. They are listed in Table 3.1



(D: chromephore group of dye, P: polypeptide chain of collagen)

Scheme 3.3 Reaction of chrome-tanned leather with reactive dye [Han, 1990]

Table 3.1 Leather Samples

Sample No.	Name	Specifications	Supplier
1	Retanned sheepskin*	Chrome pretanned and Mimosa retanned	British School of Leather Technology (BSLT) tannery
2	Rewetted wet-blue or wet-blue (from bovine hide)	Chrome tanned	Garston and Highfield Leathers Ltd, Liverpool, UK
3	Crust leather (from bovine hide)	Wet-blue fatliquored using Remsynol ESI	BSLT tannery
4	Resin retanned leather	Chrome tannage combined with an acrylate resin retannage	BSLT tannery

* Detail see Appendix I

3.2.2 Dyestuffs and other chemicals

Two different classes of dyestuffs (i.e., acid and reactive dyes) were used in the dyeing process. Their properties are listed in Table 3.2. The pH indicators and neutralising agents used are listed below.

(1) pH indicator: Bromocresol Green (colour change at pH 3.6-5.2)

(2) pH indicator: Bromocresol Purple (colour change at pH 5.2-6.8)

(3) pH indicator: Bromophenol Blue (colour change at pH 2.9-4.2)

(4) Sodium formate (purity > 97%), East Anglia Chemicals.

(5) Sodium bicarbonate (purity > 97%), Timstar Laboratory Suppliers Ltd.

3.3 EXPERIMENTAL

3.3.1 Dyeing Processes

3.3.1.1 Dyeing of leather samples

As described before, the pH of wet-blue leathers ranges from 3 to 3.5, much lower than the pH required for dyeing. All the samples were therefore neutralised before dyeing. In the present study, two different neutralising solutions were prepared. The first one was composed of 1% sodium bicarbonate (based on the wet weight of leather) and 2% sodium formate and the second one was composed of 2% sodium bicarbonate only. All samples were neutralised for 2 hours at 35°C in a rotating flask. The progress of neutralisation was monitored by regularly checking the pH over the cross-section of the leather using Bromocresol green and Bromocresol purple as pH indicators. The neutralisation continued until the final pH of the samples reached

Table 3.2 The dyestuffs used in the dyeing process

Dyestuff	Colour Index	Chemical Class	Molecule weight	Penetration	Solubility Rating	Light fastness	Perspiration resistance	Washing fastness	Water fastness	Supplier
Airedale Brown 3RG	Acid Brown 80	monosulfonated disazo	573-613	2-3	3	3-4	4-5 4 4-5	5 5 3	4 4 4-5	Yorkshire Chem.
Airedale Brown ER	Acid Brown 75	disulfonated trisazo	637	2	4	4	3-4 1			Yorkshire Chem.
Airedale Brown DS	Acid Brown 73	disulfonated trisazo	626	4	1	4-5	4 4 2-3	3 4 2-3	3 2 3-4	Yorkshire Chem.
Airedale Black E793	Acid Black 210	trisazo	859	3-4	-	1-2	/	3-4 - -	2-3 2-3 2	Yorkshire Chem.
Procion Blue MX-7RX	Reactive Blue 161	phenazine	/	2-3	110 g/l	3-4	5 5 5	5 5 5	5 5 5	ICI Fine Chem.

Numerical rating scale: 1 - poor or low, 5 - good or high

6.0~6.5. The pH distribution over the cross-section is very critical for the even penetration of dyestuff. So the neutralisation and pH checking continued until an even pH distribution over the leather cross-section was reached. Of the above two neutralisation solutions, the first one gave a good neutralisation over the whole cross-section of the leather whereas the second one could only give a sandwich neutralisation, i.e. the pH in the surface was about 6 but in the inner layers was still around 4. So the first neutralisation solution was selected and used for all the samples in the experiment.

Dyeing was carried out with and without ultrasound at different temperatures. In order to make the results from the dyeing experiments with and without ultrasound comparable, all the samples were cut with a standard die from the same part of the original leather samples supplied. All the samples were rewetted in distilled water for 12 hours and the excess water was removed by a dry tissue. Dye solutions of different concentrations were prepared for use in the dyeing vessel (a metal drum or a glass container). In accordance with the practice adopted by the leather industry, the amount of chemical used is expressed as the weight percentage of wet hides or leathers. When the glass container was used as a dyeing vessel, two different concentrations were used: one was 4% dyestuff and 1500% water; the other was 6% dyestuff and 1500% water. The samples (typically, 10-20 g) were dyed at 30, 50 and 60°C respectively. In the metal drum only one concentration (4% dyestuff and 200% water) and two different temperatures (25 and 40°C) were used.

Dyeing processes were also investigated in three different modes when ultrasonic irradiation was applied. These were:

1. for a one hour dyeing process, the ultrasound was applied in either the first 20 minutes or the last 20 minutes of the dyeing process,
2. dyeing processes were carried out with mechanical stirring in the presence or absence of ultrasound,
3. dyeing processes were conducted in a glass vessel or a metal drum in the presence or absence of ultrasound

3.3.1.2 Dyeing of chrome tanned hide powder

Besides the above leather samples, some chrome-tanned leather powders were also dyed with and without ultrasound. The leather powders were neutralised for 60 minutes with 2% sodium bicarbonate before dyeing at 30°C. The final pH was about 6.0-6.5. The neutralised powders were then squeezed with a dry nylon cloth to remove excess water. After that, 20 g of the wet powder was transferred into the dyeing vessel containing a dyeing solution of 3 g dm^{-3} concentration. The dyeing process was carried out at 25 and 40°C with and without ultrasound. Changes of the dye concentration in the dyeing bath were monitored by using a UV/visible spectrophotometer.

3.3.2 Determination of dye uptake

Dye uptake was determined on the basis of dye consumption in the dyeing bath. When the initial concentration and the concentration in the dyeing bath at a certain time are known, the dye uptake can be worked out from equation (3-1).

$$W_t = \frac{C_0 V_0 - C_t V_t}{G_0} (\%) \qquad (3\text{-}1)$$

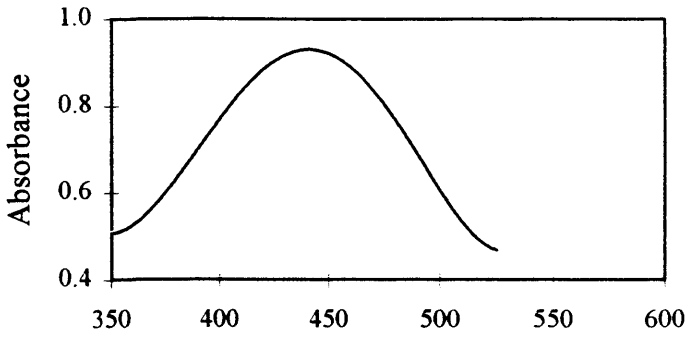
where W_t is dye uptake of leather expressed as milligram of dyestuff per gram of the wet leather (mg/g), C_0 and C_t are the initial concentration of dye solution and the

concentration at time *t* respectively, V_0 and V_t are the volumes of dye solution at the initial and time *t* respectively and G_0 is the weight of the wet sample.

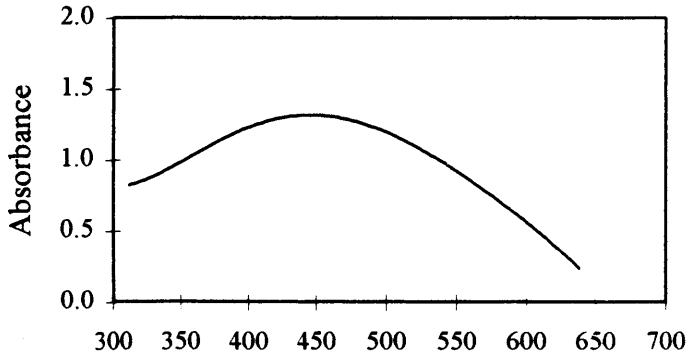
C_0 and C_t were determined by the following procedure. 1 mL of dye solution was taken out regularly from the dyeing bath and diluted by 50 times with distilled water for measuring absorbance at a wavelength with maximum absorption using a UV/visible spectrophotometer. The wavelength at which maximum absorption occurs for each dye is listed in Table 3.3 (spectra are shown in Fig. 3.1a-f). Concentrations were then determined from a concentration-absorbance calibration curve. The calibration curves shown in Fig. 3.2a-f were constructed by measuring the absorbance of a series of dye solutions with known concentrations.

Table 3.3 Wavelengths of maximum absorption for the dyes used

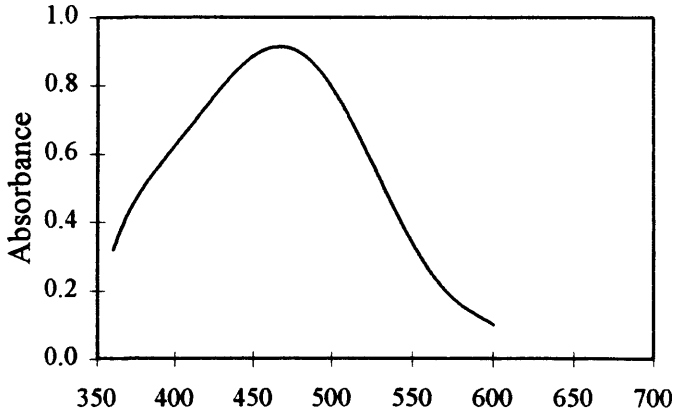
Dyestuff	Wavelength (nm)
Airedale brown, 3RG	443
Airedale brown, DS	474
Airedale brown ER	428
Airedale black, E793	459
Procion blue, MX-7RX	577



a. Airedale brown 3RG

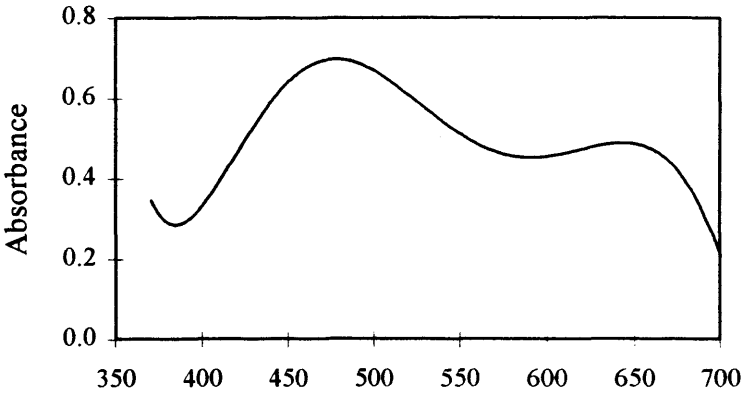


b. Airedale brown ER

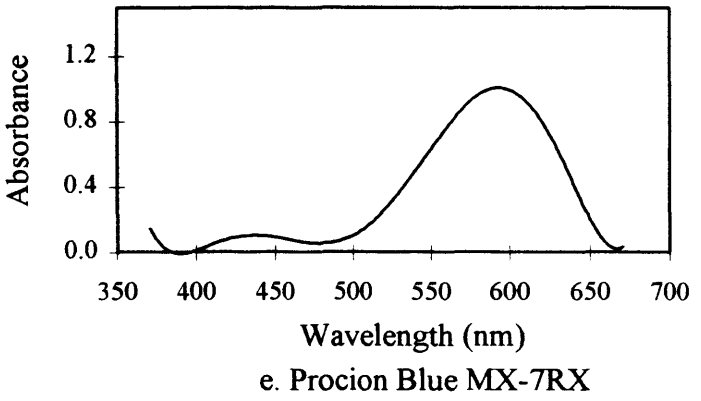


c. Airedale brown DS

Fig. 3.1 UV/visible spectra of dyestuffs

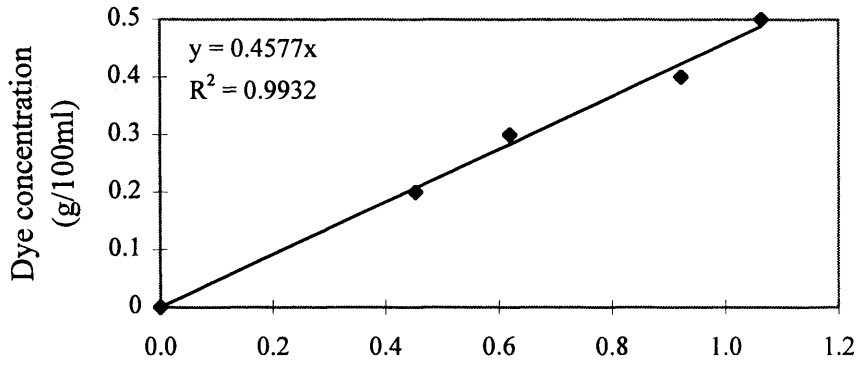


d. Airedale black E793

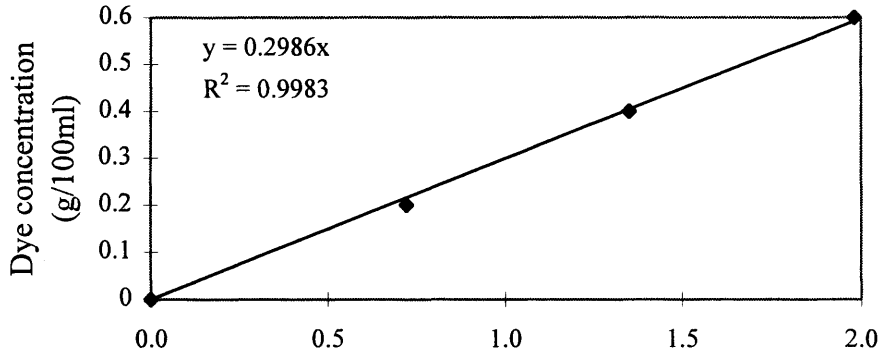


e. Procion Blue MX-7RX

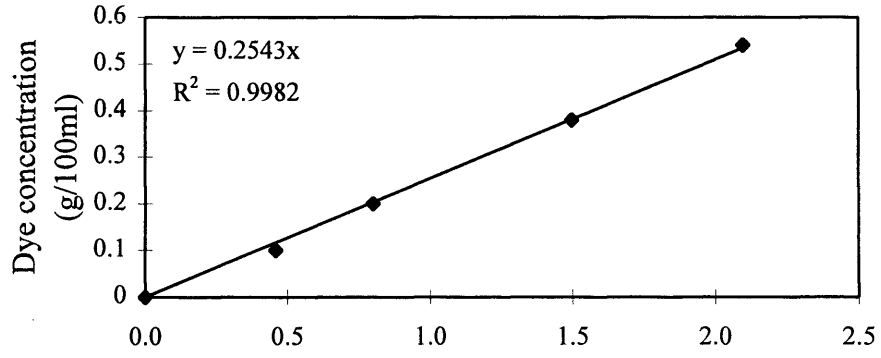
Fig. 3.1 UV/visible spectra of dyestuffs



(a) Airedale brown 3RG

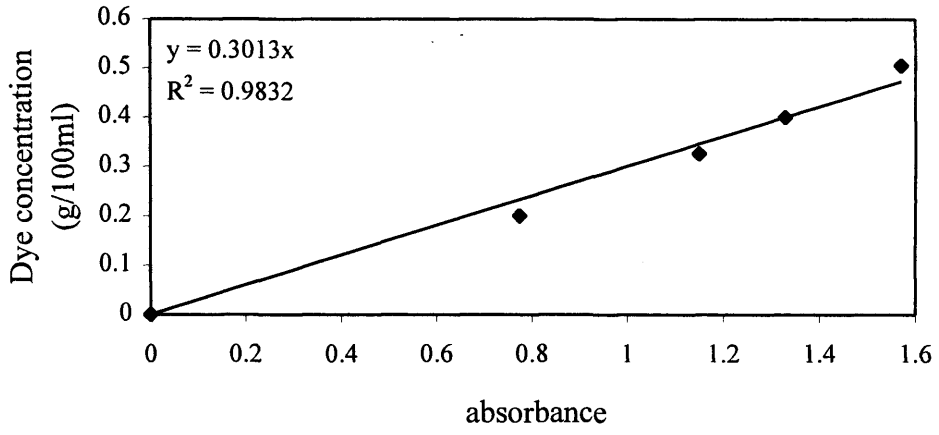


(b) Airedale brown ER

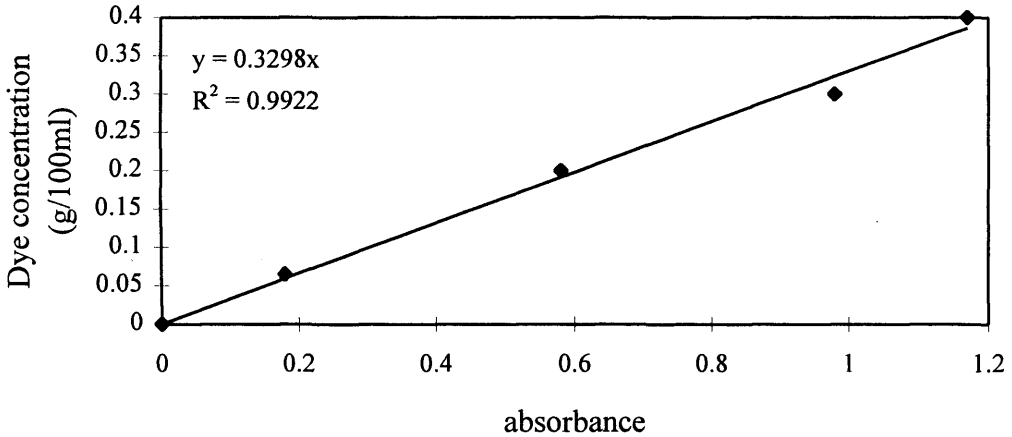


(c) Aireadale brown DS

Fig. 3.2 The relationship of dye concentration to absorbance



(d) Airedale black E793

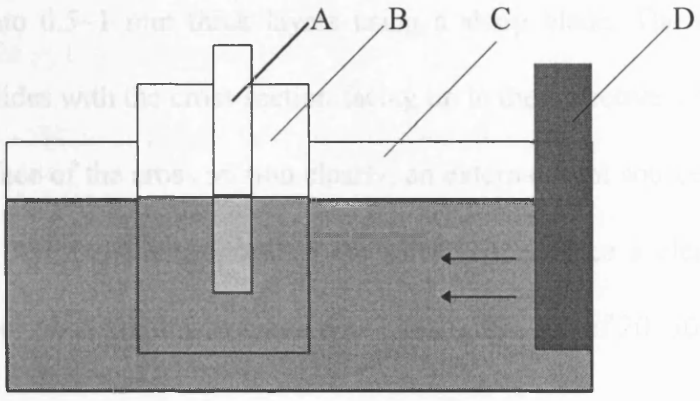


(e) Procion MX-7RX

Fig. 3.2 The relationship of dye concentration with UV absorbance

3.3.3 Dye diffusion through a cellophane membrane

Diffusion is one of the most important factors affecting the leather dyeing process. In order to study the effect of ultrasonic irradiation on dye diffusion, the diffusion coefficient was measured using Barrer's method [Vickerstaff, 1957, p97] The apparatus is illustrated schematically in Fig. 3.3. The experiments were carried out with and without ultrasonic irradiation.



A- dialysis tubing (cellophane) B dyeing vessel

C- water bath D ultrasound transducer

Fig. 3.3 The membrane diffusion apparatus

A tubular dialysis membrane (A) made by Visking (Medicell International Ltd) was used as a diffusion membrane in which one end was sealed with a clip and the other was kept open. The tubing (ϕ19×80 mm) was filled with 20 mL distilled water. The water-filled tubing was then immersed into a dyeing vessel (B) which contained 300 mL dye solution with a concentration of 3 g dm^{-3}. The liquid levels inside and outside the tubing were kept the same all the time during the course of diffusion. The temperature of the dyeing bath was kept at either 25 or 40°C. The

concentration changes inside the tubing during the diffusion were measured by UV/visible spectrophotometry at different time intervals. The kinetics of dye diffusion with and without ultrasound were studied. The diffusion coefficient (D) was also calculated.

3.3.4 Dye penetration

The degree of dye penetration in dyed leather samples was examined using an optical microscope (Olympus 796069). The dyed samples were cut through their cross section into 0.5~1 mm thick layers using a sharp blade. The samples were mounted onto slides with the cross section facing up to the objective lens. In order to observe the surface of the cross section clearly, an external light source was directed at the samples. A camera was fixed on the microscope. Once a clear image was obtained, a colour photograph was taken with a magnification of 20~30.

3.3.5 Testing for rub fastness

Rub fastness of dyed samples was determined by a rub fastness tester (STM 461, SATRA Footwear Technology Centre). Samples were cut into a size of approximately 25×4 cm. There are two different rub fastness tests, i.e., dry and wet rub fastness test. For the dry rub fastness test, the dyed sample was placed on the testing plate and clamped around the edge of the sample. A dry felt pad was placed on the top of the sample with a 2.5 Kg load. Then the sample was rubbed with the stated number of revolutions, 128, 256, 512 or 1024. Each rubbing was carried out by using a new pad in a new position of the sample. After testing, each of the pads was cut in half. One half was reversed and mounted together with the other half on a black card for visual assessment. Grey Scale was used to compare the staining on the

side of the half pads with the reverse unstained side. Changes in visual appearance of the tested leather samples at different number of revolutions, with and without ultrasound, were noted [Official method SLF 5].

The procedure for the wet rub fastness test was similar, except that the pad was boiled in water to moisten it fully before the test, and the pre-load was 0.73 Kg.

3.4 RESULTS AND DISCUSSION

3.4.1 Dye uptake and dyeing rate

The four different leather samples (Table 3.1) were dyed with and without ultrasound at various temperatures. Five different dyes were used (Table 3.2). The dyeing rate was studied at different dye concentrations and at different temperatures. The protocol for ultrasound application was also varied

3.4.1.1 Effect of temperature

Dyeing rate and dye uptake was studied at 30, 50 and 60°C. In each case two parallel experiments were carried out, i.e. with and without ultrasonic irradiation.

Plots of dye uptake against dyeing time are shown in Figs 3.4-9: a significant increase in dye uptake can be seen when power ultrasound (ULT) was applied.

In all cases, dyeing rates in the initial stages (i.e., the initial 10 minutes) are the fastest in any process. This is because, in the beginning, the dye concentration gradient between the leather sample and dyeing bath is the highest, and so the dyeing rate will be very fast at that time. As the dyeing process proceeds, the concentration gradient will reduce gradually and the dyeing rate would also be reduced accordingly. Another factor responsible for this slow-down in dyeing rate

might be the change in the charge difference between dye molecules and leather fibres. Although the leather samples were neutralised before dyeing, there was still a certain degree of difference in pH between the leather fibres and the dye solution. As the dyeing process proceeds, dye molecules penetrate gradually into the leather fibres, the pH in the dye bath and the leather becomes more and more closely matched and the reaction between the dye molecules and the leather fibre slows down.

It is also apparent that the effect of ultrasound on the dyeing process depends on the dyeing temperature. Figs. 3.10 and 11 show plots of the dye uptake ratio (dye uptake with ultrasound to dye uptake without ultrasound) against dyeing time. For the samples prepared from sheepskin, higher temperature makes the ultrasonic process more effective in respect of the relative increase of dye uptake (Fig. 3.10). For the rewetted wet-blue leather made from bovine hide, a reverse temperature effect was observed (Fig. 3.11). This may be due to the difference between both the tanning process and the structure of these two samples. Firstly, because mimosa retanned sheepskin had less affinity for the acid dye, the dye molecules more easily penetrated deep inside the leather. In addition, sheepskin has a more loose fibre structure than bovine wet-blue leather. In other words, the activation energy for the penetration for bovine wet-blue leather is higher than that for the mimosa retanned sheepskin. This means that temperature will have a greater effect on the rate of dyeing for the wet-blue leather than for the retanned sheepskin. Thus, when dyeing at a higher temperature for the bovine wet-blue leather, the effect of ultrasound becomes less predominant..

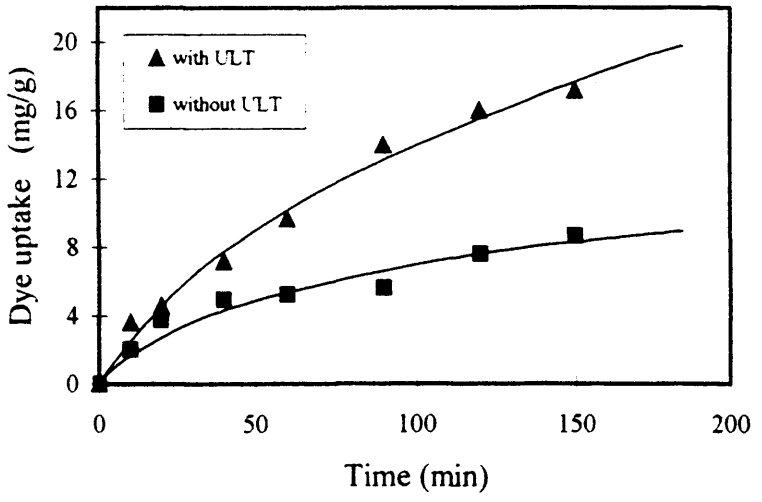


Fig. 3. 4 Effect of ultrasound on dye uptake of retanned sheep skin at 30°C (Airedale brown 3RG)

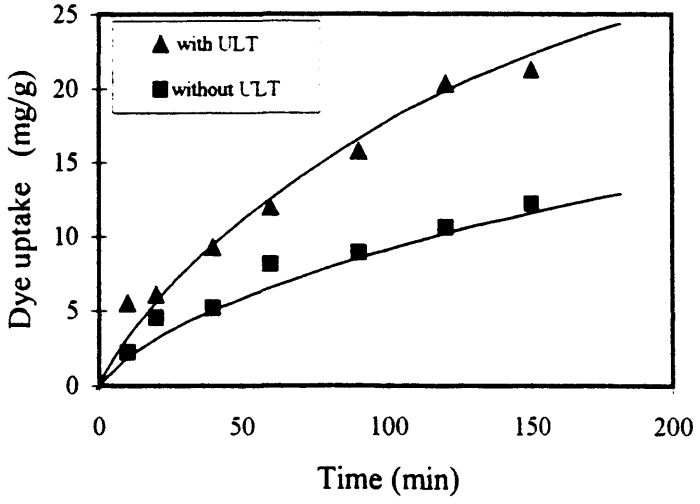


Fig.3.5 Effect of ultrasound on dye uptake of retanned sheepskin at 50°C (Airedale brown 3RG)

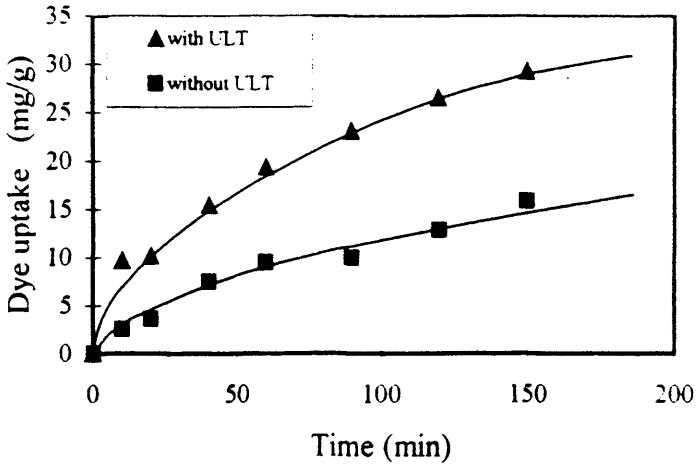


Fig. 3.6 Effect of ultrasound on dye uptake of retanned sheepskin at 60°C (Airedale brown 3RG)

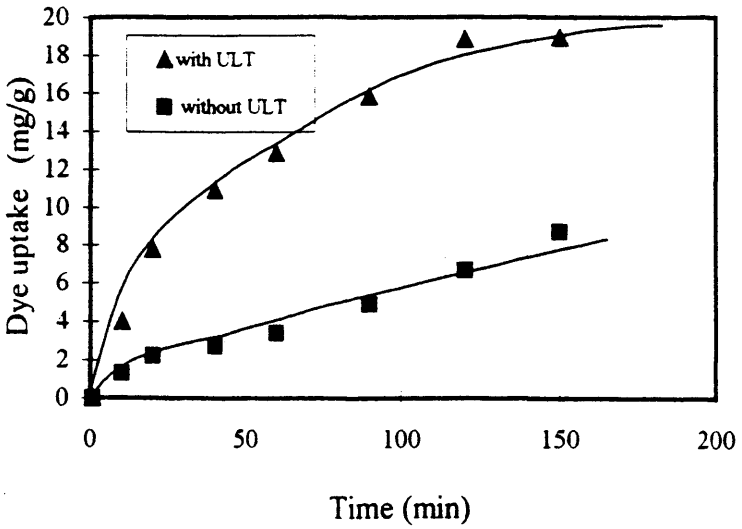


Fig. 3. 7 Effect of ultrasound on dye uptake of rewetted wet-blue leather at 30°C (Airedale brown 3RG)

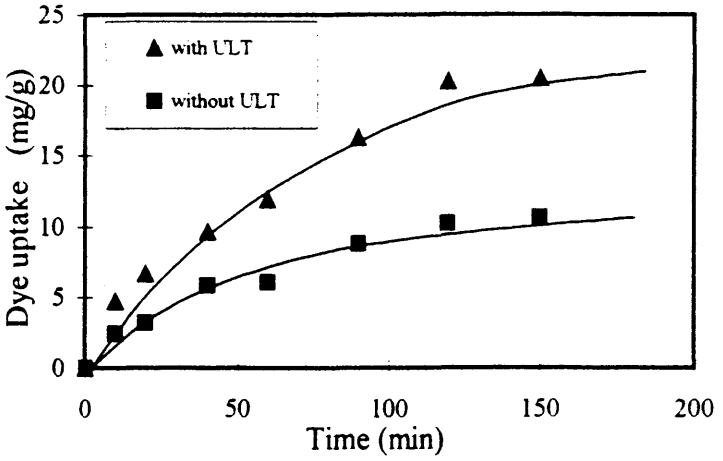


Fig. 3.8 Effect of ultrasound on dye uptake of rewetted wet-blue leather at 50°C (Airedale brown 3RG)

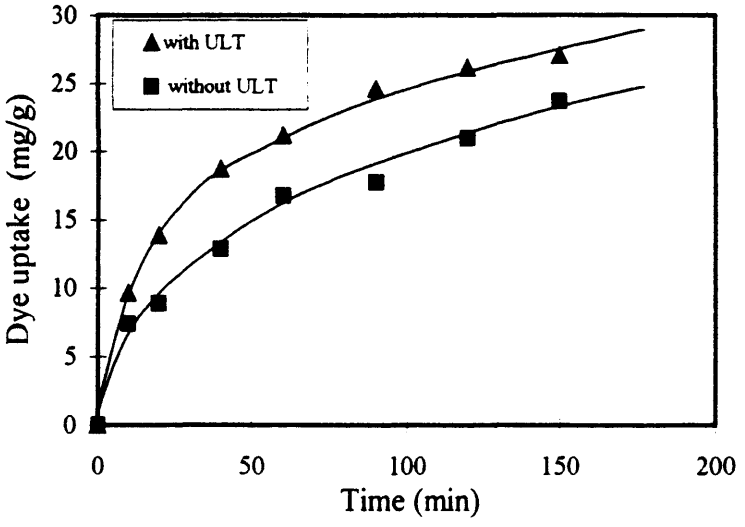


Fig. 3. 9 Effect of ultrasound on dye uptake of rewetted wet-blue leather at 60°C (Airedale brown 3RG)

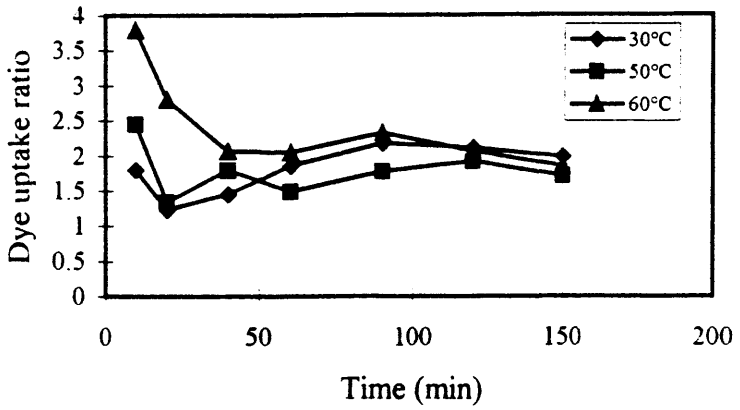


Fig. 3. 10 The ratio of dye uptake with ultrasound to that without (retanned sheep skin)

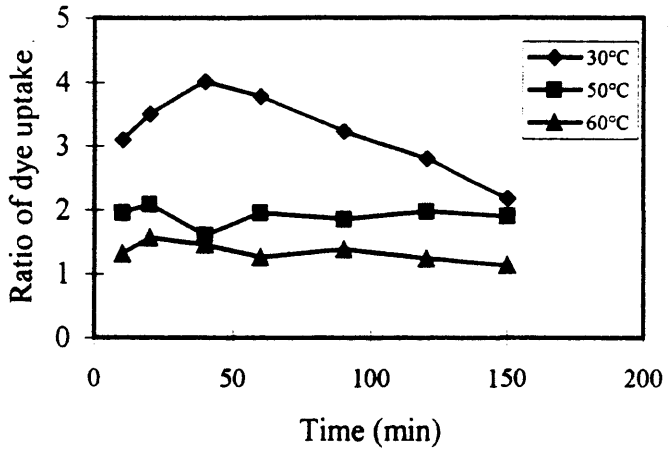


Fig. 3. 11 The ratio of dye uptake with ultrasound to that without ultrasound (rewetted wet-blue)

Due to the accelerating effect of ultrasound on the dyeing process, another advantage might be derived from its application, that is, dyeing could be conducted at a lower temperature with ultrasound. For instance, the dye uptake in the retanned sheep skin dyed at 30°C with ultrasound for 60 minutes is 9.6 mg/g, which is similar to that in the sample dyed for 60 minutes without ultrasound at 60°C. In addition, the application of ultrasound can also shorten the time of dyeing. This can be seen clearly in Tables 3.4 and 3.5.

Table 3.4 Time savings for dyeing retanned sheepskin due to ultrasound (ULT).

Temperature	Dyeing without ULT		Dyeing with ULT		Time saved (%)
	Time (min)	Dye uptake (mg/g)	Time (min)	Dye uptake (mg/g)	
30°C	150	8.66	60	9.64	60%
50°C	150	12.21	60	11.96	60%
60°C	150	15.81	40	15.40	73%

Table 3.5 Time savings for the dyeing of rewetted wet-blue bovine leather due to ultrasound

Temperature °C	Dyeing without ULT		Dyeing with ULT		Time saved (%)
	Time (min)	Dye uptake (mg/g)	Time (min)	Dye uptake (mg/g)	
30°C	150	8.7	30	9.6	80%
50°C	150	10.64	60	11.88	60%
60°C	150	23.6	60	22	60%

From the results, it is clear that if the dye uptake required is 8.66 (mg/g) for the retanned sheepskin, then a normal dyeing process (at 30°C) needs 150 minutes whilst an ultrasonic dyeing process (at 30°) takes less than 60 minutes. In the case of the rewetted wet-blue bovine leather, such a dye uptake is achieved in only 30 minutes (cf. 150 min for non ULT). Clearly the dyeing time can be shortened by 60%-80% by using ultrasound.

In addition to the experiments using a 4% dye offer as described above, a 6% dye offer was also used for the retanned sheepskin. Similar results were obtained. The dye uptakes were increased in the presence of ultrasound in all cases. After dyeing for 150 minutes, the dye uptake in each of the samples was tested using the same method as described above. In order to compare data conveniently, the results for both 4% and 6% concentrations are listed in Table 3.6. It can be seen that the application of ultrasound allows the dye offer to be reduced, whilst at the same time achieving the same or even higher dye uptake. The dye uptake in the case of 4% dye offer with ultrasound is higher than that for 6% offer without ultrasound. This could be beneficial in terms of reducing the consumption of dyestuff and hence the overall cost of the dyeing process.

Table 3.6 The dye uptake(mg/g) in retanned sheepskin after dyeing for 150 minutes.

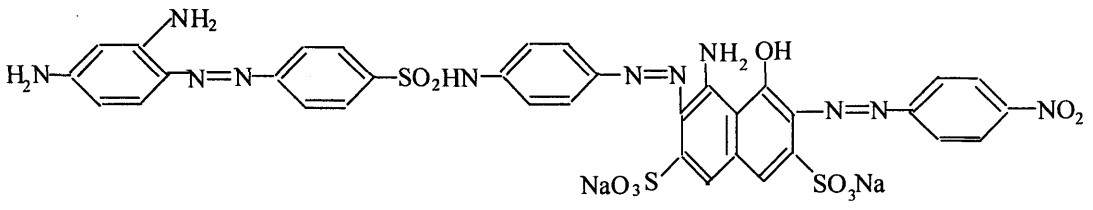
Temperature	4% Dye offer		6% Dye offer	
	with ULT	without ULT	with ULT	without ULT
30°C	17.13	8.66	17.83	10.73
50°C	21.33	12.21	24.06	14.05
60°C	29.11	15.81	39.74	21.29

3.4.1.2 Effect of the type of dyestuffs and leathers

Three different commercial dyestuffs (acid dyes Airedale brown 3RG and Airedale E793, and a reactive dye Procion MX-7RX) and three different leather samples (retanned sheep skin, crust leather from bovine hide, and resin-treated wet-blue from bovine hide) were used to examine the effect of dyestuff type and leather type on dyeing performance under ultrasonic irradiation. All the dyeing experiments were carried out at the same temperature (50°C). Fig. 3.5 and Figs. 3.12-19 show the dye uptakes of all the leather samples with the above three different dyes. Again, ultrasound significantly increases the dye uptakes for all the dyestuffs used. However, the influence of ultrasound on dye uptake varies from one dyestuff to another. Without ultrasonic irradiation, the dye uptake of the retanned sheepskin samples rank in the order of Blue (Procion MX-7RX) > Brown (Airedale 3RG) > Black (Airedale E793), while after the application of ultrasound this order was changed into Brown (Airedale 3RG) > Black (Airedale E793) > Blue (Procion MX-7RX).

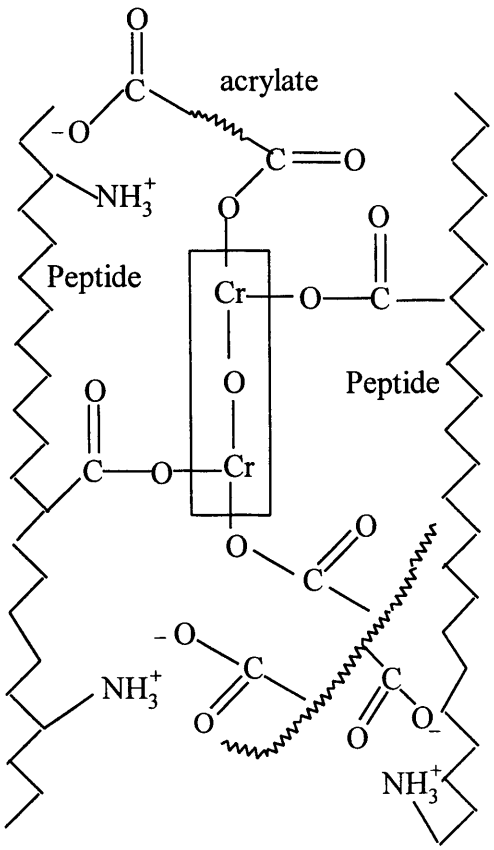
The increase of dye uptake achieved by using ultrasound can be seen more clearly by plotting the ratio of the dye uptake with ultrasound to that without against the dyeing time (Fig. 3.20-22). In the case of sheepskin, the Airedale black E793 shows the highest increase of dye uptake after using ultrasound, while Procion MX-7RX has the lowest (Fig. 3.20). This difference can be attributed to the different structures of these dyestuffs. Although the exact molecular structures of some dyestuffs used are strictly confidential, the general information disclosed by the manufacturer is still helpful for the understanding of the above difference in dyeing behaviour. From Table 3.2, it is seen that Airedale black E793 is a trisazo acid dye

with a molecular mass of 859 and Airedale brown 3RG is a disazo acid dye with a molecular mass of 573-610 (the structure of Airedale black E793 is shown in Scheme 3.4). Obviously the former has a larger molecule size than the latter. This is why the samples dyed with Airedale black E793 without the application of ultrasound give much lower dye uptake than those dyed with Airedale brown 3RG. However, after the application of ultrasound, the difference in dye uptake between these two dyes was largely reduced. This can be seen from Figs. 3.5 and 3.12: the dye uptakes of these two dyes were almost at the same level when ultrasound was used. This is because ultrasonic irradiation increases the dye diffusion rate (see section 3.4.2) by the 'jet effect' [Suslick, 1990]. The lower the dye diffusion rate without ultrasonic irradiation, the greater is the impact of the 'jet effect', and hence the larger the increase in the dye uptake obtained by using ultrasound (results from section 3.4.2). Procion MX-7RX is a reactive dye. Due to its good reactivity with the leather fibres, this dye gives a very high dye uptake even without the ultrasound (Fig. 3.13). The effect of ultrasound in this case is much less than for the other two acid dyes. Similar results were obtained by Shimizu *et al.* [1989] when they used ultrasound in the dyeing of Nylon 6 film with different dyestuffs, i.e., disperse, acid and reactive dyes. They found that with reactive dyes, there was the lowest reduction in the activation energy, as a result of the application of ultrasound to the dyeing system.



Scheme 3.4

Another factor influencing dye uptake is the type of leather. Three different samples were used to examine this factor, i.e., retanned sheep skin, crust leather from bovine hide and retanned wet-blue leather with acrylate resin (see Table 3.1). For the sample retanned with acrylate resin, the dye uptake is smaller than for the other two leathers both in the presence and absence of ultrasound. It was noted that, especially when dyeing without ultrasound, the surface colour shade was very pale although the concentration of the dyeing solution was the same in both cases with and without ultrasound. It seems that the presence of acrylate resin in the sample is the reason for the difficulty in achieving dye affinity. The interaction between acrylate resin and tanned leather was studied previously [Li et al., 1989]. It was found that the carboxyl groups in acrylate resin react with the chromium complex in chrome tanned leather and form a new combination, as shown in **Scheme 3.5.**



Scheme 3.5

At the same time, carboxyl groups in the acrylate resin may block some of the amino groups on the polypeptide chains, which would reduce the affinity of acid dyes to the leather. The dyeing process thus becomes very slow, a factor which accounts for the lower dye uptake of this sample compared to that of the other two. There may also be an acrylate resin coating on the surface of the leather, as well as the fibres. However, when ultrasound was used, the dye uptakes were significantly increased and reached the same level as obtained with the other dyes (Fig. 3.17-19). The colour shade on the leather surface and the dye penetration are improved to a large extent. Both these effects should again be attributed to the cavitation and 'jet effect' produced by ultrasound. It was found that a strong 'jet-effect' could perforate and break the passivated surface of a solid and expose the reactive sites to the solution [Suslick, 1990], which might help the dye molecules to break through the resin and attach to the collagen. In addition, this 'jet effect' could also break the weak linkages of the carboxyl group and amino group from collagen, and result in the blocked amino groups becoming reactive again to the dye molecules.

Among the three leather samples, the bovine crust leather gave the highest dye uptakes in both cases (Figs. 3.14-16). This crust leather may be expected to have been much less cationic and the charge in the middle layer can also be expected to have been reduced by the fat-liquoring process [Otto, 1950]. As a result, anionic dyes should penetrate into the leather rather than fix on the surface. Therefore as observed, a larger amount of dyestuff is absorbed by the bovine crust sample. This point will be further confirmed by the results of the penetration testing presented in the next section.

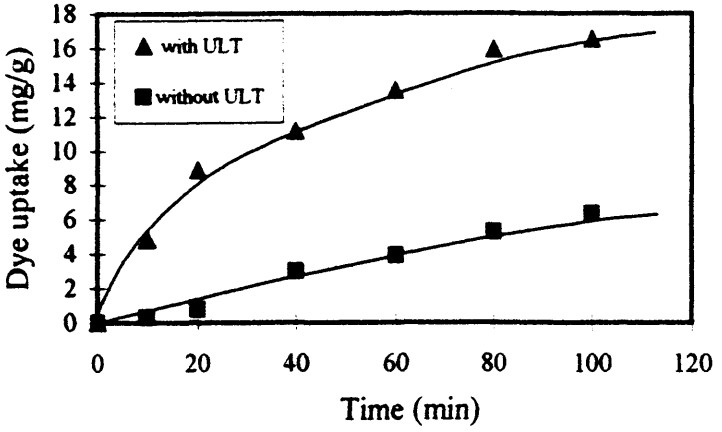


Fig. 3.12 Effect of ultrasound on dye uptake of retanned sheep skin at 50°C (Airedale black E793)

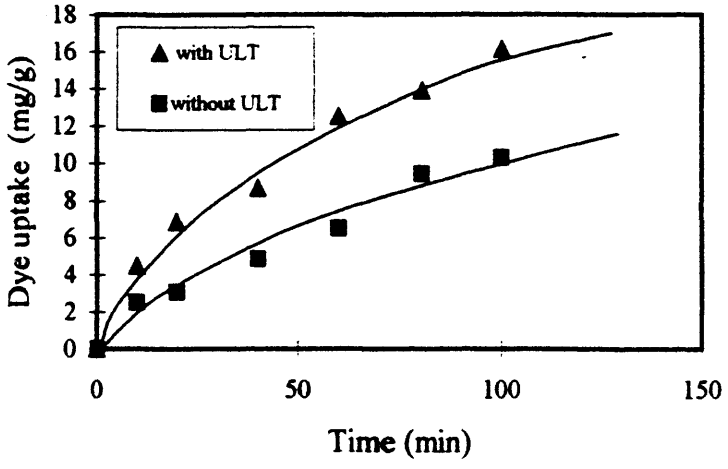


Fig. 3.13 Effect of ultrasound on dye uptake of retanned sheep skin at 50°C (Procion MX-7RX)

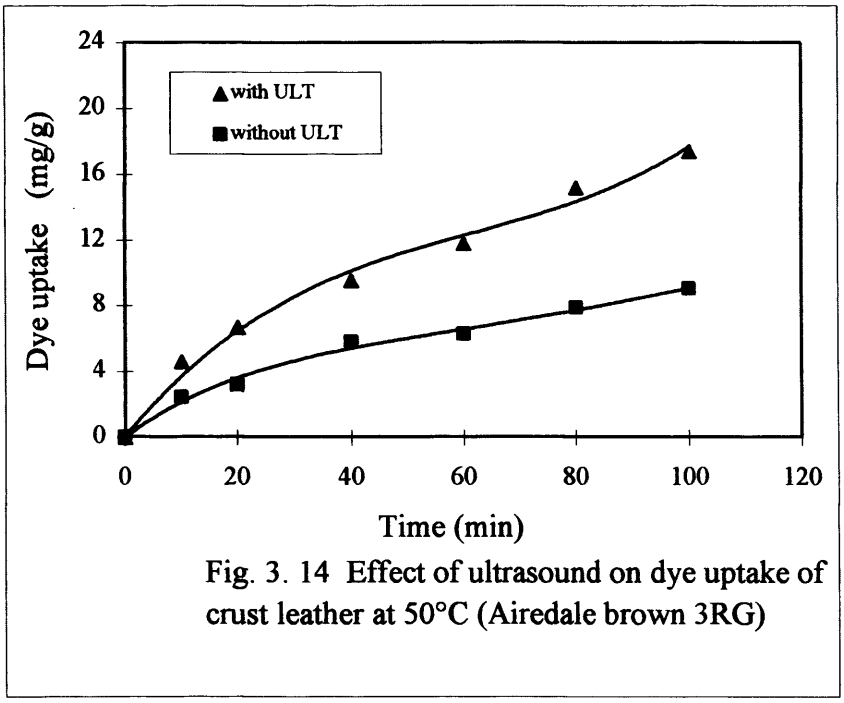


Fig. 3. 14 Effect of ultrasound on dye uptake of crust leather at 50°C (Airedale brown 3RG)

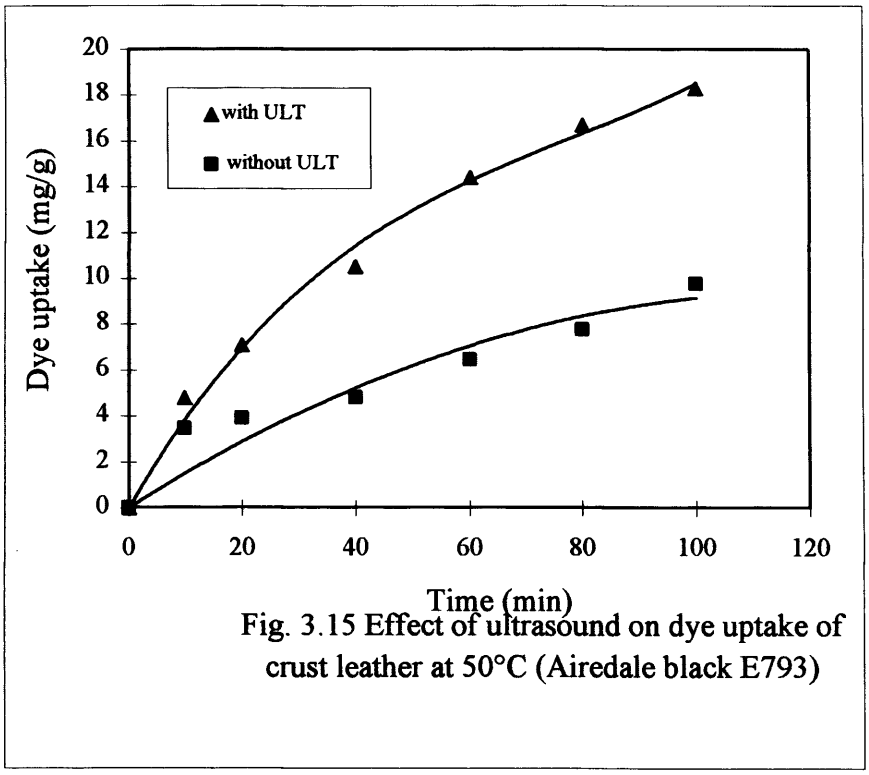


Fig. 3.15 Effect of ultrasound on dye uptake of crust leather at 50°C (Airedale black E793)

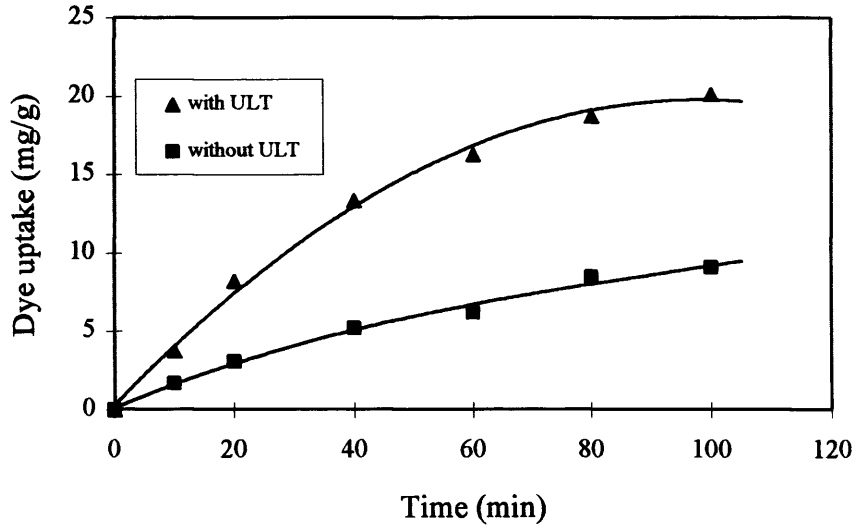


Fig. 3.16 Effect of ultrasound on dye uptake of crust leather at 50°C (Procion MX-7RX)

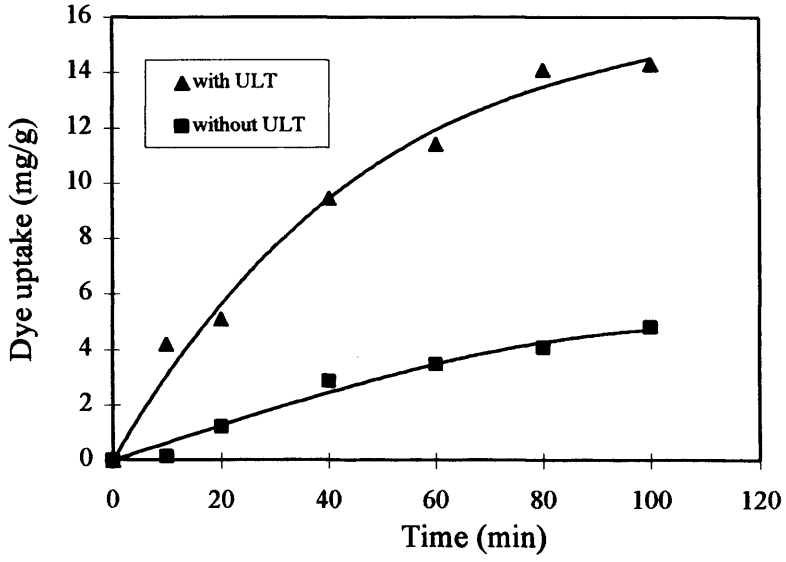


Fig. 3. 17 Effect of ultrasound on dye uptake of resin treated wet-blue leather at 50°C (Airedale brown 3RG)

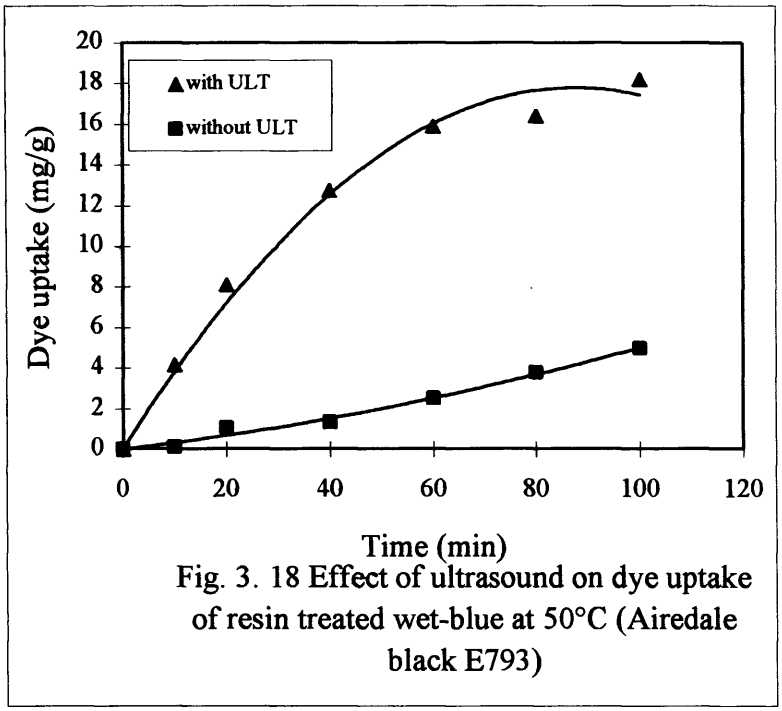


Fig. 3. 18 Effect of ultrasound on dye uptake of resin treated wet-blue at 50°C (Airedale black E793)

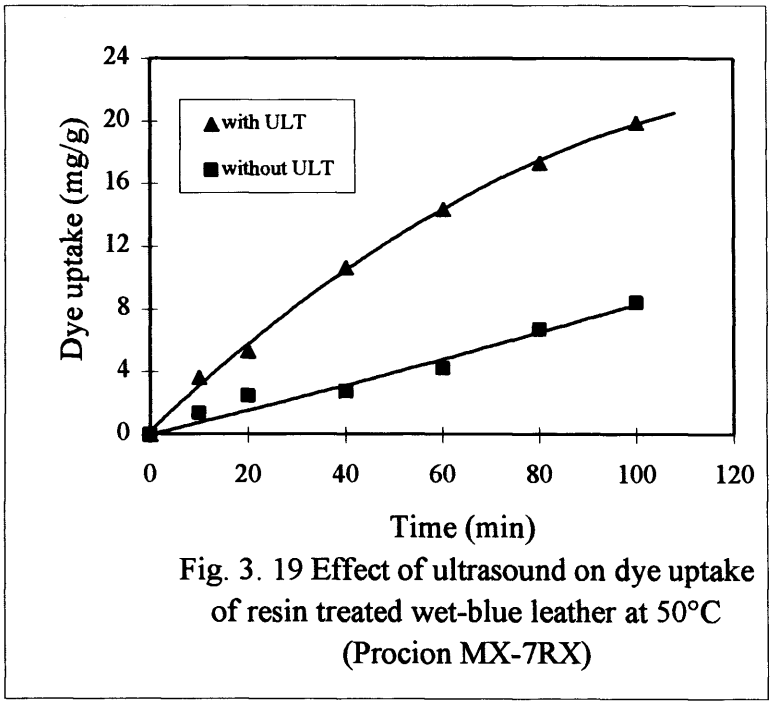


Fig. 3. 19 Effect of ultrasound on dye uptake of resin treated wet-blue leather at 50°C (Procion MX-7RX)

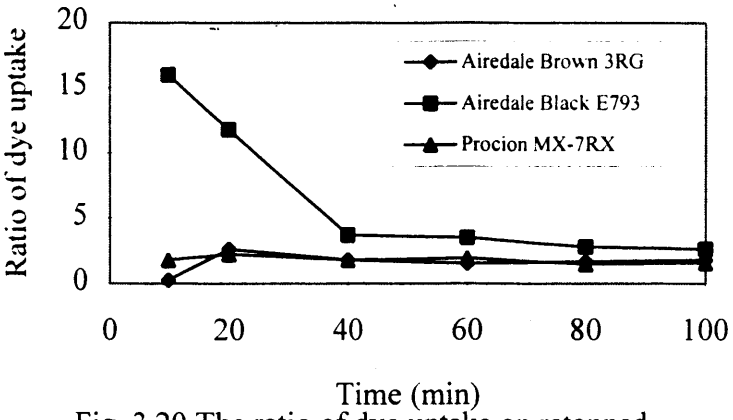


Fig. 3.20 The ratio of dye uptake on retanned sheepskin with ultrasound tothat without ultrasund

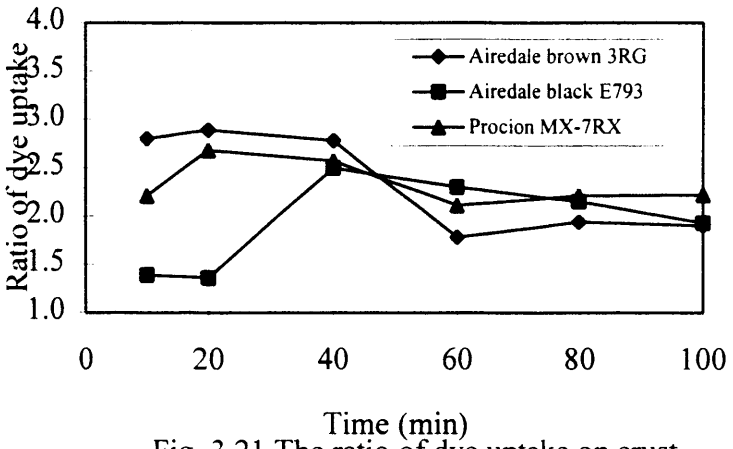


Fig. 3.21 The ratio of dye uptake on crust leather with ultrasound to that without ultrasound

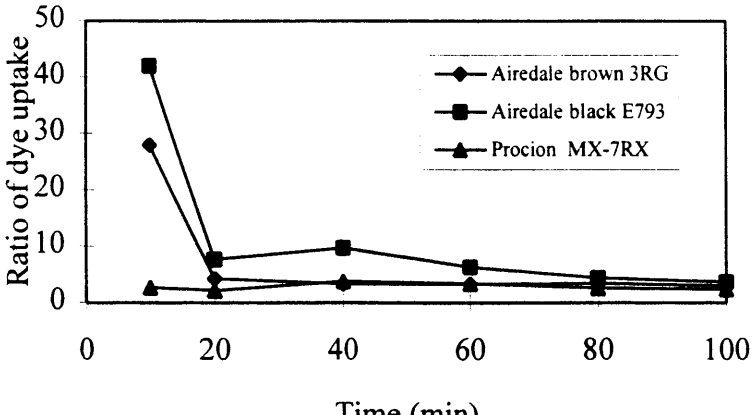


Fig. 3. 22 The ratio of dye uptake on the resin treated leather with ultrasound to that without ultrasound

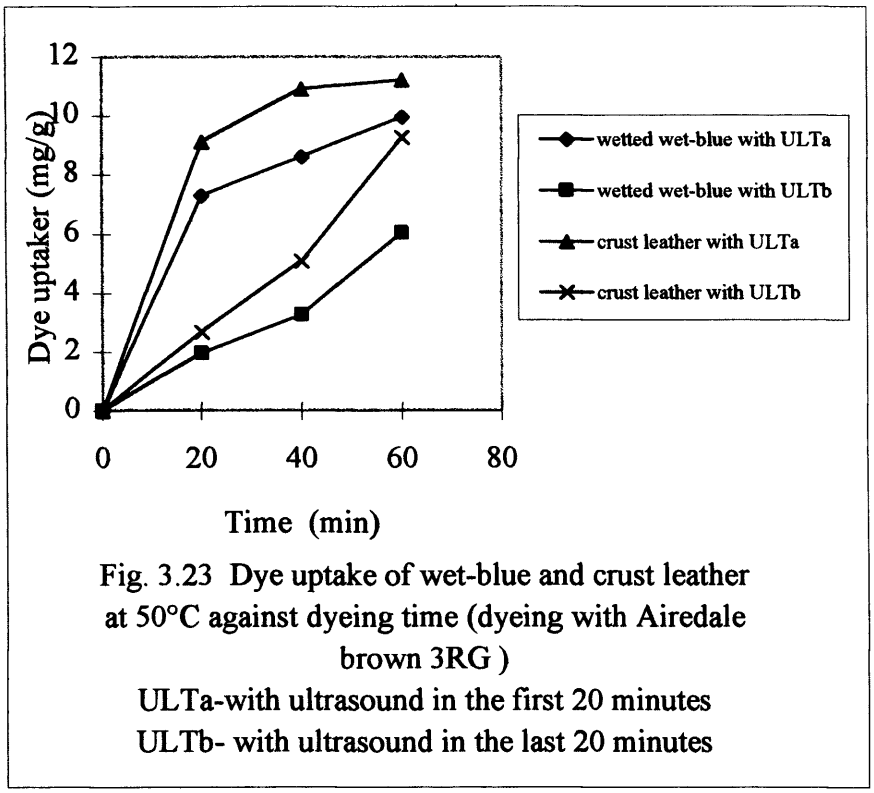


Fig. 3.23 Dye uptake of wet-blue and crust leather at 50°C against dyeing time (dyeing with Airedale brown 3RG)

ULTa-with ultrasound in the first 20 minutes

ULTb- with ultrasound in the last 20 minutes

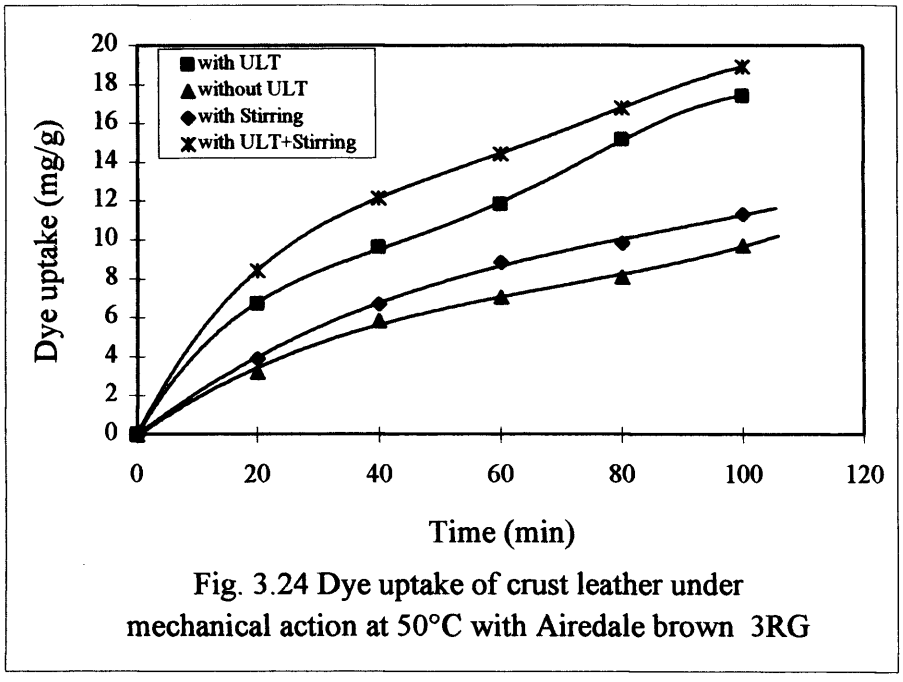


Fig. 3.24 Dye uptake of crust leather under mechanical action at 50°C with Airedale brown 3RG

From the above results and discussion, it can be concluded that the response of the dyeing process to ultrasound depends to a great extent on the type of leather and its pretanning and retanning processes. The results imply that ultrasound is very effective in increasing dye uptakes for those dyestuffs which tend to have a low penetration or weak affinity for the leather. This makes the use of ultrasound very promising for the practice of leather dyeing.

3.4.1.3 Effect of applying ultrasound at different stage of the dyeing process

In the early stages of this project, it was noticed that different results were obtained if ultrasound were applied at different stages of the dyeing process. Thus a group of experiments was conducted to examine this effect: group (a) — samples dyed in the presence of ultrasound for the first 20 minutes followed by a normal or non-ultrasonic dyeing process for the next 40 minutes; group (b) — samples dyed in the opposite way with the first 40 minutes a non-ultrasound process and then the last 20 minutes with ultrasound. The results are plotted in Fig. 3.23. A noticeable difference was observed between these two groups for both the bovine wet-blue sample and the bovine crust leather. Group (a) shows a much higher dye uptake than Group (b). This means that the application of ultrasound in an early stage of the dyeing process is more effective than in a later stage. For instance, the dye uptakes for Airedale Brown 3RG are 9.97 mg/g and 6.03 mg/g for Group (a) and (b) respectively for the wet-blue leather, and 11.22 mg/g and 9.27 mg/g respectively for Group (a) and (b) for the crust leather.

The above results can be understood from a consideration of the dye concentration differences between the earlier and later stages of the dyeing process. The results obtained in section 3.4.2 (diffusion study) indicates that ultrasound could

reduce the particle size of dye aggregates in aqueous solution and speed up the diffusion and hence the dyeing process. In the early stage of the dyeing process, the concentration gradient between the dye solution and leather samples is at its highest point, so this stage is the most effective period for diffusion and penetration. As discussed before, the most important effect of ultrasound on dyeing is its ability to accelerate diffusion and penetration, so if ultrasound is applied at this early stage, full advantage of this effect will be taken. This can be seen more clearly from the dye uptakes at the end of this stage of ultrasonic irradiation. In the first 20 minutes, 73% (rewetted bovine wet-blue) and 80% (bovine crust leather) of the final dye uptakes were achieved for Group (a) (Fig. 3.23).

In contrast to this, the samples in Group (b) which were dyed with ultrasound only in the last 20 minutes clearly missed using ultrasound during the optimum period of dye diffusion. Although the rate of dye uptake was speeded up when ultrasound was applied for the last 20 minutes, the final dye uptake at the end of the 60 minutes period was lower than that of Group (a).

From the above discussions, clearly the earlier the ultrasound is applied in the dyeing process, the higher the dye uptake will be achieved. After a short period of ultrasonic irradiation in the initial stage of dyeing, the dye uptake could reach a considerable level (over 70% of the final dye uptake in a 60 minutes process). This means that a full period of irradiation with ultrasound may not be necessary or economical. In addition, a deeper penetration of the dye in samples from Group (a) was also observed.

3.4.1.4 Dyeing with mechanical stirring and ultrasonic irradiation

As indicated in the experimental section, the dyeing processes discussed above were carried out in a glass vessel and no mechanical stirring was used. However in industry, most leather is made with certain types of mechanical action, i.e. stirring or drumming. Obviously mechanical action is a very important factor for the practical dyeing process. In order to check the applicability of ultrasound to practical use in the tannery, some dyeing experiments were carried out with both mechanical stirring (50 rpm) and ultrasonic irradiation. The crust leather sample made from bovine hide was selected again for these dyeing experiments. The samples were dyed at 30 and 50°C with Airedale brown 3RG whilst being stirred. The results are shown in Fig. 3.24. The dye uptakes are ranked in the following order: ultrasound + stirring > ultrasound > stirring > no ultrasound or stirring.

Table 3.7 shows the difference in dye uptakes between samples dyed with and without ultrasound, either in the presence or absence of mechanical stirring. In the presence of mechanical stirring, the differences of dye uptakes are higher than those without mechanical stirring. This is especially noticeable in the first 60 minutes; after that the difference is minimal.

Table 3.7 The differences of dye uptake (mg/g) between the sample dyed with and without ultrasound

Time (min)	20	40	60	80	100
Stirring	4.5	5.5	5.6	7.1	7.6
No stirring	3.5	3.8	4.7	7.1	7.7

In the tannery leathers are often dyed in drums. In order to simulate this practical process, a small metal drum was made and used in the present study (see Fig. 2.2). The drum was fixed to an electrical stirrer which had different speeds. The experimental unit is shown in Fig. 2.1. Wet-blue bovine leather samples were dyed in this metal drum with Airedale brown 3RG and Airedale brown DS and results are shown in Figs. 3.25-26. The effects of ultrasound on dyeing in this metal drum were not as obvious as on dyeing in the glass vessel (cf. Fig. 3.8). The increase in dye uptake when ultrasound was used was only 3-12%, compared with the glass vessel where this increase was 91%. When the drum rotated, the leather sample was lifted up by the internal pegs and stayed out of dyeing liquor for a period until it fell off the pegs and back into the liquor again. In practice, about one third of the time the sample was not in the dyeing liquor so the actual time of ultrasonic irradiation was much shorter. When the aluminium foil was used to check the local intensity of ultrasound, pits in the aluminium that could be traced in the metal drum are about 40% fewer than those in the glass vessel. Metals are good reflectors of sound waves, so it appears that much less energy is actually transmitted into the metal drum. This must be a factor which accounts for the less effectiveness of ultrasound for the metal drum dyeing than for the glass vessel dyeing. It is also apparent that the overall dye uptake in the metal drum was still higher than that in the glass vessel. This is due to the vigorous mechanical action of drumming, and due to a higher dye concentration in the metal drum as a result of shorter float length (200% *vs.*1500% in the glass vessel).

3.4.1.5 Effect of ultrasound on chrome tanned hide powder

The results presented in the above sections show that ultrasound can accelerate penetration of dyestuff into the fibrous network of leather, and hence increase the dye uptake. In order further to clarify this point, some chrome tanned hide powders were dyed with and without ultrasound at 25 and 40°C. Hide powders are essentially constituted of loose fibres rather than the tight entangled fibrous assembly. They have a smaller particle size and larger surface area, so the dye molecules should find it much easier to penetrate compared with a normal leather. The dyeing process would be adsorption controlled rather than diffusion controlled. If the major effect of ultrasound is to increase the diffusion, then there will not be much difference in dye uptake between an ultrasonic and a non-ultrasonic process in this case. A dyeing experiment using hide powders was therefore carried out.

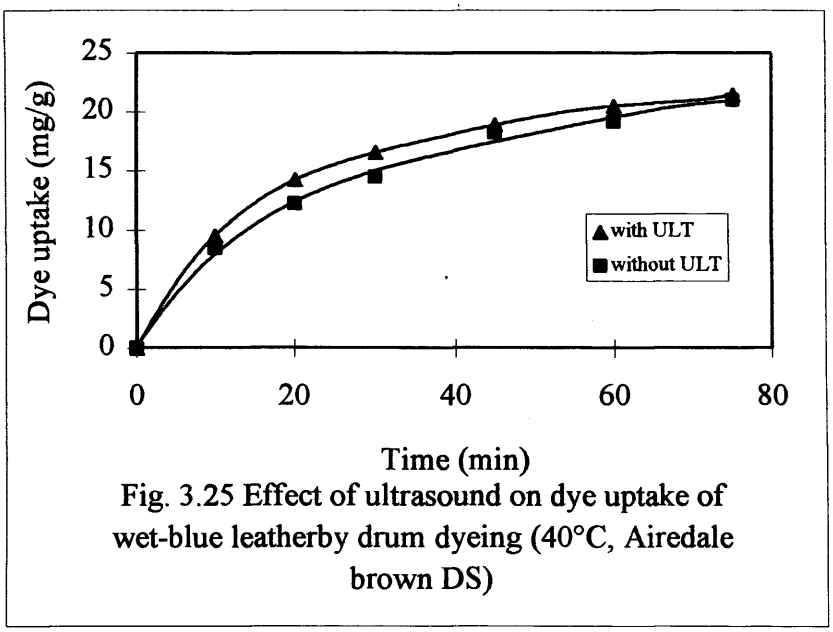


Fig. 3.25 Effect of ultrasound on dye uptake of wet-blue leatherby drum dyeing (40°C, Airedale brown DS)

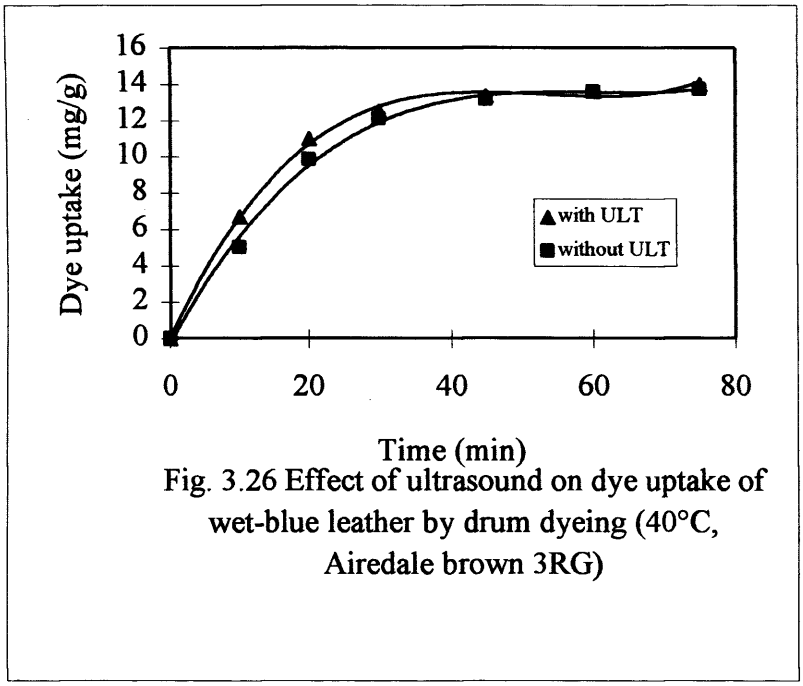


Fig. 3.26 Effect of ultrasound on dye uptake of wet-blue leather by drum dyeing (40°C, Airedale brown 3RG)

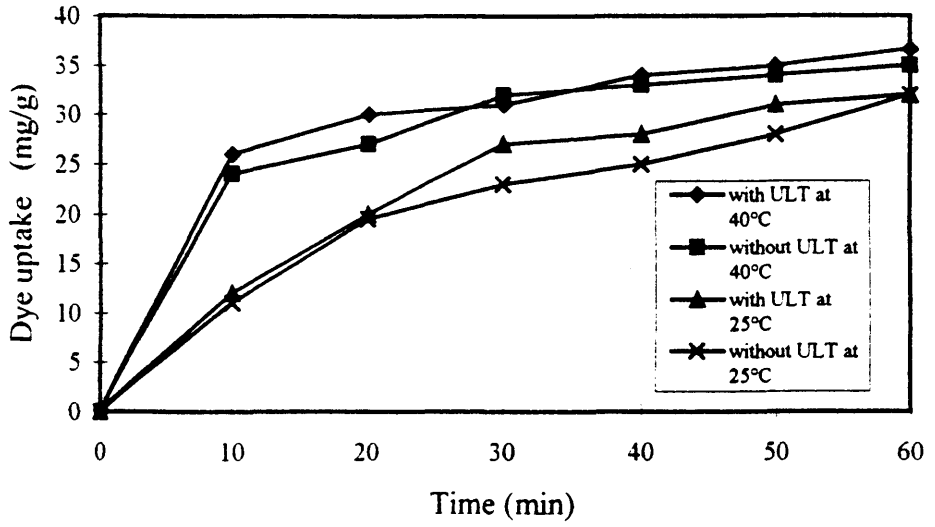


Fig. 3. 27 Effect of ultrasound on dye uptake of chrome tanned hide powder at 25 and 40°C (Airedale brown 3RG)

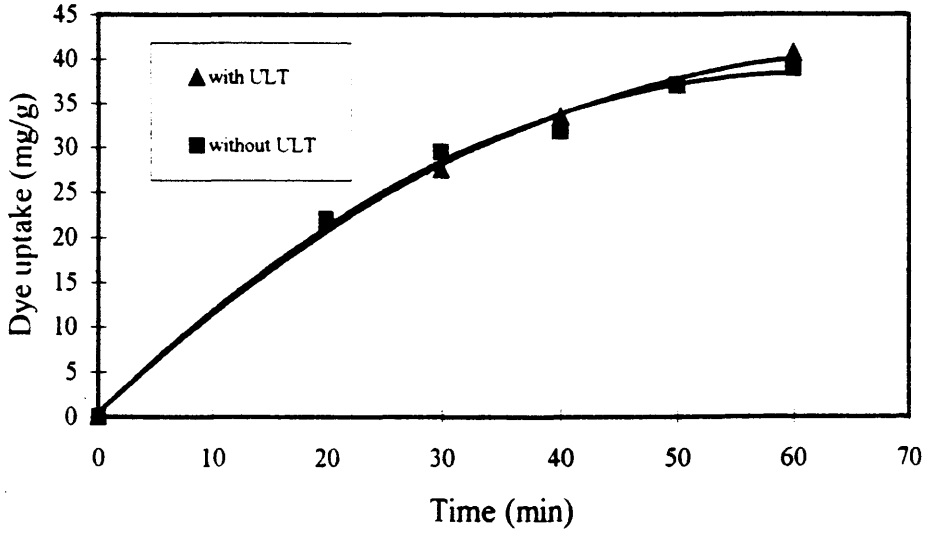


Fig. 3.28 Effect of ultrasound on dye uptake of chrome-tanned hide powder at 40°C (Airedale brown DS)

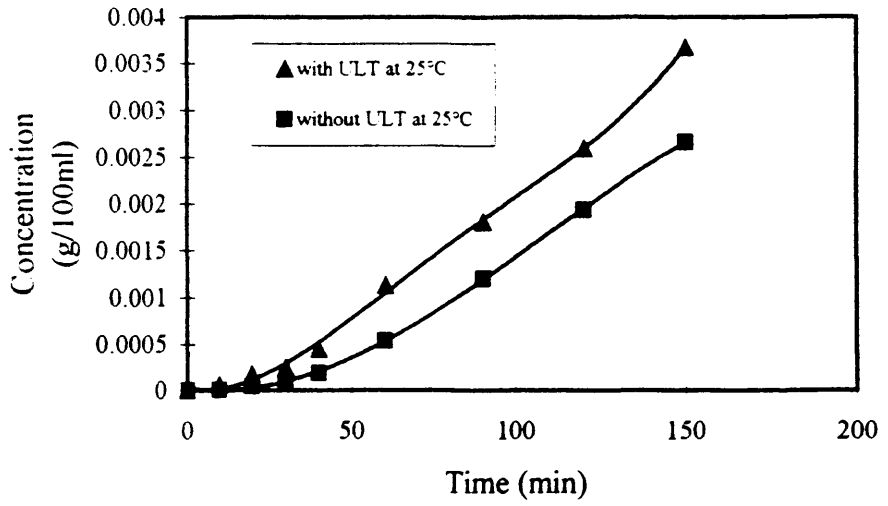


Fig. 3. 29 Dye diffusion curve (dialysis apparatus)
(Airedale brown 3RG at 25°C)

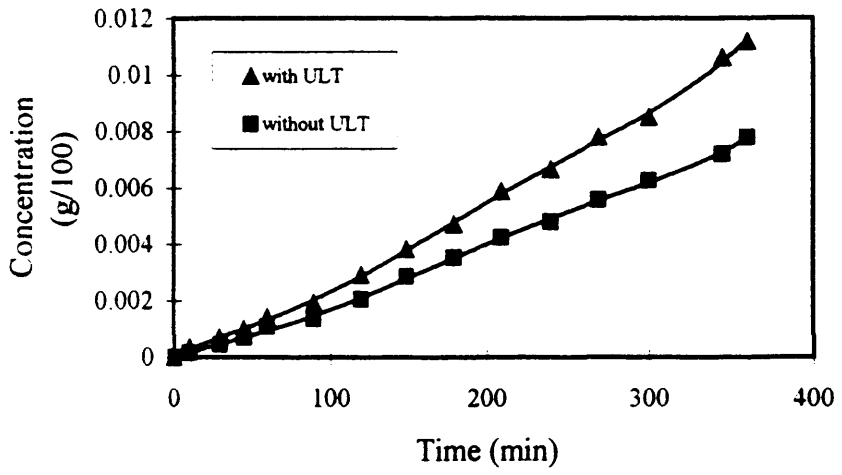


Fig. 3. 30 Dye diffusion curve (dialysis apparatus)
(Airedale brown ER at 25°C)

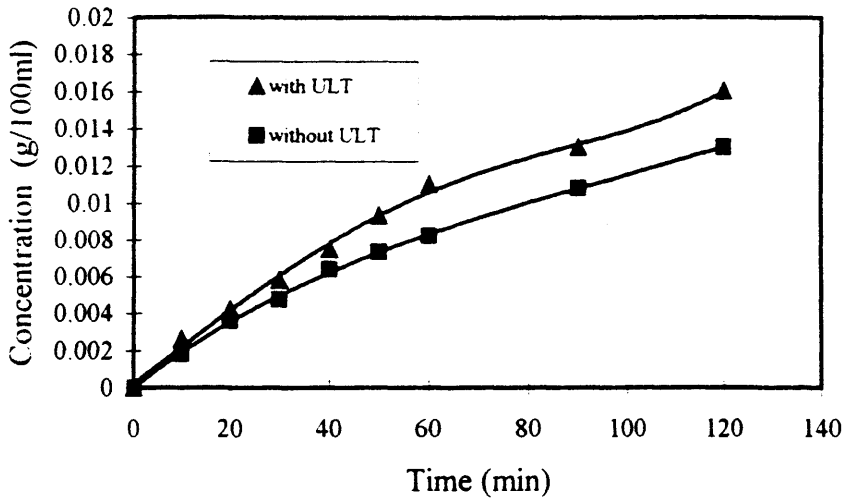


Fig. 3. 31 Dye diffusion curve (dialysis apparatus)
(Airedale brown DS at 25°C)

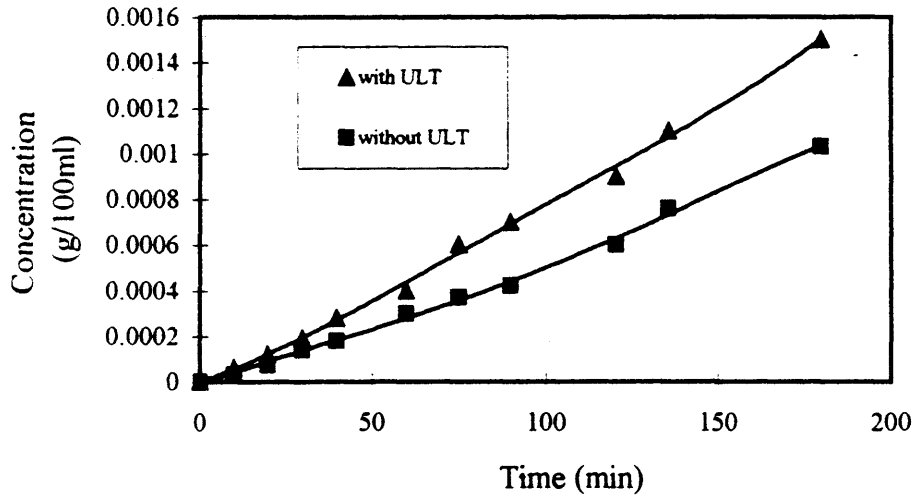


Fig. 3. 32 Dye diffusion curve (dialysis apparatus)
(Airedale black E793 at 25°C)

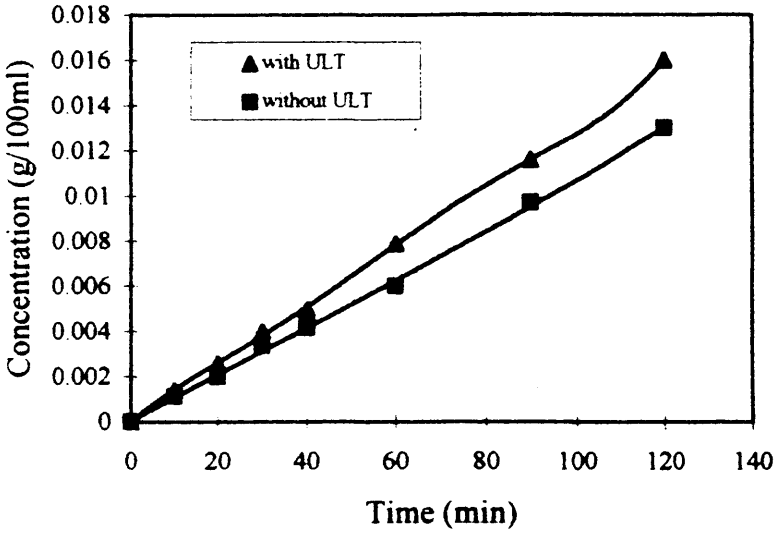


Fig. 3.33 Dye diffusion curve (dialysis apparatus)
(Procion MX-7RX at 25°C)

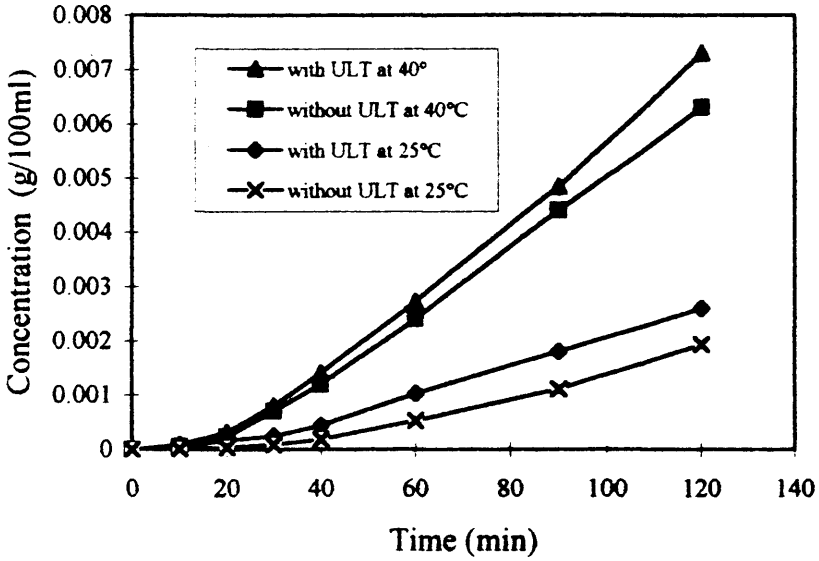


Fig. 3.34 Dye diffusion curve (dialysis apparatus)
(Airedale brown 3RG at 25 and 40°C)

Figs. 3.27-28 show the dye uptakes of hide powder samples dyed with and without ultrasound at 25 and 40°C. Over the 60 minute observation period, there is no significant difference between the ultrasonic and non-ultrasonic processes. It is concluded that the main effect of ultrasound on the dyeing process is to increase dye diffusion or penetration into the fibrous structure of leather, which consequently increases the dye uptake.

3.4.2 Dye diffusion coefficient measured using a dialysis tube

In order to confirm the conclusion of the last section, a dye diffusion experiment using a dialysis membrane was carried out in the glass vessel. Because of the much thinner cross-section of the membrane, adsorption is negligible in the experiment.

The concentrations of dyestuffs in the dialysis tube at 25°C during the diffusion process are plotted against the diffusion time in Figures. 3.29~3.33. In order to investigate the temperature-dependence of dye diffusion under ultrasonic irradiation, an acid dye (Airedale brown 3RG) was selected to repeat the above experiment at 40°C. The result is shown in Fig. 3.34. All the results clearly show that the concentration in the dialysis tube increases after using ultrasound irradiation, especially at 25°C. The reactive dye (Procion blue MX-7RX) has the highest concentration in the tube and the acid dye (Airedale black E793) has the lowest, for the same period of diffusion.

According to Fick's first law of diffusion, the diffusion rate can be expressed as follows [McBain *et al.*, 1931].

$$\frac{ds}{dt} = -DA\frac{dc}{dx} \qquad (3\text{-}2)$$

where $\frac{ds}{dt}$ is the rate of transference of the solute through an area A, across which there is a concentration gradient $\frac{dc}{dx}$. D is the diffusion coefficient, which is the most important parameter characterising the diffusion rate because it is independent of the concentration gradient. Based on the equation (3-2) and the present experimental conditions and system, the following equation was derived to calculate the diffusion coefficient, D (detail is given in Appendix II):

$$D = \frac{K}{t\,(1+\lambda)} \ln\left[\frac{C_0}{C_0 - (1+\lambda)C_1}\right] \qquad (3\text{-}3)$$

$$K = \frac{d\,l}{4},\ \lambda = \frac{V_2}{V_1}$$

where, d - dialysis tubing diameter (1.9 cm)

l - dialysis tubing thickness (0.03 cm)

V_1 - volume of dye solution in the vessel

V_2 - volume of dye solution in the dialysis tube

Table 3.8 lists all the results from equation (3-3). It can be seen that the diffusion coefficients in the presence of ultrasonic irradiation are 19~68% higher than that without ultrasonic irradiation. The dyestuff Procion MX-7RX has the highest value of diffusion coefficient but the lowest increase (24%) after using ultrasound. In contrast, the dyestuff Airedale black E793 has the lowest value of diffusion coefficient, about 5-10 times lower than the other dyestuffs. As described before, Airedale black E793 is a trisazo dye and has a higher molecular mass (859) than the others. Its structure is shown in **Scheme 3.4**. The large size and poor solubility are probably responsible for the low diffusion rate. However, for Airedale black E793, the increase of diffusion coefficient after using ultrasound is quite high (70%). Thus the effect of ultrasound on this type of dye (Airedale black E793) is more profound.

As might be expected, the diffusion rate at 40°C (Fig. 3.32) is higher than that at 25°C for dyestuff Airedale brown 3RG. The diffusion coefficients in the presence and absence of ultrasound are 4.43×10^{-8} and 3.82×10^{-8} cm^2/s respectively at 40°C, and 2.03×10^{-8} and 1.25×10^{-8} cm^2/s respectively at 25°C. The ratios (D_{ult} /D_{nult}) are thus 1.15 (at 40°C) and 1.62 (at 25°). It can therefore be seen that, at least for Airedale brown 3RG, a higher temperature tends to reduce the effect of ultrasound on the diffusion coefficient. It is likely that, at higher temperatures, the dye aggregations have a smaller size and so they can diffuse more easily even without ultrasound. Also at high temperature the dye molecule movement is faster and hence an increase in D is expected.

Table 3.8 Diffusion coefficients (cm^2/s) of different dyestuffs at 25°C.

Dye stuffs	Airedale Brown 3RG	Airedale Brown DS	Airedale Brown ER	Airedale Black E793	Procion MX-7RX
With ULT ($D_{ult}\times10^8$)	2.03	8.58	1.96	0.63	9.84
No ULT ($D_{nult}\times10^8$)	1.25	7.20	1.42	0.38	7.92
Ratio (D_{ult}/D_{nult})	1.62	1.18	1.38	1.70	1.24

Note: D_{ult} is the diffusion coefficient with ultrasound; D_{nult} is the diffusion coefficient without ultrasound.

Considering the above diffusion coefficients, it is clear that ultrasound speeds up the diffusion process significantly and hence the overall dyeing rate. The underlying reasons for this acceleration are very complex. However some of the factors which might influence the effect are discussed below.

Firstly, the suggested reduction of dye aggregate or micelle size may be expected owing to the high shear forces caused by ultrasound. Assuming no charge and a spherical shape for the dye micelle, the relationship between the diffusion coefficient (D), the micelle radius (r) and temperature (T) can be expressed as [Vikerstaff, 1957]:

$$D \propto T/r \qquad (3\text{-}4)$$

In other words, the diffusion coefficient is inversely proportional to the micelle radius. The larger the micelle radius is, the lower the diffusion coefficient. Thus, from the results in Table 3.8, it may be inferred that the particle size of dyestuff Black E793 is the largest and that of Procion MX-7RX and Airedale brown DS is

the smallest. This may explain the difference in the diffusion behaviours of these dyestuffs.

Nevertheless, the micelles of dye molecules are normally charged particles due to the dissociation of the ionizable groups in the micelles. The above relationship between diffusion coefficient and particle radius, i.e., equation (3-4), therefore should be modified. Based on the theory of Nernst-Haskell [Vikerstaff, 1957, p97], the following equation can be established:

$$D = \frac{K}{1 + K'r} \mathrm{T} \qquad (3\text{-}5)$$

where D is the diffusion coefficient, K and K' are the system constants which depend on temperature, valences of the dye ion and its gegenion, and the mobility of the ions. Although equation (3-5) is more complicated than equation (3-4), the inverse proportion relation between D and r is still the case, so a higher diffusion coefficient still indicates a smaller particle size.

Another important factor that may be responsible for the acceleration of dye diffusion is the ultrasound induced cavitation near a solid surface as illustrated in Fig. 1.3. As described in Section 1.2.2, the speed of the moving jet is >100 m/s [Lauterborn *et al.,* 1975] and the pressure of the jet is in the order of 10,000 atm [Lorimer, 1987]. Such a high speed jet and high pressure will push the dye molecules strongly into the surface of the membrane and so enhance the diffusion and penetration. It can therefore be imagined that, in the case of leather dyeing, this jet works like a tiny needle punching into the fibrous substrate. Obviously dye molecules would migrate into the inner layers of the leather in the presence of the

jet. Jetting has been demonstrated by Watmough [1993] in his experiments in which a dye solution in a bath was irradiated by a 50 kHz ultrasonic unit and a white paper sheet was used as an indicator of the jet effect. After a certain period of irradiation, many dense colour spots were observed on the sheet (Fig. 3.35). The formation of these spots was interpreted as being the result of the jet effect [Watmough, 1993].

A further factor which may influence the diffusion process during ultrasonic irradiation is the localised high temperature and pressure produced when cavitation collapse occurs suddenly on the diffusion cell surface. This will reduce the surface tension between the dye and the diffusion cell thus reducing the restraining forces between them and accelerating the movement of dye molecules into the cell [Thakore, 1990].

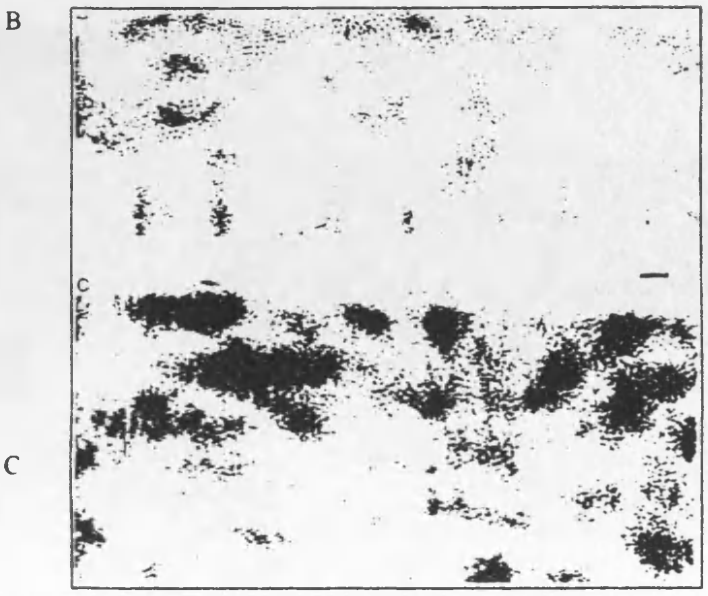


Fig. 3.35 Dye spots caused by ultrasonic "jet effect" [Watmough, 1994]

B-15 minutes, card exposed along the main diagonal axis of the tank

C- 15 minutes, card exposed parallel to the base of the tank

(32.5 litre ultrasonic cleaning bath, 50 kHz, 150 W)

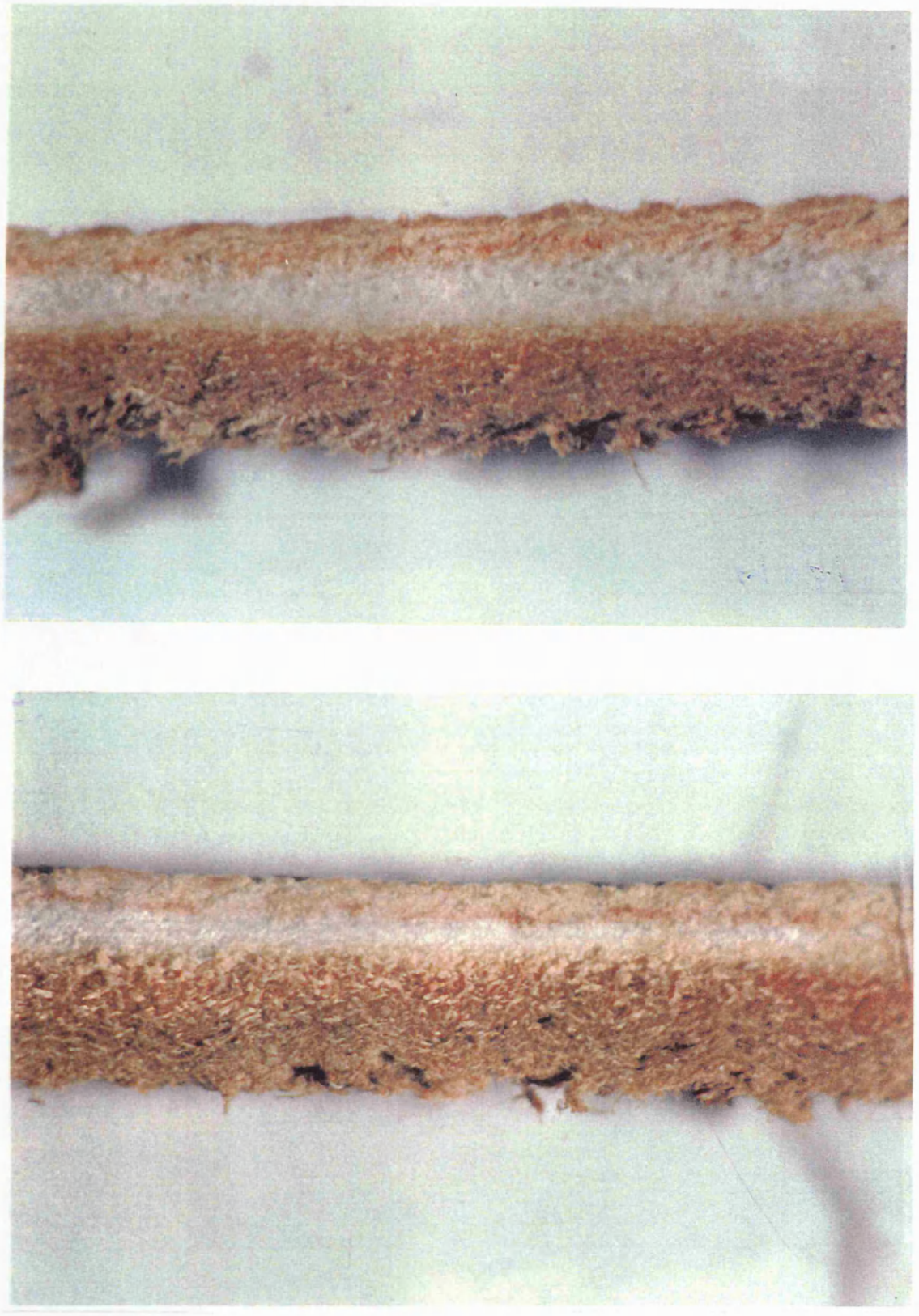


Fig. 3.36 Optical micrographs of retanned sheepskin dyed with (bottom) and without (top) ultrasound (20°C, 100 minutes, Airedale brown 3RG magnification ×25)

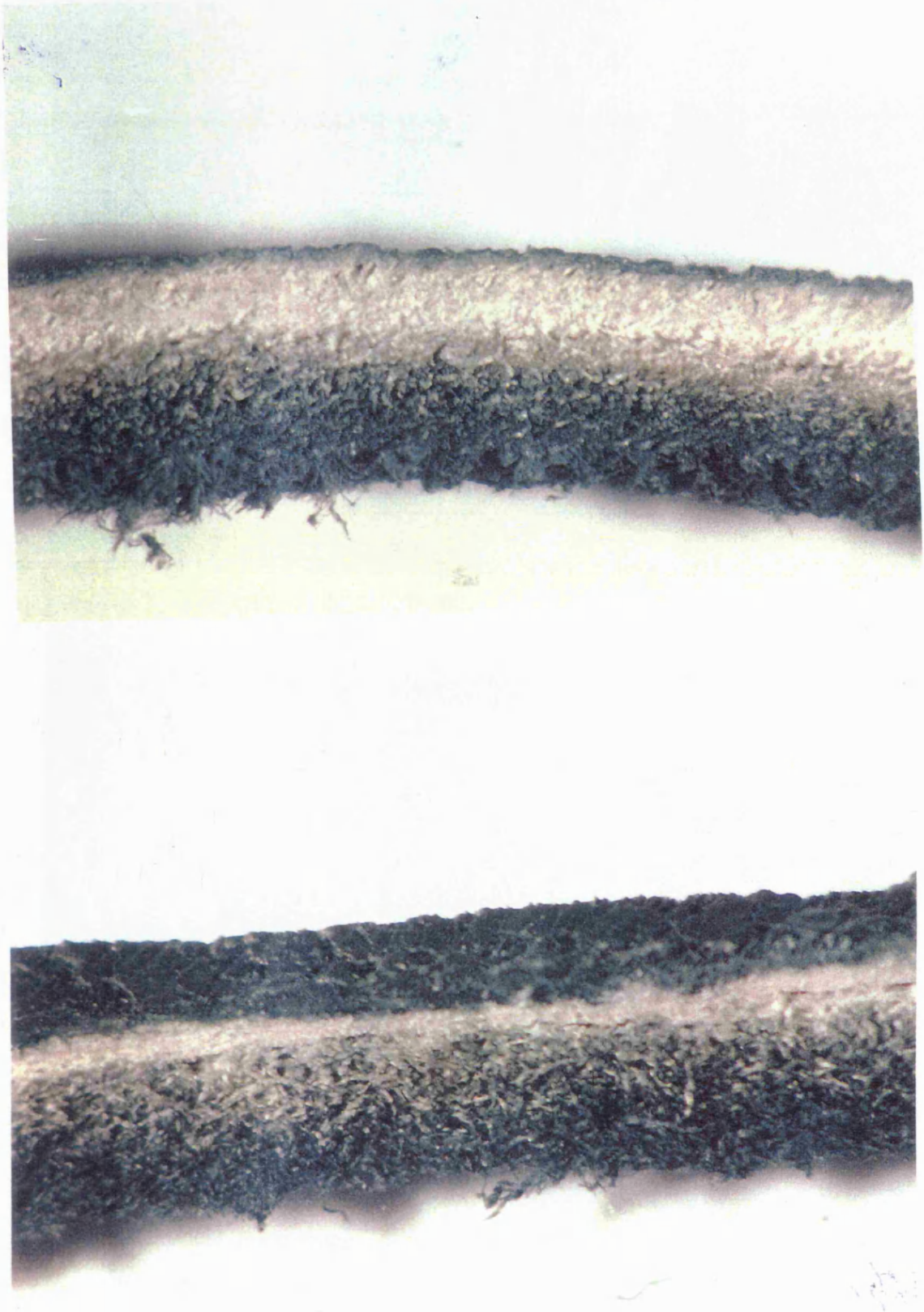


Fig. 3.37 Optical micrographs of retanned sheepskin dyed with (bottom) and without (top) ultrasound (60°C, 40 minutes, Airedale black E793, magnification ×25)

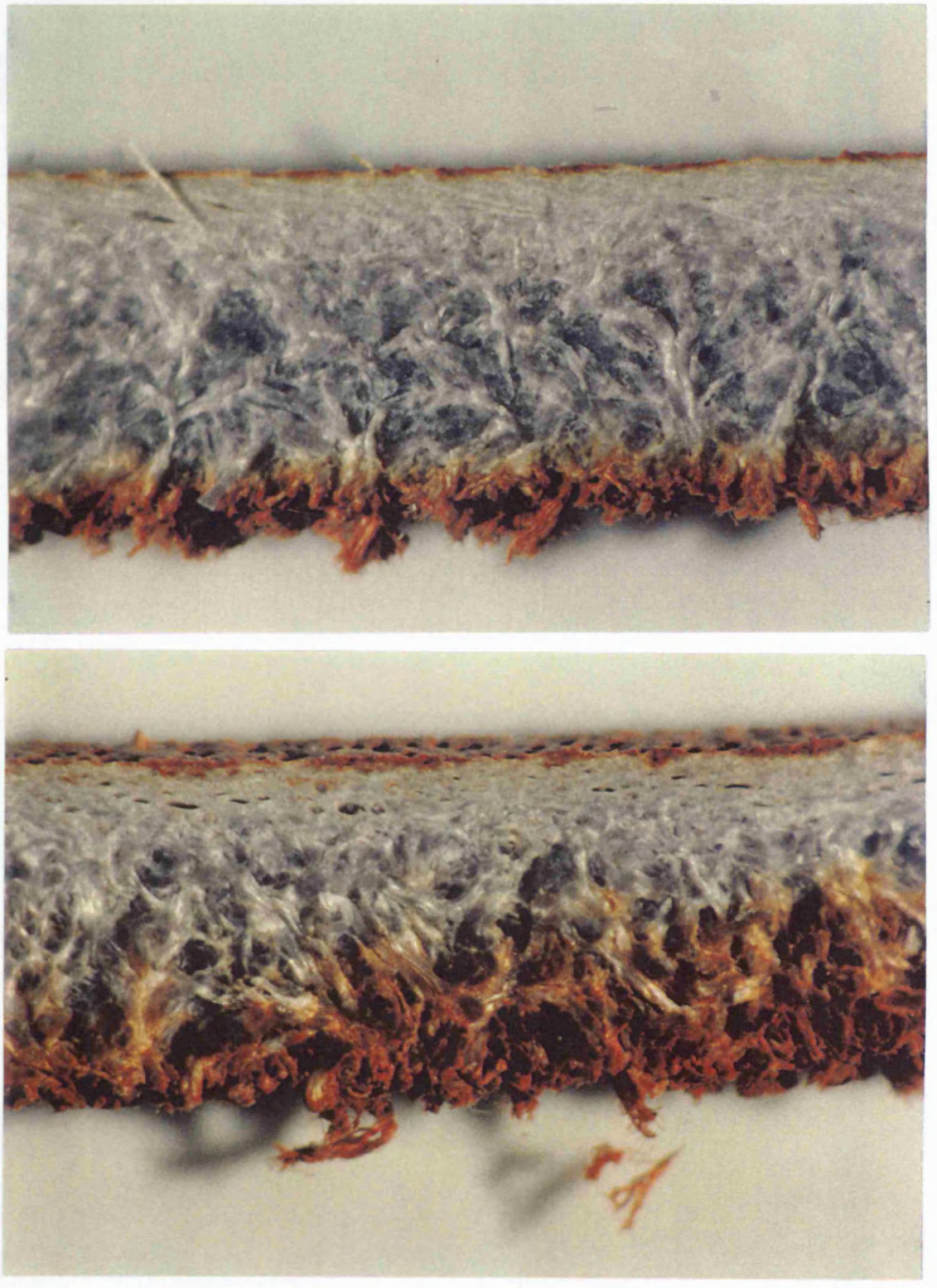


Fig. 3.38 Optical micrographs of rewetted wet-blue leather dyed with (bottom) and without (top) ultrasound (50°C, 100 minutes, Airedale brown 3RG, magnification ×25)

Fig. 3.39 Optical micrographs of resin retanned wet-blue dyed with (bottom) and without (top) ultrasound (50°C, 100 minutes, Airedale brown 3RG, magnification ×25)

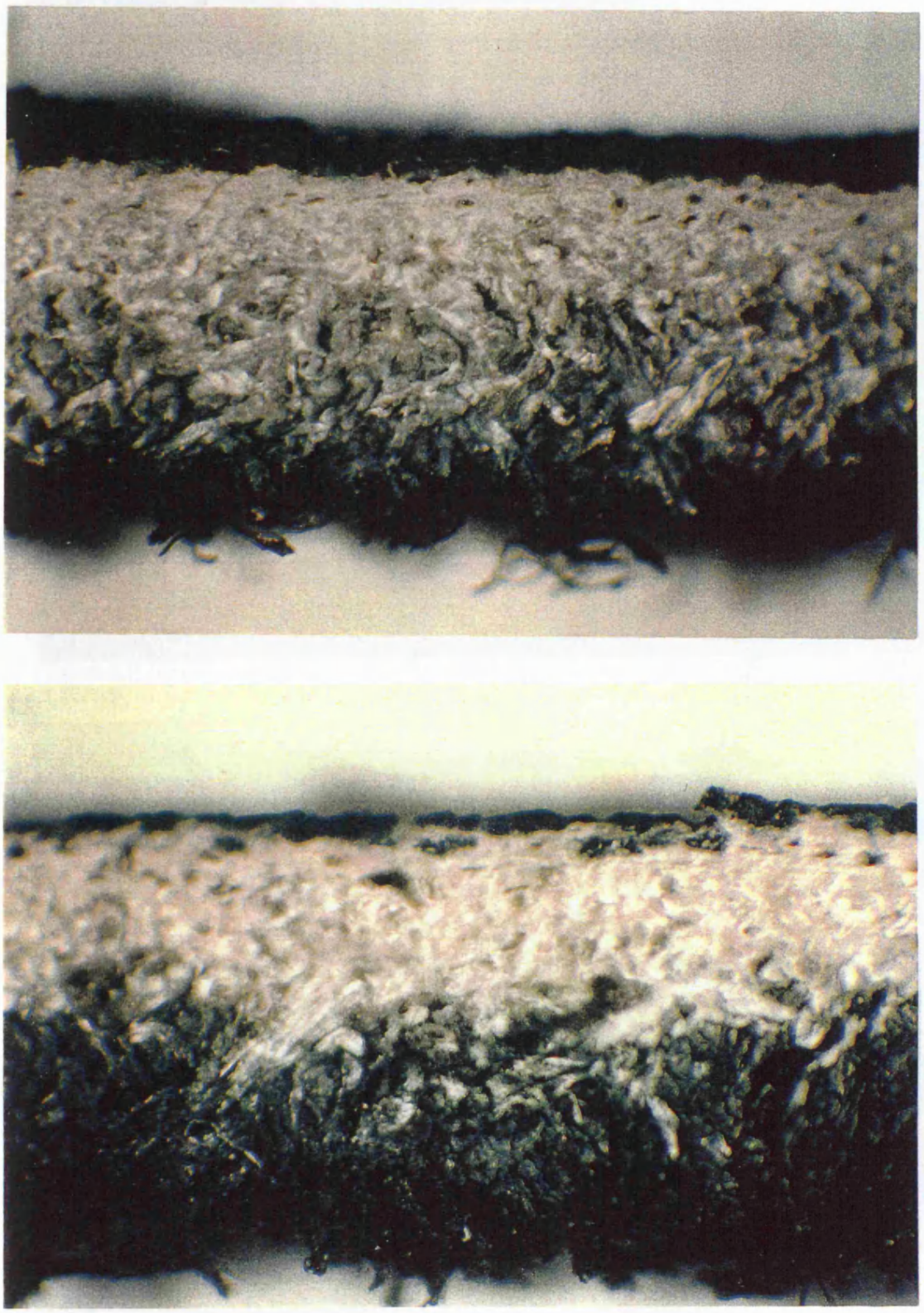


Fig. 3.40 Optical micrographs of crust leather from bovine hide dyed with (bottom) and without (top) ultrasound (50°C, 100 minutes, Airedale black E793, magnification ×25)

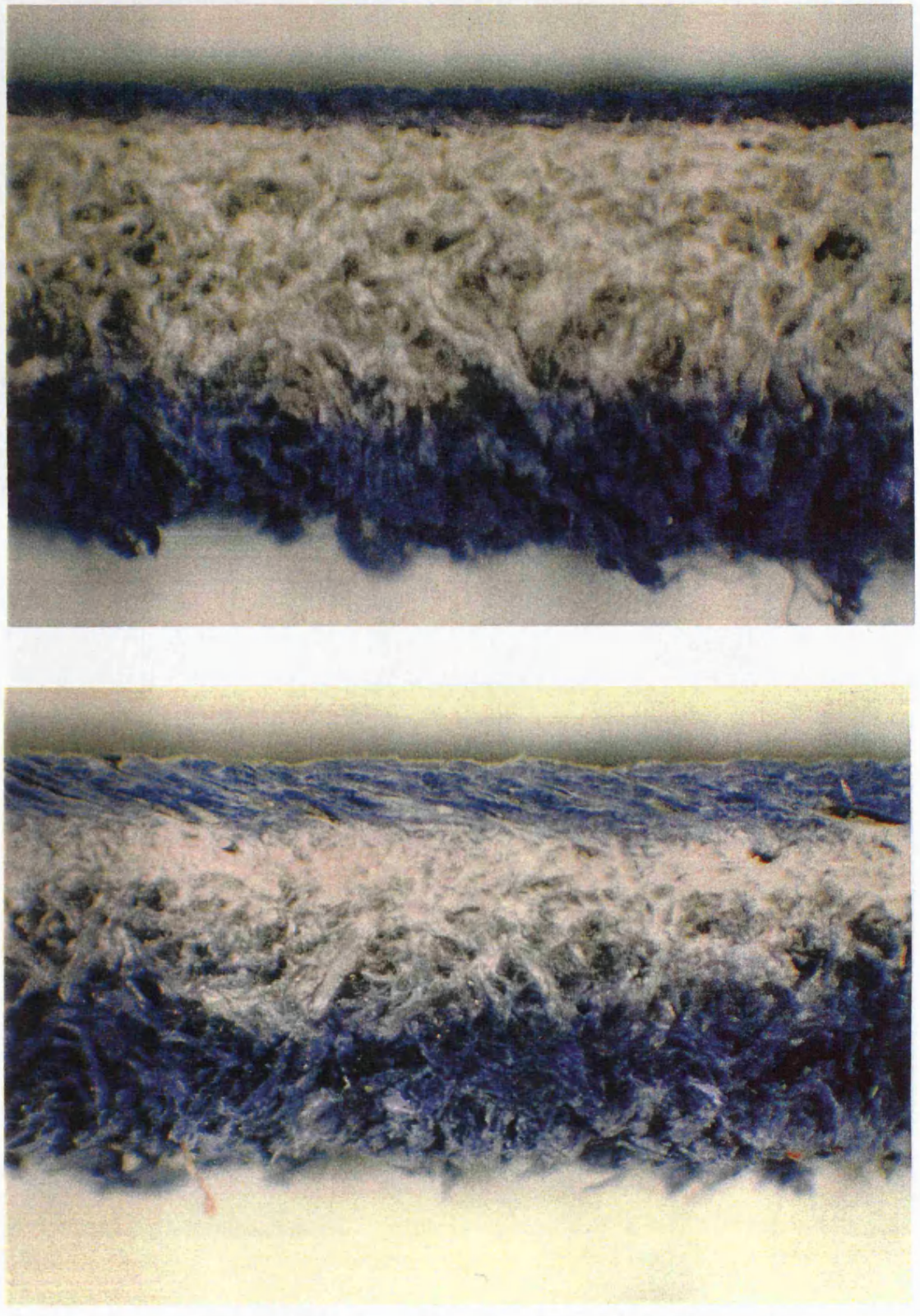


Fig. 3.41 Optical micrographs of crust leather dyed with (bottom) and without (top) ultrasound (50°C, 100 minutes, Procion MX-7RX, magnification ×25)

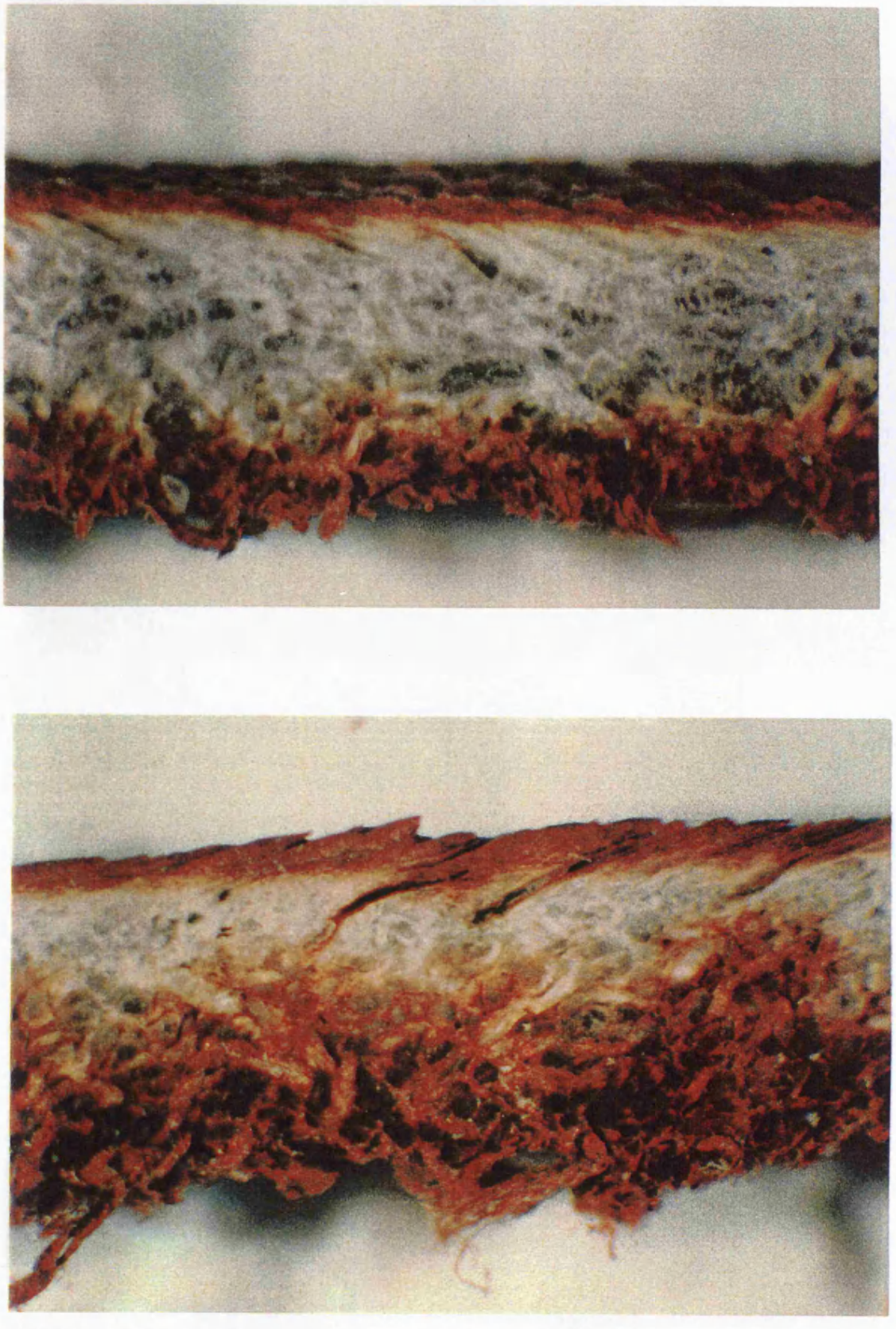


Fig. 3.42 Optical micrographs of wet-blue from bovine hide dyed with (bottom) and without (top) ultrasound (50°C, 100 minutes, Airedale brown 3RG, magnification ×25)

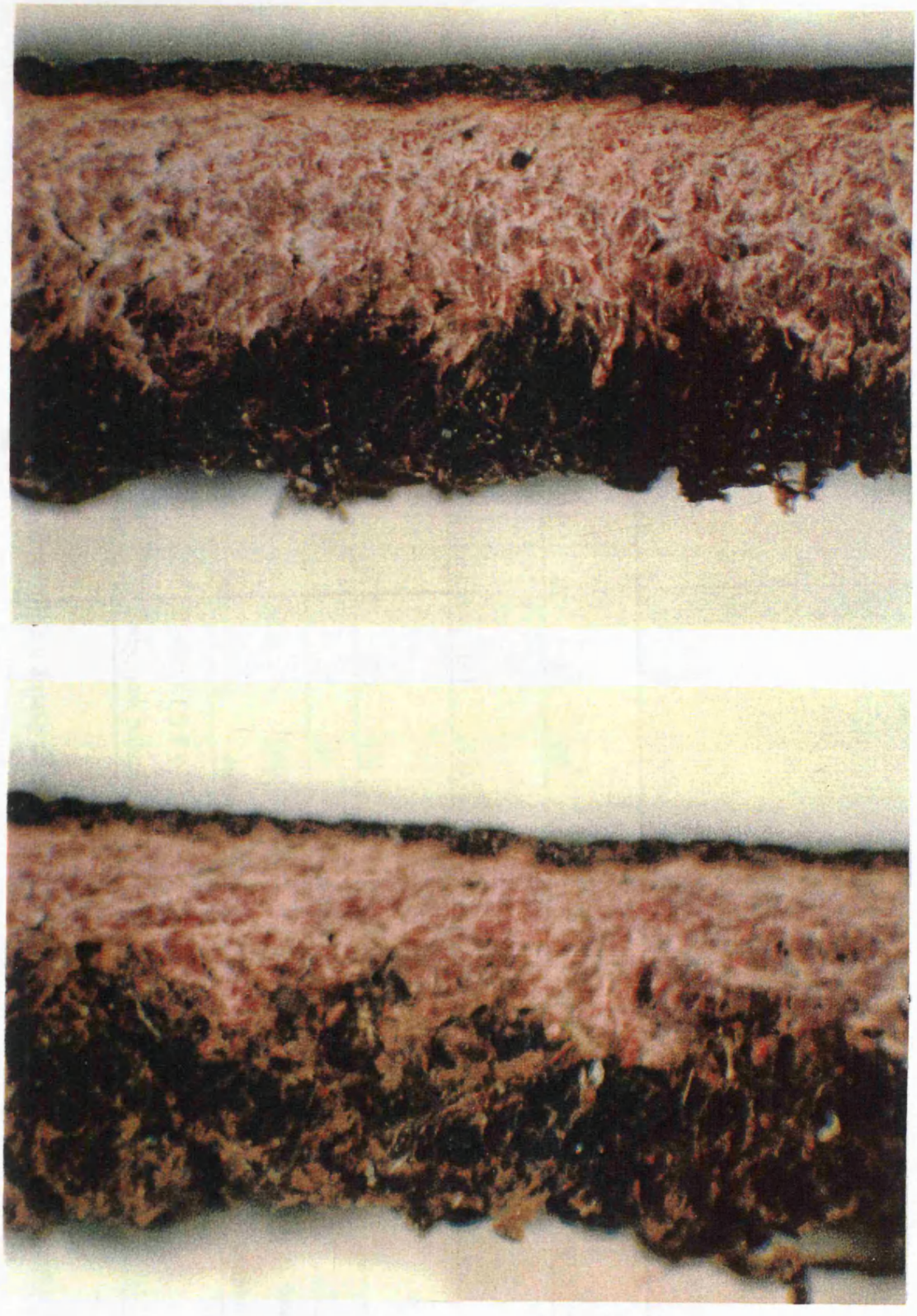


Fig. 3.43 Optical micrographs of wet-blue from bovine hide dyed with (bottom) and without (top) ultrasound (25°C, 75 minutes in drum, Airedale brown DS magnification ×25)

Table 3.9 Dye penetration in the leather samples after dyeing for 100 minutes at 50°C in the glass vessel.

Sample	Retanned leather from sheepskin (1.9 ± 0.1 mm)						Rewetted wet-blue (2.6 ± 0.1 mm)				Resin treated wet-blue (2.7 ± 0.1 mm)					
Dyestuff	Airedale brown 3RG		Airedale black E793		Procion MX-7RX		Airedale brown 3RG		Procion MX-7RX		Airedale brown 3RG		Airedale black E793		Procion MX-7RX	
Ultrasound	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
From grain side (mm)	/	0.4	/	0.35	/	0.4	0.2	0.1	0.2	0.2	0.6	0.3	0.3	0.1	0.6	0.5
From flesh side (mm)	/	1.2	/	1.0	/	1.3	0.9	0.55	1.0	0.7	0.7	0.5	1.4	0.6	1.0	0.7
Penetration (%)	100	84	100	71	100	89	42	25	46	35	50	27	65	29	62	44

A - with ultrasound B - without ultrasound

3.4.3 Effect of ultrasound on dye penetration

As described before, apart from dye uptake, ultrasound can also increases dye penetration. The depth of dye penetration into the leather from both the flesh and grain side was examined by optical microscopy (see section 3.3.4). The results obtained with the glass vessel are listed in Table 3.9 and the optical micrographs are shown in Fig. 3.36-43.

It can be seen that in each case, dye penetration into the leather was increased after sonicating with ultrasound. However, the depth of dye penetration depends on the sample type and the dyestuff used. For retanned leather from sheepskin, the dye penetration with ultrasound was about 50% deeper than that without ultrasound (Figs 3.36 and 3.37, Table 3.9) and the dye nearly completely penetrated the full cross-section of the leather. For resin treated leather using ultrasound, the degree of dye penetration was 50, 65 and 61% for dyestuffs Airedale brown 3RG, black E793 and Procion blue MX-7RX respectively, and they were about twice those obtained without ultrasound (Fig. 3.39, Table 3.9). It was surprising to find that the resin retreated bovine wet-blue had a better dye penetration than the bovine wet-blue leather, although its overall dye uptake was less than the wet-blue leather (see Fig. 3. 15). In addition, these two samples had a totally different surface colour. The wet-blue leather had a dark brown surface colour whereas the resin treated one had a pale brown surface colour. For the bovine crust leather and bovine wet-blue, similar observation were also made (Figs. 3.38-41).

Table 3.10 Dye penetration into bovine wet-blue leather at 25°C for 75 minutes in the metal drum

Dyestuff	Airedale brown 3RG		Airedale Brown DS	
	with ULT	without ULT	with ULT	without ULT
From grain side (mm)	0.2	0.2	0.25	0.2
From flesh side (mm)	1.4	1.0	1.2	0.7
Penetration (%)	61	46	58	35

The above table shows results for the metal drum and it is clear that, even though ultrasound transmission to the metal drum was poor, there was an improvement in dye penetration with ultrasound. The dye penetration in the samples subjected to ultrasound was about 40% deeper than that without ultrasound.

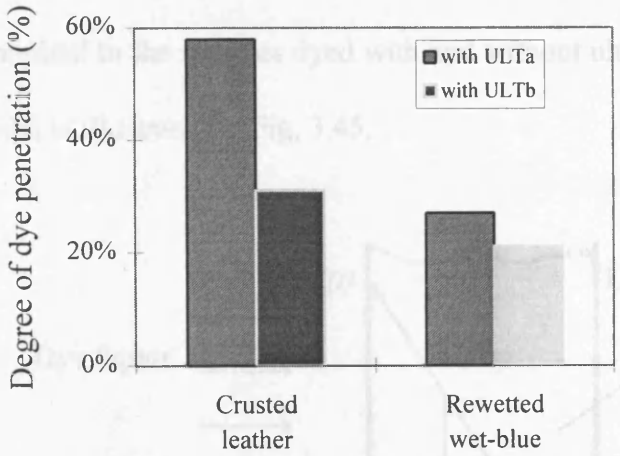


Fig. 3. 44 The dye penetration on sample treated with ultrasound in different stages

Fig. 3.44 shows the dye penetration difference between the different ultrasonic irradiation modes. It was found that the dye penetration in the sample treated by ultrasound in first 20 minutes (ULTa) was greater than that in the sample

treated by ultrasound in the last 20 minutes (ULTb). These results are consistent with those for dye uptake shown in Fig. 3. 23.

As described earlier, leather dyeing occurs by a gradual diffusion of dye molecules from the dyeing bath to deep inside the leather and collagen fibre bundles or fibres. It has been seen that the dye uptake and penetration are markedly increased when ultrasound is used (Table 3.9 and Fig. 3.4-17). From the dye diffusion experiments in the dialysis tube (See section 3.4.2), it was shown that the diffusion coefficients of all types of dyes are higher in the presence of ultrasound. This explains the better penetration achieved by using ultrasound. However, the diffusion process in real leather is much more complicated than that in a dialysis tube because of the large dye absorption which can not be ignored in terms of the effect on diffusion. In order to study the quantitative relationship between diffusion coefficient and dye penetration in the real leather dyeing system, Fick's first law of diffusion is applied to the samples dyed with and without ultrasonic irradiation. The diffusion model is illustrated in Fig. 3.45.

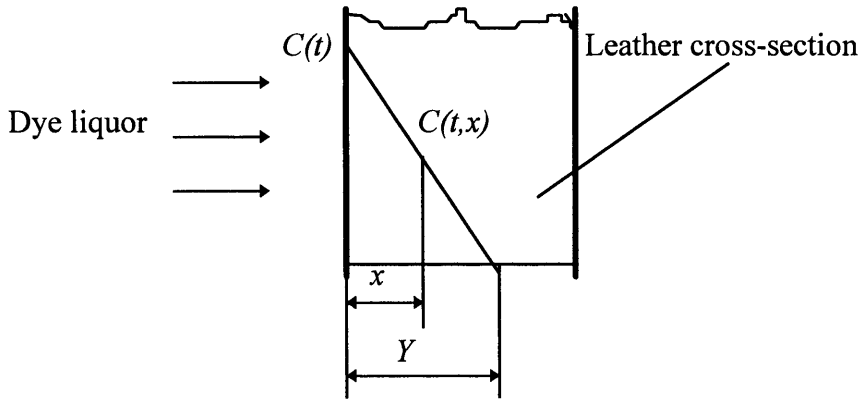


Fig. 3.45 A diffusion model for leather

In this model, at time t, the dye concentration in the dyeing bath is $C(t)$ and the dye penetration depth is Y. At the same time, the dye concentration at x is $C(t,x)$.

Based on Fick's first law, the amount of dye (*s*) diffusing through a unit area should follow equation (3.6).

$$\frac{ds}{dt} = -D\frac{dC(t,x)}{dx} \tag{3-6}$$

where D is the diffusion coefficient of the dye in leather. According to previous investigations [Rys, 1989], it is reasonable to assume a linear distribution of dye concentration within the leather cross section. In other words,

$$C(t,x) = \frac{Y-x}{Y}C(t) \tag{3-7}$$

Therefore,

$$s = \int_0^Y C(t,x)\,dx = \int_0^Y \frac{C(t)\,(Y-x)}{Y}dx = \frac{1}{2}C(t)\,Y \tag{3-8}$$

From equations (3.6~3.8), the following equation can be established.

$$\frac{d}{dt}\left[C(t)\,Y\right] = 2D\frac{C(t)}{Y} \tag{3-9}$$

According to Vickerstaff's work [1954], *C(t)* can be expressed as follows.

$$C(t) = C_\infty + (C_0 - C_\infty)\,e^{-kt} \tag{3-10}$$

where C_0 and C_∞ are the initial and equilibrium concentration in dyeing bath respectively. k is the arbitrary velocity constant [Vickerstaff, 1954]. However, within

the time limit in the present experiment, equation (3-10) may be approximated to equation (3-11), which is found to have a very good fit to experimental data.

$$C_t = C_0 e^{-k t} \ (0<t<\infty) \qquad (3\text{-}11)$$

where k can be determined by the experiment data. Through a series of mathematical treatments, the diffusion coefficient D can be derived from equations (3.9) and (3.11).

$$D = \frac{k Y^2}{2(e^{2kt} - 1)} \qquad (3\text{-}12)$$

Equation (3-12) indicates that the square of the depth of the dye penetration is proportional to the diffusion coefficient. The higher the value of D, the deeper the dye penetration inside the leather. According to equation (3-12), diffusion coefficients of dyes in leathers can be obtained from the dye penetration results (Table 3.9 and Figs. 3.36-43). This was done and all results are shown in Table 3.11. The results in Table 3.11 indicate that the effect of ultrasound on the dye penetration depends on the properties of leather. When ultrasound was used, for example, the dye penetration into the sheepskin sample had the smallest increase, whereas the dye penetration into the resin treated wet-blue had the largest increase.

Table 3.11 The dye penetration (Y) and diffusion coefficient (D) of leather samples dyed with and without ultrasound

Sample		K (1/sec)	Y (mm)	D (cm^2/sec)
Sheepskin/ Airedale brown 3RG at 50°C	with ULT	0.00009	1.4	4.50×10^{-7}
	without ULT	0.00005	1.0	3.04×10^{-7}
Sheepskin /Airedale black E793 at 50°C	with ULT	0.000098	1.1	2.76×10^{-7}
	without ULT	0.00003	0.9	2.65×10^{-7}
Sheepskin /Procion blue MX-7RX at 50°C	with ULT	0.000056	1.4	5.70×10^{-7}
	without ULT	0.00004	1.2	3.96×10^{-7}
Wet-blue / Airedale brown 3RG at 50°C	with ULT	0.000096	1.5	10.2×10^{-7}
	without ULT	0.000047	0.6	1.11×10^{-7}
Resin retanned bovine hide / Airedale brown 3RG at 50°C	with ULT	0.00006	1.8	8.70×10^{-7}
	without ULT	0.000013	0.6	1.38×10^{-7}
Resin retanned bovine hide/ Airedale black E793 at 50°C	with ULT	0.000116	1.4	3.76×10^{-7}
	without ULT	0.00002	0.6	1.32×10^{-7}
Resin retanned bovine hide/ Procion Blue MX-7RX at 50°C	with ULT	0.00008	1.0	2.34×10^{-7}
	without ULT	0.0000316	0.7	2.24×10^{-7}
Crust bovine hide / Airedale black E793 at 50°C	with ULT	0.0000816	1.6	6.28×10^{-7}
	without ULT	0.000028	0.8	2.24×10^{-7}
Crust bovine hide /Procion blue MX-7RX at 50°C	with ULT	0.00008	1.2	3.57×10^{-7}
	without ULT	0.000032	0.8	2.18×10^{-7}

3.4.4 Dye fastness

Rewetted wet-blue leather from bovine hide was dyed at 50°C for 100 minutes in the glass vessel then used for the dye fastness test. Table 3.12 gives the results for dry and wet rub fastness testing. The dry rub fastness for samples dyed with and without ultrasound is nearly the same level, but the wet rub fastness values of samples dyed with ultrasound are better than those dyed without ultrasound. When the stain on the pads after different numbers of revolutions was examined, a deeper coloured stain on the wet pads for the sample dyed without ultrasound was found. This means that the amount of dye on the surface of the sample treated with ultrasound is less than that without ultrasound. This result also confirms the conclusion that a better dye penetration is obtained when ultrasound is applied.

Table 3.12 Wet and dry rub fastness test results (Grey Scale)

Condition	wet-blue from bovine drum dyed with Airedale brown 3RG				wet-blue from bovine drum dyed with Airedale brown DS			
ultrasound	with		without		with		without	
Rub/revolution	wet	dry	wet	dry	wet	dry	wet	dry
256	3	5	3	5	4	5	3	5
512	2	5	2	5	3	5	2	5
1020	1	5	1	4	1	5	1	5

3.5 CONCLUSIONS

The results from this chapter allow the following conclusions to be drawn:

1. By using ultrasound the dyeing process can be either shortened by 40-70% or the same amount of dye uptake can be obtained in the same time at a reduced dyeing temperature.
2. Dye diffusion rate can be accelerated by 20-65%.
3. Dye penetration into leather with ultrasound treatment was about 1.5-2 times deeper than that without ultrasound.
4. Ultrasound is very effective with those dyestuffs that tend to give a poor penetration or dye uptake.
5. For a one hour dyeing process, the dye uptake of leather that is treated with ultrasound in the first 20 minutes of the dyeing process can be twice as high as that of leather treated with ultrasound in the last 20 minutes.
6. Ultrasound is more effective than mechanical agitation in enhancing the dyeing process.

CHAPTER 4

EFFECTS OF ULTRASOUND ON THE FATLIQUORING PROCESS

4.1 INTRODUCTION

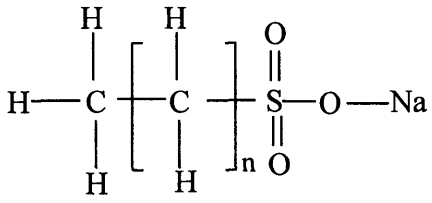
Before the tanning process, natural fat has to be removed from the hide or skin in the degreasing process. Once the fat is removed, the collagen fibres and fibre bundles will stick together after the water trapped between them is evaporated during drying [He, 1981]. This will make the leather very stiff and hard after drying, rendering it unsuitable for producing flexible, soft and strong leathers. Fat thus needs to be re-introduced by a process known as fatliquoring to enhance the softness and flexibility of leather by preventing the collagen fibres from sticking together during drying [Heideman,1993].

Most commercial fatliquoring agents are supplied as a mixture of raw oil and a certain type of surfactant. Based on the properties of the surfactants used, fatliquoring agents can be divided into three groups, i.e., anionic, cationic and non-ionic fatliquors. Among them, anionic fatliquors are the most widely used in the leather industry. Anionic fatliquors are composed of a sulfated or sulfited oil, the neutral oil and some free fatty acids. The sulfated and sulfited oil, containing respectively the water-soluble groups $-OSO_3Na$ and $-SO_3Na$, work as a surfactant to emulsify the neutral oil so that they become dispersed in water as droplets. The degree of sulfation or sulfitation is an important factor in determining the behaviours of these fatliquors. The higher the degree of sulfation or sulfitation, the better the penetration of the emulsion, but the less

the lubricating effect on the leather due to the reduction in neutral oil content. So the selection of the type of fatliquor is dependent on the end use of the product.

Sulfo groups in the fat molecules may bond with amino groups in the collagen fibres and strong ionic linkages are thereby formed [Han, 1990]. At the same time, the neutral oil component precipitates as a hydrophobic layer on the surface of the fibre. As a result, an oily hydrophobic layer will be formed between the wet fibre surfaces. During the course of drying, this layer works as a barrier to prevent inter-fibre cross-links from forming and imparts to the leather a degree of lubrication, bringing about the softness and flexibility that are the essential characteristics of quality leather products [Sharphouse, 1983].

In the present study, a commercial sulfited oil was selected for the fatliquoring process in all the experiments. Sulfited oil is more acid-stable than sulfated oil because the sulfur atom is directly attached to a carbon atom and is therefore a better () of raw oil, resulting in better, deeper lubrication. This oil is normally applied to suede and gloving leathers and other soft leather products. A typical molecular structure for a sulfited fatliquor component is shown in **Scheme 4.1** [Sharphouse, 1983].



Scheme 4.1

The softness of the leather is influenced by a number of factors, such as the fatliquoring conditions and the properties of the fatliquor themselves, i.e. the particle size and the stability of the fatliquor emulsion [Diharce, 1979, Covington, 1989]. These latter two characteristics of the emulsion can be changed by the preparation process. For many years ultrasound has been widely used as a homogeniser in the preparation of highly stable oil/water emulsions and dispersions, especially in the food industry. Previous researchers have done some interesting work in this area in the 1950s and 1960s. Their work has been described in section 1.3.3.3. For the reasons given earlier, i.e. limited availability and high cost of ultrasound equipment, this technique has never been properly applied in the tannery, although it is clearly relevant in the case of fatliquoring. It is necessary to re-assess the feasibility of using ultrasound to enhance the process. It was expected that ultrasound would reduce the particle size, the viscosity and the local interfacial tension of a fatliquor emulsion [Gourlay,1959 and Kotlyarevskaya, 1964] and, as a result, the fatliquor should more easily penetrate and more evenly distribute into the leather to give end products that would have better softness. Based on this hypothesis, a series of experiments was conducted within the present study in order to examine the effects of ultrasound on the fatliquoring process.

4.2 EXPERIMENTAL

4.2.1 Materials

Two types of leather samples were used in the present experiment. One was a wet-blue split from bovine hide with a thickness of 1.9-2.3 mm, which was supplied by Highfield Leathers Ltd (Liverpool, UK). The other was a retanned sheepskin

leather with a thickness of 1.2-1.5 mm, which was made in BSLT tannery (see Appendix I). In order to make the study comparable to industrial practice, a commercial synthetic fatliquor, Remsynol ESI (Hodgson Chemicals Ltd), was used throughout the experiments. The properties of this fatliquor are listed in Table 4.1. The other chemicals used in the process are listed in Table 4.2. Sudan IV was diluted to 2% by weight using 70% ethanol. Dichloromethane and other chemicals were used without further purification.

Table 4.1 The properties of Remsynol ESI fatliquor [Hodgson Chemicals Ltd]

Description	An excellent replacement for sulfited sperm oil based on synthetic esters
Appearance	A clear amber, free flowing oil
Solubility	Readily emulsifiable in cold or warm water forming a fine white emulsion
Active Content	80%
pH	5.0-6.5 for a 10% aqueous emulsion
Charge	Anionic
Stability	Stable to hard water and dilute formic acid

Table 4.2 Other chemicals used in the fatliquoring process (general purpose grade, purity > 97% unless otherwise specified)

Chemicals	Supplier
Sudan IV	BDH Laboratory Supplies
Dichloromethane	BEECROFT & PARTNERS
Ethyl alcohol	BDH Laboratory Supplies
Sodium bicarbonate	East Anglia Chemicals
Sodium formate	Trimstar Laboratory Suppliers Ltd

4.2.2 Fatliquoring procedure

All the leather samples were neutralised by alkaline solutions before fatliquoring. The reason for this is similar to that described for dyeing. The gradient of pH across the leather cross section is critical for the penetration and deposition of fatliquor. The neutralisation solutions were prepared in the same way as that for the dyeing process (section 3.3.1.1.).

The fatliquoring processes was carried out with an 8% offer of Remsynol ESI and 700% water (float) based on the wet weight of leather (typically 15-25 g of leather) using the same experimental device as that for dyeing (see Fig. 2.1). From the dyeing results, it was concluded that mechanical stirring affected the influence of ultrasound on the dyeing behaviour, the fatliquoring experiments in the present study were carried out with mechanical stirring (50 rpm). Ultrasound was used either in the preparation of the fatliquor emulsion or in the fatliquoring process itself. The experiments proceeded in three groups distinguished by the timing and manner of ultrasound application.

1. In the first group, the fatliquor emulsions were prepared by magnetic stirring and leather samples were fatliquored in the presence of ultrasound for 30, 60 and 90 minutes at temperatures of 20, 40 and 60°C respectively.
2. In the second group, the oil emulsions were prepared by magnetic stirring and ultrasound either was used in the first 30 minutes or in the last 30 minutes of the fatliquoring process at 40°C

In the third group, the samples were fatliquored at 40°C for 30 and 60 minutes using a Remsynol ESI emulsion that had been prepared by ultrasound or magnetic stirring for 30 and 60 minutes.

In order to compare the results with those obtained in a normal fatliquoring process, each group of experiments was repeated without using ultrasonic irradiation under otherwise the same conditions. To study the distribution of the fatliquor across the cross section of the leather, the fatliquored samples were sliced into three layers using a bandknife-splitting machine (located at BLC The Leather Technology Centre). Each layer had a thickness of about 0.6-0.7 mm. From flesh to grain sides, these layers were named as outer corium (OC), inner corium (IC), and grain (GN) layers respectively. The oil contents (also referred to as fat contents) of three layers were measured individually.

4.2.3 Measurement

In order to evaluate the effects of ultrasound on fatliquoring, the properties of the fatliquor and the fatliquored samples were measured, i.e. the particle size of the fatliquor emulsion, the oil content and the distribution of the oil within the leather.

4.2.3.1 Particle size

About 100 mL of the aqueous fatliquor emulsion with a 1% (w/v) concentration of Remsynol ESI was prepared using ultrasound irradiation for different periods of time at 20, 40 and 50°C respectively in a glass vessel mounted on the ultrasonic unit (Fig. 2.1). After irradiation the samples were kept at the same temperature as that at which they were prepared. The control samples were prepared at the same temperature with magnetic stirring instead of ultrasound irradiation. Samples were added to the test cell (~5 mL each time) of the particle size analyser (Coulter Counter particle size analyser, located in BLC). Ten readings were taken for each sample and an average value was obtained based on these readings.

4.2.3.2 Viscosity of Remsynol ESI emulsion

Emulsions of 5% and 10% concentrations (w/v) of the fatliquor oil (Remsynol ESI) were prepared at 25°C with either ultrasound or magnetic stirring for 30 minutes, then the viscosity of the emulsion was measured over a range of shear forces and at 20, 30 and 40°C using a Brookfield DV-III Rheometer.

4.2.3.3 Oil content test

The oil content of the fatliquored leather was measured by the standard official method [SLC 4:1966]. The fatliquored samples were air-dried to a constant weight and then ground in a milling machine (APEX Construction Ltd). About 10 ± 0.1 g of ground leather was placed in a thimble filter which was then covered by a thin layer of cotton wool (grease free) and placed inside a Soxhlet extraction apparatus. Before extraction, the solvent flask was dried at 102±2°C for 30 minutes, cooled in a desiccator, and its weight (W_0) recorded. The extraction was carried out with dichloromethane for 5 hours. The extract was then distilled to removed the dichloromethane. The flask with residue was dried in an oven for four hours at 102 ± 2°C and cooled down for 30 minutes in a desiccator. The final weight was W_1. The oil content in leather can be expressed as follows:

$$F(\%) = \frac{W_1 - W_0}{W_s} \times 100 \qquad (4\text{-}1)$$

where W_s is the weight of the original leather sample.

4.2.3.4 Penetration of fatliquor

After drying at room temperature for a week, small pieces of leather were taken from the fatliquored samples. These pieces were then cut through their cross section into very thin layers using a freezing microtome (Cryocut 1800, located at BLC). All the cut slices were placed in a distilled water bath first and then rinsed in a 50% ethanol solution. After this preliminary treatment they were then transferred into a saturated solution of Sudan IV in 70% ethanol. The samples were stained for one hour and then moved into a 50% ethanol solution [Koppenhoefer et al., 1940]. After these steps the samples were ready for examination. A gradient in the depth of the reddish colour was apparent and reflected the distribution of oil along the cross section of fatliquored leathers. The samples were sandwiched between a slide and a cover glass and fixed with glue. Photographs were taken as appropriate.

4.3 RESULTS AND DISCUSSION

4.3.1 Effects of ultrasound on the properties of fatliquor emulsion

4.3.1.1 Particle size of fatliquor emulsion

Particle size is one of the most important factors characterising the nature and performance of an emulsion and influences the stability and penetration of the fatliquor. In general, the smaller the particle size of a fatliquor emulsion, the better is the penetration into leather [Heidemann 1980].

1% aqueous fatliquor emulsions were prepared at 20, 40 and 50°C using either ultrasound irradiation or magnetic stirring for different periods of time. The particle sizes of the samples were measured by a Coulter Counter particle size analyser. The

results show that the particle size was reduced by 18%, 14 % and 22% at 20°C, 40°C and 50°C respectively after 30 minutes ultrasound treatment (Table 4.3). Figure 4.1 shows the changes of particle size after sonicating for different period of time. For a 15 minute irradiation, the particle size is 71 nm which is nearly the same as that of the sample prepared by magnetic stirring. When the irradiation time increases to 30 minutes, the particle size is reduced to 61 nm. However after another 30 minutes irradiation, the particle size remains nearly the same. This implies that there is an optimum irradiation time which gives the minimum particle size and further irradiation may not generate any significant effect (Fig. 4.1).

Table 4.3 The mean particle size of ESI fatliquor emulsion obtained either with a 30 minutes application of ultrasound or magnetic stirring

Temperature °C	20		40		50	
Preparation method	ULT	Stirring	ULT	Stirring	ULT	Stirring
d (nm)	65.44	80.4	61.2	71	53	68.3
SD	26	22	24	20	14	19

Note: ULT - ultrasound; Stirring - magnetic stirring;
d - average diameter of oil emulsion (from 10 readings)
SD - standard deviation

When ultrasound is used to prepare fatliquor emulsions, it is expected that cavitation at the interface between the immiscible phases results in the breakdown of the oil/water barriers with the generation of very high speed jets from one liquid into the other. Such fast moving jets will speed up the formation of the oil/water emulsion (Fig. 4. 2) [Mason, 1991]. The sudden collapse of the cavitational bubbles at or near

the interface of particles causes enormous shear forces which will be sufficient to fragment the droplets of oil and produce a finer particle size emulsion [Boudjouk, 1988]. It is further expected that the reduction of the droplet size will change the physical or chemical properties of the emulsion, such as solubility and stability. The relationship between droplet size and solubility can be expressed as follows:

$$\ln\frac{S_1}{S_2} = \frac{\gamma V}{RT}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \qquad (4\text{-}2)$$

where S_1 and S_2 are the solubility of particles with radii of r_1 and r_2 respectively, γ is interface tension and V is the molar volume of the liquid in the droplet. From this equation, it can be seen clearly that the smaller the particle size, the higher the solubility.

When the oil containing an emulsifier is dispersed in water and the concentration of the emulsifier reaches a certain critical level, three different types of molecular 'complex' may be formed in the system. In one, the emulsifiers themselves aggregate to form micelles. In the second, the so called 'soluble micelles' (diameter ~40-100 Å) form a very small amount of oil packed inside the micelle. In the third, a small droplet of oil forms with emulsifiers being adsorbed on its surface (Fig. 4.3) [Jilin, p505]. Due to the irradiation by ultrasound, a finer fatliquor emulsion may be produced. The number of smaller particles would increase and more "soluble" micelles would be formed. Such "soluble" micelles can form a thermodynamically stable solution [Durham, 1961]. This type of micelles has a markedly smaller diameter of about 4-10 nm which could penetrate into the collagen fibril bundle and help to keep the fibrils separate. In addition, a large number of the smaller particles should give a more uniform oil distribution for the fatliquored leather.

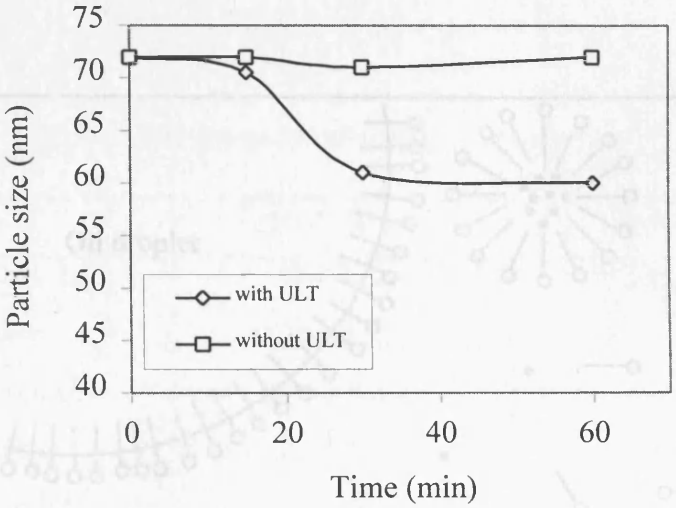


Fig. 4.1 The particle size of fatliquor emulsion (ESI) obtained with and without ultrasound treatment

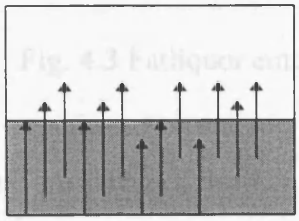


Fig. 4.2 The schematic presentation of cavitational jet effect at the water-oil interface

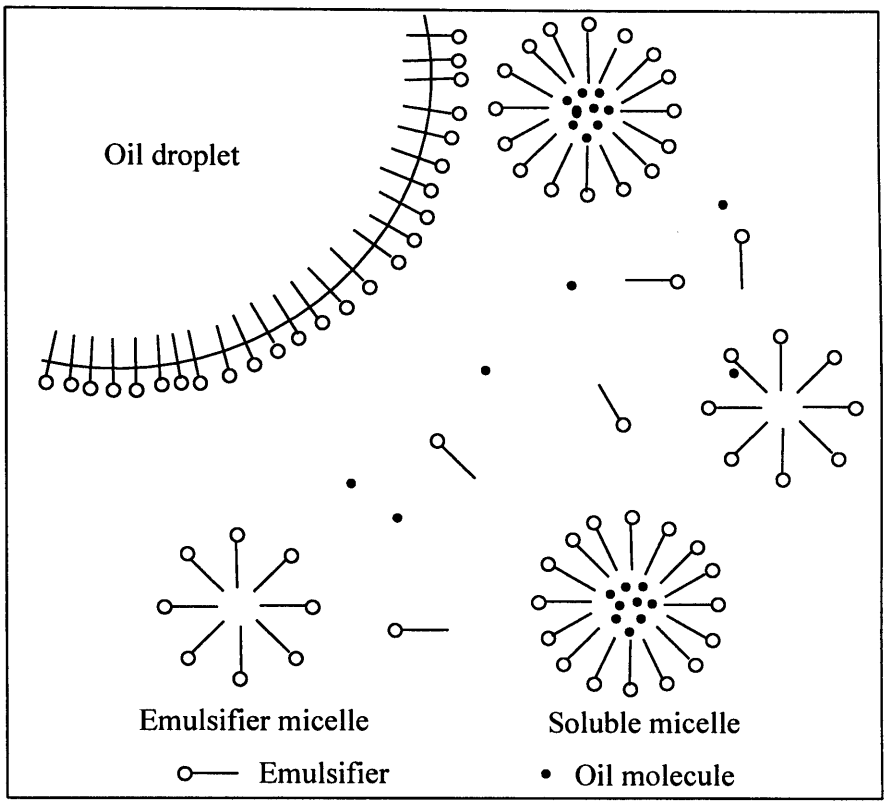


Fig. 4.3 Fatliquor emulsion in water

Obviously the physical structure of leather means that only a fatliquor emulsion below a certain particle size can get through. Generally speaking, leather can be considered as a porous material. It is well known that the triple helices of polypeptide chains have a diameter of ~15 Å and form microfibrils which in turn form fibrils. A fibril contains ~7000 collagen molecules and has a diameter of ~100 nm [Heidemann, 1980]. These fibrils may be seen as basic units which combine further to form fibril bundles (fibres) and finally fibre bundles. The hierarchy of

collagen structures in the corium layer is shown in Table 4.4 [Alexander, 1993]. Within this fibrous structure, there are many spaces which are potentially the pathway for the penetration by the fatliquor emulsion particles.

Table 4.4 The hierarchy of collagen structure

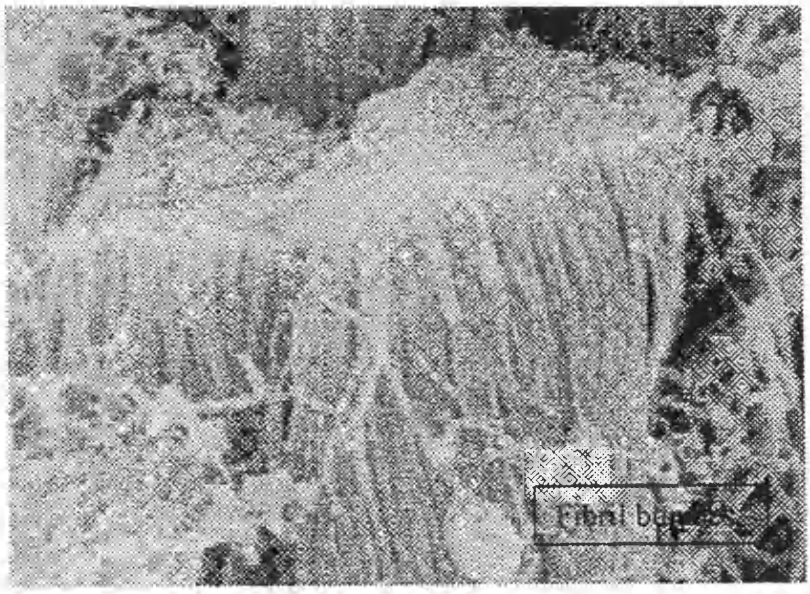
Unit	Typical diameter	Average gaps
Fibre bundle	60-200μm	*500-1000 nm
Fibre	30-60 μm	/
Fibril bundle	3-6μm	/
Fibril	100-200 nm	*10-50 nm
Microfibril	10 nm	

* estimate values

From previous investigations, it is known that the average distances between fibrils are in the order of 10~50 nm and between fibril bundles are the order of 500~1000 nm (Fig. 4.4) [Heidemann p29-30, 1993]. However, in order to penetrate into these spaces, fatliquor particles have to be much smaller than those average distances. The fatliquoring behaviour of fatliquor emulsions with different particle sizes has been intensively studied by Covington and Alexander [1993]. Their results indicated that only those emulsion particles of ~5 nm could penetrate into the fibril bundles, to reach the surfaces of fibrils, while those emulsion particles larger than 25 nm can only reach the surfaces of the fibril bundles [Covington and Alexander, 1993]. Because of the three dimensional network of fibres, it is almost impossible for a fatliquor droplet to find a passage which maintains the average distance mentioned above all the way from the leather

surface to the deep inside. Unless they are very small, therefore, fatliquor droplets are stopped before they can reach deep inside the leather. Only very tiny drops would have the chance to get deep inside of leather. Consequently, particle size is extremely important for fatliquor penetration. The present results indicate that ultrasound is very useful in preparing a fine emulsified fatliquor with very small particle size.

It is clear that the reduction in the particle size of fatliquor emulsions will be beneficial in several respects. As mentioned above, it will increase the oil penetration into the leather and give a more uniform distribution of the oil across the whole cross section. As a result, a softer leather should be produced.



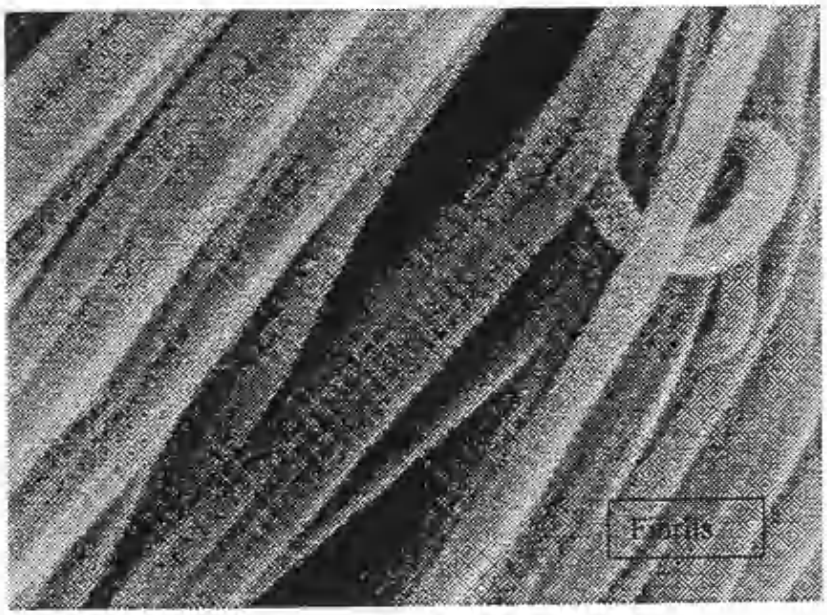


Fig. 4.4 Fibrils (×50,000) and fibril bundles (×1,000) [Heidemann, 1993]

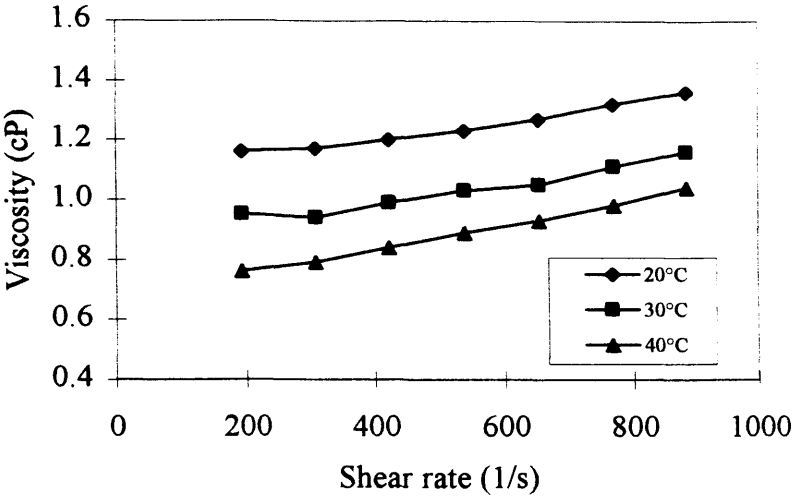


Fig. 4. 5 The viscosity of a fatliquor (Remsynol ESI) against shear rate, 5% (w/v) concentration emulsion prepared by 30 min. ultrasound treatment

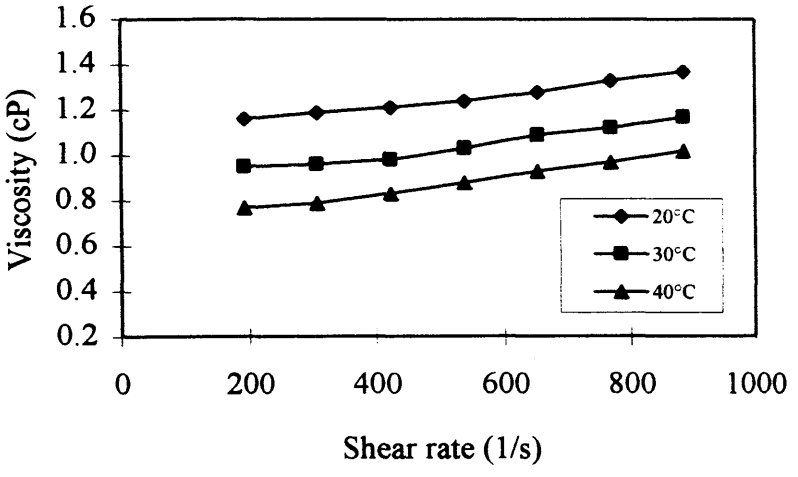


Fig. 4.6 The viscosity of a fatliquor (Remsynol ESI) against shear rate, 5% (w/v) concentration emulsion prepared by 30 min. magnetic stirring

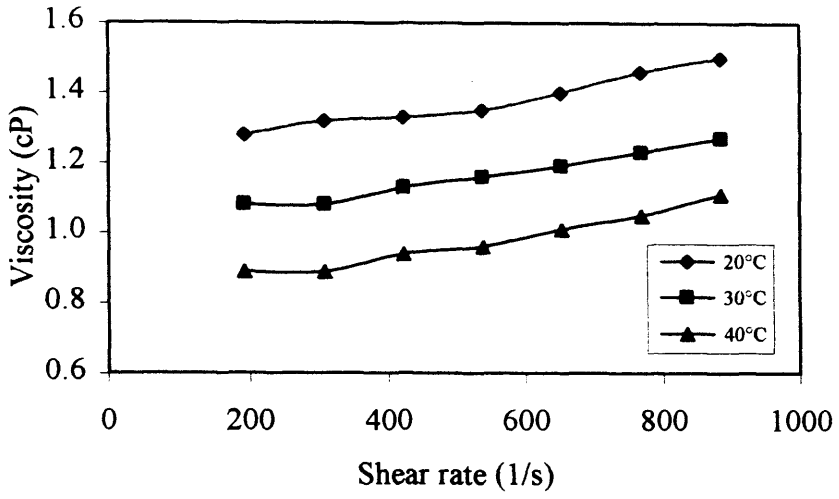


Fig. 4.7 The viscosity of a fatliquor (Remsynol ESI) against shear rate, 10% (w/v) concentration emulsion prepared by 30 min. ultrasound treatment

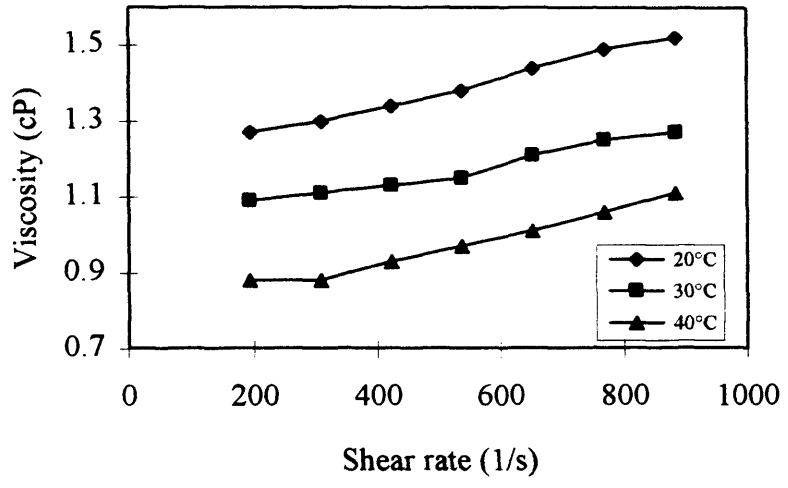


Fig. 4.8 The viscosity of a fatliquor (Remsynol ESI) against shear rate, 10% (w/v) concentration emulsion prepared by 30 min. magnetic stirring

4.3.1.2 Viscosity of fatliquor

The viscosity of a fatliquor is also a very important property, since it will directly affect the oil penetration into the leather. It is well known that the lower the viscosity of a fatliquor, the higher its mobility will be and the better its penetration. As described in the last section, the particle size of ESI emulsion became smaller after ultrasound treatment and it is known that emulsion particles size can affect emulsion viscosity; it was therefore necessary to measure the change of viscosity of fatliquor after ultrasound treatment.

The viscosity (η) is defined by the quotient S/V (where S is the shear stress and V is the shear rate) and it can vary as a function of V (non-Newtonian liquids). 5% and 10% concentrations of Remsynol ESI fatliquor emulsion were prepared either by ultrasonic agitation or by magnetic stirring for 30 minutes. The results for their viscosities are presented in Figs. 4.5-4.8. It can be seen that the viscosity of the fatliquor emulsion produced by ultrasound treatment is only slightly different from that prepared by magnetic stirring, and they are both non-Newtonian liquids (the viscosity slightly increased when the shear rate increased). It can also be seen that the viscosity of fatliquor emulsion decreased as the temperature increased. For instance, when the temperature increased from 20 to 40°C, the viscosity of the fatliquor emulsion prepared with ultrasound for 30 minutes dropped from 1.22 to 0.89 cP, and that prepared without ultrasound dropped from 1.27 to 0.88 (at a shearing rate of 192 s^{-1}). In addition, the higher the concentration, the higher is the viscosity. When the concentration changed from 5% to 10%, the viscosity increased from 1.36 to 1.5 cP at 20°C, and from 1.04 to 1.11 cP at 40°C (Figs. 4.5-4.8). These effects of temperature, shear rate and concentration are all consistent with the generally observed behaviours

of emulsion [Becher, 1965]. From the results it can be seen that the viscosity of Remsynol ESI emulsion is low (the viscosity of water at 20°C is 1 cP) even at a concentration of 10%. As far as viscosity is concerned, it does not pose a problem for the emulsion to penetrate inside the leather. However, the degree of oil penetration depends heavily on the conditions of the leather sample, i.e. the surface charge, pH across the cross section and temperature. It has been reported that neutralisation is not always even across the cross-section [Otto, 1958] and if this is the case with that there is uneven fat distribution in the leather. Although the particle size of the emulsion is reduced by ultrasound, this does not seem to greatly affect the viscosity.

4.3.2 The influence of ultrasound on the oil content of the leather

Two types of leather sample were fatliquored either with or without ultrasound and in each case with or without mechanical stirring. The oil contents in the fatliquored leather samples were then measured. From the results in Table 4.5, it can be seen that, as may be expected, the oil contents are higher with stirring than without. The highest oil contents were achieved in the sample fatliquored in the presence of ultrasound and mechanical stirring (speed 50 rpm). In the case of wet blue, for instance, they are 7.79% at 40°C and 10.25 % at 60°C. The lowest values were found for the samples which had been fatliquored without either ultrasound or mechanical stirring. The amount of oil in these samples was only 2.60% at 40°C and 3.59% at 60°C. It was also found that the amount of oil in the sample subjected to mechanical stirring was higher than that in the sample which had been fatliquored in the presence of ultrasound irradiation only. The overall order of oil contents was thus as follows:

ultrasound + stirring > stirring > ultrasound > without ultrasound or stirring.

On the basis of these results, it appears that mechanical action is highly important for fatliquoring. Therefore, in the present study, all the fatliquoring processes were carried out in the presence of mechanical stirring (50 rpm).

Table 4.5 The oil content of bovine wet-blue and retanned sheepskin leather after treatment at 40°C and 60°

Temperature (°C)	40				60			
Ultrasound/ Stirring	U+S	S	U	N	U+S	S	U	N
Wet-blue leather	7.79	6.11	4.44	2.60	10.25	8.57	5.59	3.59
Retanned sheepskin	8.03	7.13	6.65	/	17.26	14.17	13.44	/

S - mechanical stirring; U - Ultrasound; N - without ultrasound or stirring

While subjected to mechanical stirring, the wet-blue bovine leather was fatliquored either conventionally or with ultrasound under a series of different conditions. In the first group of experiments, the samples were treated with ultrasound at the same temperature for different periods of time. The oil contents of wet-blue leather which had been subjected to ultrasound at 60°C for 30, 60, and 90 minutes are given in Fig. 4.9; the results for the samples not exposed to ultrasound are also shown in this figure. Several points may be noted. Firstly the relative increases in oil content obtained by using ultrasound are 42%, 20% and 13% for 30, 60 and 90 minutes, respectively. Secondly, the oil content after ultrasound treatment for 60 minutes is 10.25%, almost the same as that found after ultrasound treatment for 90 minutes (10.27%). This indicates that after 60 minutes fatliquoring with ultrasound irradiation the oil level has reached its equilibrium value (i.e. increasing fatliquoring time beyond

60 minutes is not necessary). On the other hand, the oil content in the leather treated with ultrasound for 30 minutes is similar to that processed without ultrasound for 60 minutes. This clearly demonstrates that by using ultrasound it is possible to shorten the fatliquoring time significantly.

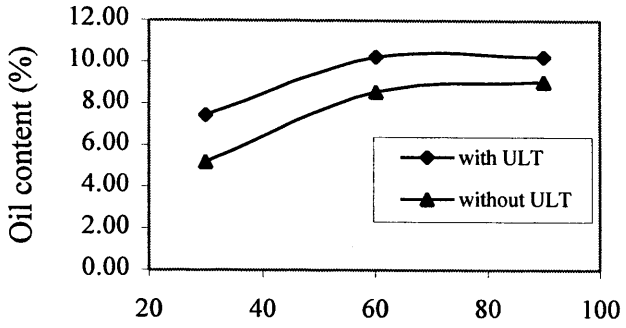


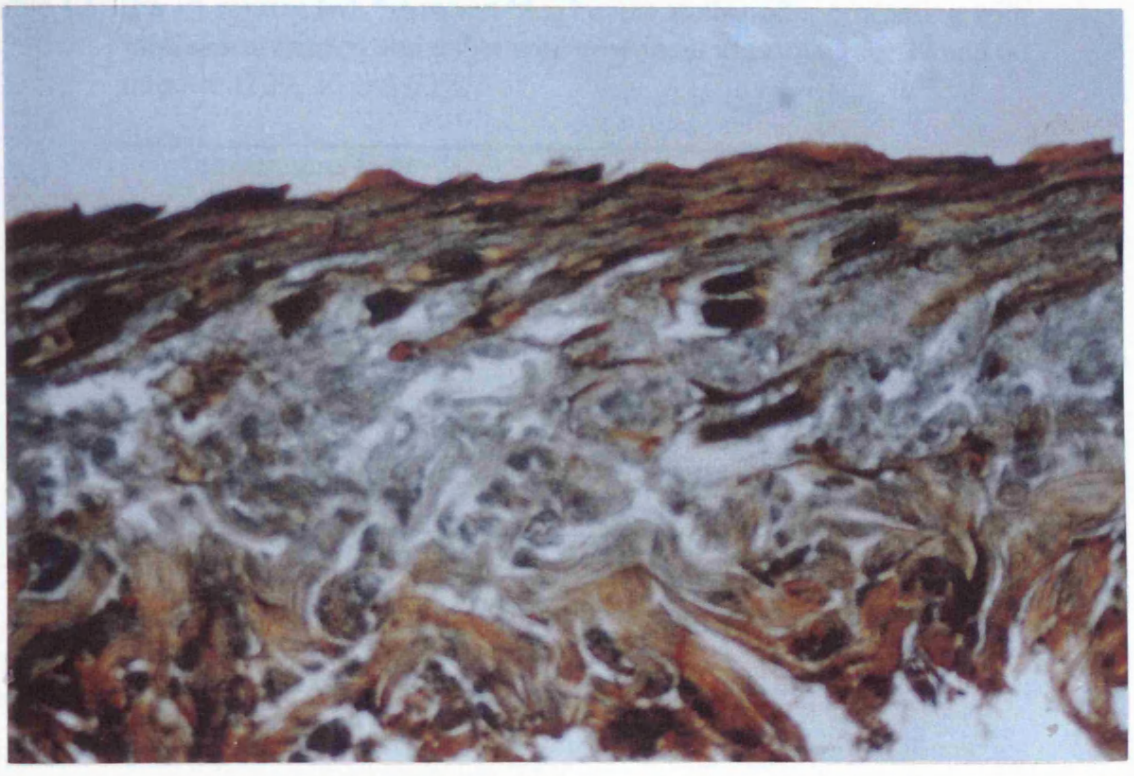
Fig. 4.9 Oil content in wet-blue bovine leather after treatment at 60°C (with mechanical stirring)

The effect of ultrasound on the oil content has also been examined after treatment at different temperatures. The results are shown in Table 4.6. In all cases, the oil content of the leather increases as the temperature is increased. The oil contents in the samples treated with ultrasound at a lower temperature can reach the same level as those in the samples processed without ultrasound treatment at a higher temperature. For instance, the oil content after processing at 20°C for 30 minutes with ultrasound is 5.61% which is higher than that found after processing at 40°C without ultrasound (4.97%). For a 60 minutes process time a similar pattern is also apparent. Clearly the application of ultrasound can achieve the same or ever higher oil contents either at lower process temperatures or shorter process times compared with a normal

fatliquoring process. This conclusion is supported by the micrographs shown in Fig. 4.10. The oil deposited in the sample was stained by the dye Sudan IV. Fig. 4.10a shows the leather fatliquored with ultrasound treatment. It is clear that the fatliquor is much better distributed throughout the whole cross-section of the leather, compared with the sample processed without ultrasound treatment (Fig 4.10b). It is clear that in this latter case, only a relatively thin layer of oil is observed on the flesh and grain sides.

In the case of retanned sheepskin, use of ultrasound can also increase the oil contents but the observed increases are much lower than that for wet-blue bovine leather, e.g., from 7.13% (40°C, 60 min without ultrasound) to 8.03% (40°C, 60 min with ultrasound). It would seem that the reasons for this difference between bovine hide and sheep skin are: (i) that the fibre structure of the sheep skin is looser than that of bovine hide, and (ii) the thickness of the sheepskin was only 70% of that of bovine hide. Both these factors meant that it was easier for oil droplets to penetrate into the sheepskin leather and so good penetration could be obtained even without ultrasound. Thus this suggests that ultrasound is more effective in improving the fatliquoring of thicker bovine leathers.

A



B

Fig. 4.10 Optical micrographs of oil distribution within the cross section of leather fatliquored for 60 minutes at 40°C (A-with ULT, B-without ULT; magnification x30)

Table 4.6 The oil content (wt. %) in wet-blue bovine leather after processing with mechanical stirring and either with or without ultrasound for 30 and 60 minutes at 20, 40 and 60°C

Temperature/Time		With ULT	Without ULT
20°C	30 minutes	5.61	4.45
	60 minutes	6.07	5.57
40°C	30 minutes	6.42	4.97
	60 minutes	8.26	6.15
60°C	30 minutes	7.45	5.21
	60 minutes	10.25	8.57

As described in the experimental section (section 4.2.2), another group of experiments were conducted where ultrasound was applied at the different stages (either in the first 30 minutes or in the last 30 minutes) of the fatliquoring process. Fig. 4.11 gives the results for the oil contents obtained with samples from this group. It can be seen that higher oil contents were achieved for the samples exposed to ultrasound for the last 30 minutes compared with those exposed in the first 30 minutes. When ultrasound was used in the first 30 minutes of the fatliquoring process, the fast moving jet formed from the collapse of cavitation bubbles may have forced some of the larger oil droplets into the voids between fibres and fibrils. Such droplets could have become a barrier for the further penetration of oil emulsion (Fig. 4.11). This will be discussed further below.

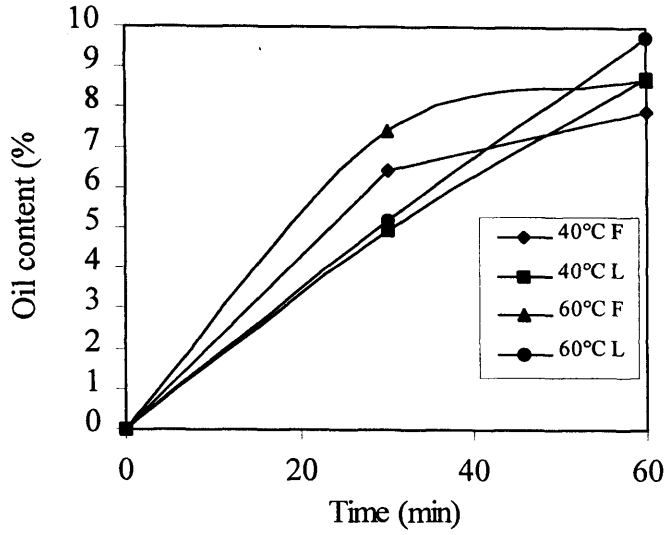


Fig. 4.11 The oil contents of samples fatliquored in the presence of ultrasound applied at different stages (F- first 30 min. L- last 30 min.)

As described in section 4.3.1.1, the mean particle size of the ESI fatliquor emulsion generated using ultrasound was clearly reduced and a finer emulsion was obtained. In the last group of experiments, the fatliquor emulsions were prepared either using ultrasound or magnetic stirring and then wet blue samples were fatliquored with mechanical stirring (50 rpm) for 30 or 60 minutes. The oil contents in the fatliquored samples were measured and the results are shown in Table 4.7. Clearly the oil contents of the leather fatliquored with an emulsion which had been pre-treated using ultrasound were higher than those fatliquored with an emulsion prepared by magnetic stirring. By using the emulsions pre-treated with ultrasound for 30 and 60 minutes, the amount of oil in the leather after fatliquoring was increased by about 35% and 40% respectively.

Table 4.7 The oil content (%) of leather fatliquored at 40°C

	ULT (30 min)	stirring (30 min)	ULT (60 min)	stirring (60 min)
Fatliquoring for 30 minutes	6.89	5.077	7.52	5.17
Fatliquoring for 60 minutes	8.94	6.59	9.08	6.57

Average results from five experiments.

ULT - fatliquor emulsion was pre-treated by ultrasound

Stirring - fatliquor emulsion was prepared by magnetic stirring

Another interesting point is that the amount of oil present in the sample fatliquored using an emulsion pre-treated with ultrasound for 30 minutes is nearly the same as that fatliquored with an emulsion pre-treated for 60 minutes. For example, these values are 8.94 % and 9.08 % respectively after a fatliquoring process lasting for 60 minutes at 40°C. These results indicate that the characteristics of the fatliquor emulsion, such as particle size, solubility and stability, have reached an optimum level after 30 minutes exposure to ultrasound. This result confirms the conclusion of section 4.3.1.1, that is, the particle size of a fatliquor emulsion reaches a stable level after 30 minutes ultrasound treatment.

From the results obtained in this section, it is clear that the particle size of the fatliquor emulsion is one of the most important factors affecting the amount of oil deposited in the leather. The oil absorbed by leather has been increased significantly by the application of ultrasound. This may reduce the consumption of fat used in this process. In addition, an increase in oil content can favourably affect the mechanical properties of the final product in various aspects. For example, Matttei and Roddy

[1957] examined the effects of fatliquor concentration on the mechanical properties of leather. They found that the tensile strength was increased by as much as 42% and the elongation at rupture increased by up to 34% by increasing the oil content of leather. They attributed their results to the increases in fibre mobility resulting from the higher oil content.

4.3.3 The distribution of oil in leather

The distribution of oil across the different strata of the cross section is another important factor affecting the flexibility of leather products. The more the oil is deposited in the inner layers, the softer the leather [Heidemann, 1993]. As described previously, the oil distribution across the cross-section of the leather is normally more or less uneven. In this section, the oil distribution in three different layers from grain to flesh of the leather samples was studied. Fatliquor emulsion (Remsynol ESI) was prepared either by magnetic stirring or by ultrasonic irradiation and then the fatliquoring process was carried out either with only mechanical stirring (50 rpm) or with a combination of ultrasound and mechanical stirring. After fatliquoring, all the samples were air-dried and split into three layers each with a thickness of about 0.6~0.7 mm, i.e. outer corium (OC), inner corium (IC), and grain (GN) layers (section 4.2.2). Table 4.8 summarises all the oil contents under different fatliquoring conditions. It can be seen that for each layer the oil content was increased when ultrasound was used either in preparing the fatliquor emulsion or in the fatliquoring process itself. This can be seen clearly by comparing Processes 1 and 2. It can be seen that the relative increases of oil contents were 54%, 87% and 3% in the GN, IC and OC layers respectively when ultrasound was used for the fatliquor emulsion

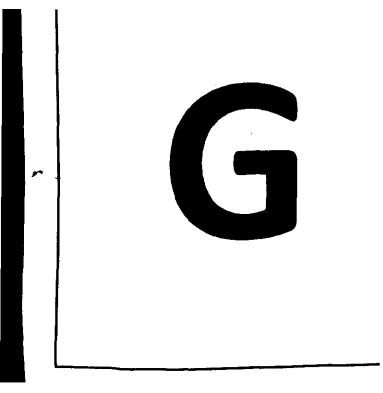
preparation. Similar results were obtained from Processes 3 and 4 or 1 and 6 (Table 4.9). It can be confidently stated that the reason for this is the reduction of the particle size of the fatliquor emulsion obtained when ultrasound is used.

Another feature to note in Table 4.8 is that the oil contents vary greatly between the three layers. GN and OC layers have much higher oil contents than IC layers. Obviously the outer-skirt location of the GN and OC layers is the most important reason for this irregularity. On the other hand, even GN and OC layers still have different oil contents under the same fatliquoring conditions. This can be attributed to the difference in the density of fibre packaging between grain and corium layers.

Leather may be thought of as consisting simply of two layers which have distinctly different structures, i.e. grain and corium layers (Fig. 4.12) [Bailey, 1988]. The grain layer is composed of interwoven collagen fibres with a very fine diameter (~1 μm) and contains the hair follicles [Haines, 1981]. The fibre network thus has a very high surface area which encourages the adsorption of oil molecules as long as the fatliquor particles are small enough to reach the surface of the fibres. When the cellular structures have been decomposed by chemical processing, i.e., unhairing, the resultant fibrous mat has many voids and a reduced density [Bailey, 1988].

Table 4.8 The fatliquoring processes (at 40°C) and oil contents in all samples

Fatliquoring processes	Fat emulsion prepareing				Fat liquoring process				Fat content (%)		
	stirring		ultrasound		stirring		ultrasound				
	30	60	30	60	30	60	30	60	GN	IC	OC
1	√				√				5.22	2.09	5.73
2			√		√				8.041	3.9	5.903
3	√					√			6.58	2.79	6.77
4			√			√			8.473	4.019	6.82
5				√		√			8.44	4.64	7.14
6	√				√		√		5.5	3.33	7.62
7		√				√		√	6.10	3.71	7.68



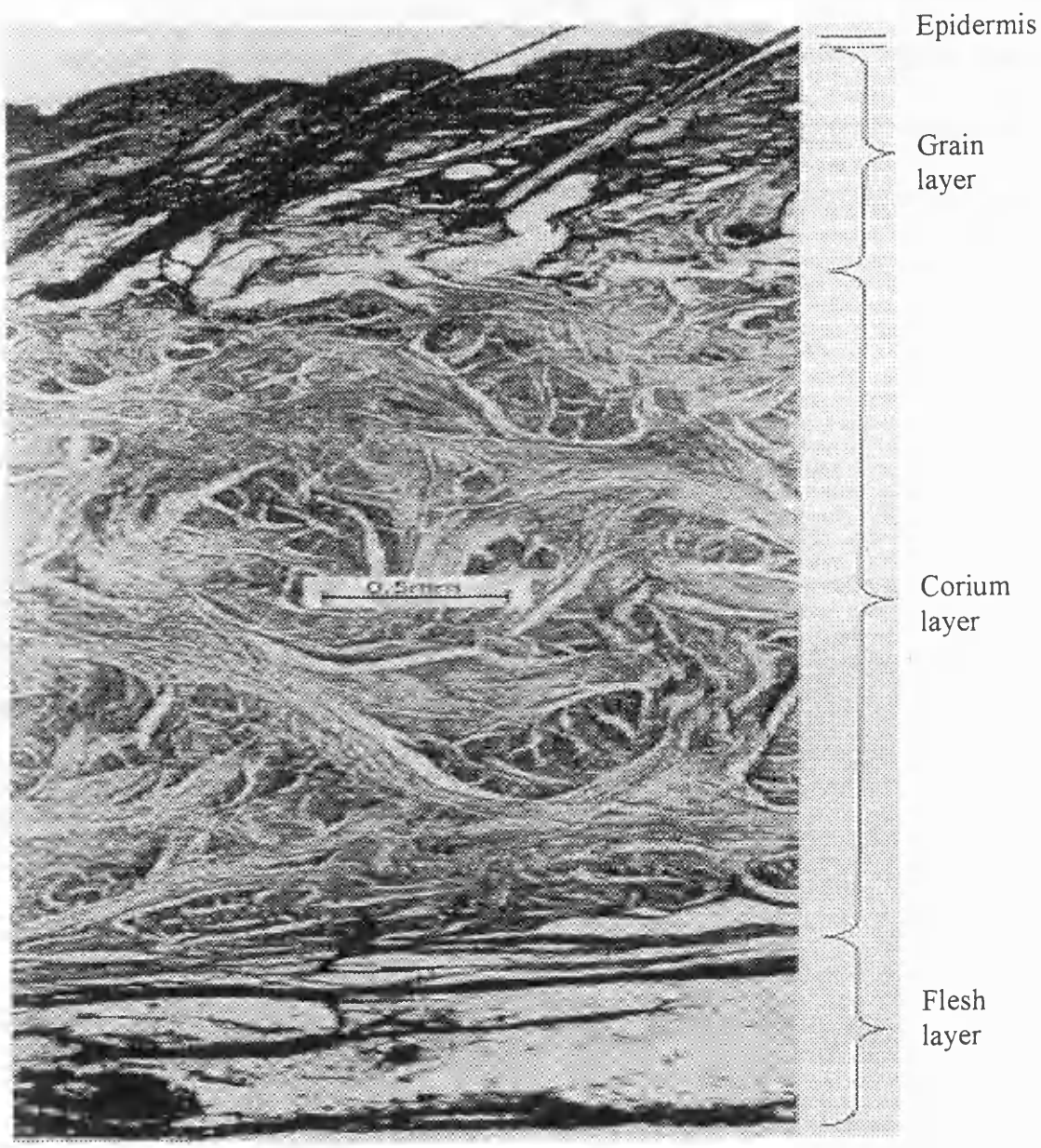


Fig. 4.12 The structure of hide [Bailey, 1988]

These factors are the physical basis for the observed high oil content in the grain layer. The corium layer has a structure rather different to that of the grain layer and is composed of thick bundles of collagen fibres. Such fibre bundles have a diameter of ~100 μm [Haines, 1981]. Obviously the fibrous network is much coarser than that of the grain layer and hence it will have a much lower surface area. In addition, within the corium layer, the fibre structure also shows a certain degree of irregularity. Towards the centre of the corium, i.e. IC layer, fibre bundles become even coarser and stronger. The fibres in IC layer are woven in a much tighter way than that in the OC layer [He, 1980]. This makes the penetration of fatliquor particles more difficult compared with the OC layer. So the oil content in the corium layer is lower than that in grain layer.

Table 4.9 The change in oil content obtained by using ultrasound

Process	1 and 2	3 and 4	1 and 6	3 and 7
GN layer	54.0%	28.7%	5.7%	-7.3%
IC layer	86.6%	44.1%	59.3%	32.9%
OC layer	3.02%	0.7%	32.8%	13.4%

In Processes 2, 4, and 5, the fatliquor emulsion was treated by ultrasound before the fatliquoring process, so the emulsion particle size had been reduced (Section 4.3.1.1). As a result, the penetration may be expected to be enhanced and the overall oil content is therefore increased. This is quite clear and easy to understand. However,

the situation in Processes 6 and 7 is much more complicated. The particle size of the emulsion becomes a very important factor in this case. From the results in section 4.3.1.1, it is known that the emulsion particles were of the order of 50-100 nm. This size is of the same order as the space between collagen fibrils [Heidemann, 1980]. Variations of the particle size in this range are therefore very critical to the penetration and hence the oil content. In Processes 6 and 7, the fatliquor emulsions were not prepared by ultrasound, so the particle size should be larger than that in Processes 2, 4, and 5. Table 4.8 shows that the oil contents for Process 7 are lower than those for Process 4 or 5, except for OC layer. This means that the effect of particle size is more significant than the direct effect of ultrasound on the fatliquoring process. If this is the case, what might be the reason? In the early stage of Processes 6 and 7, some relatively large particles might be forced into the voids on the surface of the sample, i.e. the outer layers of GN and OC layers. The salts or acid residues left on the leather by the previous processes would tend to break the emulsion and lead to the deposition of oil on the fibre or fibril surface [Otto, 1965]. A larger continuous oil phase would then occur. In addition, $-SO_3H$ groups in these deposited oil particles may form salt linkages with $-NH_2$ group in collagen [He, 1990]. Therefore it would become much more difficult for ultrasound to further emulsify the deposited oil. Those deposited oil layer will work as a barrier to block the further penetration of other fatliquor particles, even those which had been emulsified into very fine particles by the later ultrasonic irradiation. This conclusion is supported by the observation of the IC layer oil contents which could be considered as a indicator of the degree of penetration. All the oil contents of the IC layers subjected to Processes 2, 4, and 5 are higher than those subjected to in Processes 6 and 7.

Another difference between Processes 2, 4, 5 and Processes 6 and 7 can be seen from Table 4.8 when the oil contents in the GN and OC layers are compared. In Processes 2, 4, and 5, the oil contents give an order of GN>OC, while in Processes 6 and 7, the opposite is observed (i.e. OC>GN). This is most likely due to emulsion particle size differences between these two groups. In Processes 6 and 7, the emulsion particles may be expected to be larger, so it is more difficult for them to penetrate into the GN layer than into the OC layer due to the more dense structure of the GN layer. The oil content in the GN layer should thus be lower than that in the OC layer as is observed. In contrast, in Processes 2, 4, and 5, the emulsion particle size has been reduced already, so the penetration into the GN layer may be expected to be enhanced. Therefore the order of oil content has changed into GN>OC.

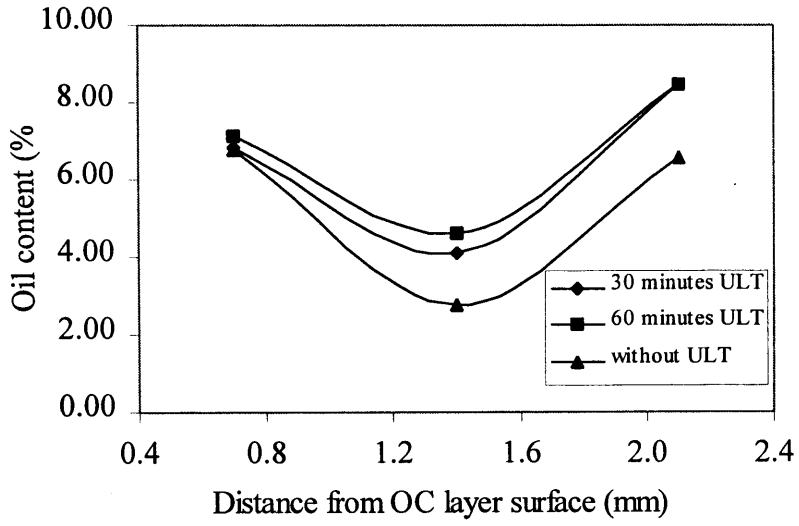


Fig. 4.13 Oil contents in different layers
(Samples fatliquored for 60 minutes with emulsion pre-treated by ultrasound for 30 and 60 minutes, 0~0.7: OC, 0.7~1.4: IC, 1.4~2.1: GN layer)

Another point which is apparent from Table 4.8 is the time dependence of ultrasound effects. When the fatliquor emulsion is prepared by ultrasound for 30 or 60 minutes, the oil contents in the leather are not much different. This can be seen clearly from the results in Processes 4 and 5 (Fig. 4.13). The reason is similar to the previous discussion of dyeing: that is, the particle size of fatliquor emulsion has reached a minimum level after treatment by ultrasound for 30 minutes (see section 4.3.1.1).

4.4 CONCLUSIONS

It is clear that the application of ultrasound indeed improves the oil penetration into the wet-blue bovine hide. Use of ultrasound on a fatliquor can produce a high quality oil/water emulsion. The particle size of such emulsions can be reduced by 20-30% by using ultrasound treatment. The oil content of leather is significantly increased after fatliquoring with an emulsion prepared by ultrasound. The increase is mainly from the middle split or inner corium layer (up to ~90%) and grain layer (up to ~50%), whereas the increase in the flesh split or outer corium layer is marginal. However, when ultrasound is directly applied to the fatliquoring process, the increase of oil content is mainly from the flesh and middle split. The results also show that ultrasound can be used to shorten the fatliquoring process time by 50% and lower the process temperature by 20°C.

CHAPTER 5

EFFECTS OF ULTRASOUND ON TANNING PROCESSES

5.1 INTRODUCTION

Tanning is the process which stabilises the collagen fibres so that they are no longer biodegradable. At the turn of the century almost all leather was tanned with plant extracts (so called vegetable tannins). Today, however, 80% of the leather manufactured in the world is made using chromium(III) as the tanning agent [Luck, 1986 and Thomson 1985]. Apart from vegetable and chromium tannages, other tannages which are widely used are based on aldehydes, oils, aluminium, zirconium and combinations of these tannages [Sharphouse, 1983]. However, the tanning process is always lengthy and time consuming, especially vegetable tanning. In some cases, such tanning takes several weeks or even longer.

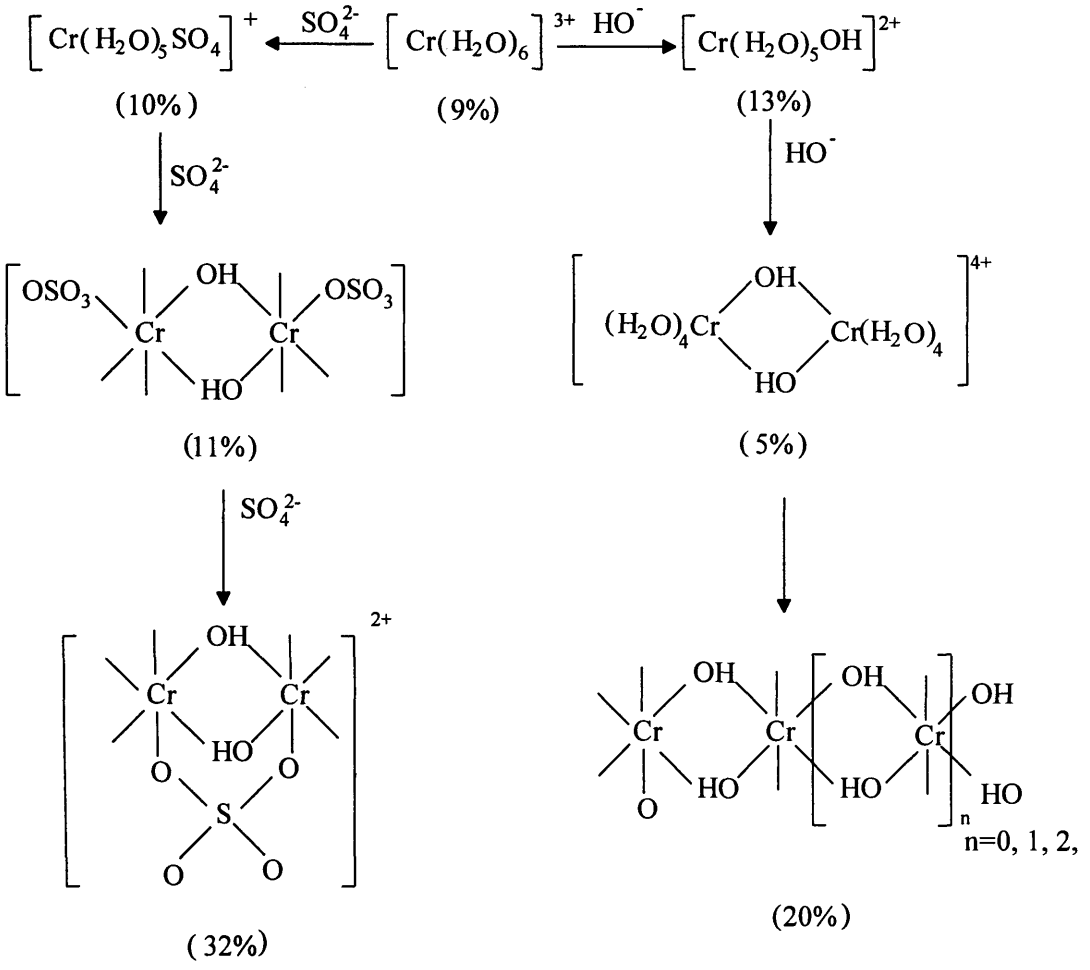
It is hypothesised that the application of ultrasound in the tanning processes can give a shortening of the process time, and an increase in the degree of fixation of tanning agents (hence reducing the effluent from the tanning discharge). In addition, the end product quality may be improved when ultrasound is used. In this Chapter, the results of using chromium, vegetable and aldehyde tannages in the presence or absence of ultrasound under different tanning conditions are reported. The properties of the tanned leather are also presented and discussed. The possible mechanisms whereby ultrasound influences different tanning processes will be discussed

5.1.1 Chromium tanning

Chromium(III) or chrome tannage has several advantages over other tannages. Among them, the high shrinkage temperature (T_s) obtainable, normally above 100°C, is perhaps the most important. In addition, chromium tanned leather has very good resistance to chemical and biological attack. No other tannages could surpass the dominant place of the chromium at present [Leather, 1996]. However chromium tanning has perceived drawbacks, the chromium-containing waste being a matter of serious environmental concern [Tang, 1993]. Although there has been no firm evidence to suggest that chromium(III) ions used in tanning are an environmental hazard, the trend is to investigate other options. Quite clearly the chromium content in the effluent from tanneries has to be minimised, and this issue has become, or is becoming, a major challenge for tanneries throughout the world. Numerous attempts have been made to solve this problem. For instance, reducing the chromium offer, changing tanning conditions, or using dicarboxylic acids during tanning can achieve a higher level of chromium exhaustion and so reduce the chromium residue in the discharged tanning liquor [Scholnick, 1992; Evans, 1987].

In chromium tanning, trivalent state chromium sulphate salts with various degrees of basicity are normally used. When dissolved in water, the chromium salts tend to form complexes with water molecules. It is found that the hydrolysis of chromium salts results in a complex mixture of basic salts of various molecular sizes. Takenouchi [1980 and 1981] has successfully separated nine species from a glucose-reduced 33% basicity chromium sulphate solution using ion-exchange chromatography and found each component had a different affinity for the collagen. The nine species are shown in **Scheme 5.1**. A 33% basicity chromium sulphate is the most commonly used chrome powder in tanneries, because this type of product has a

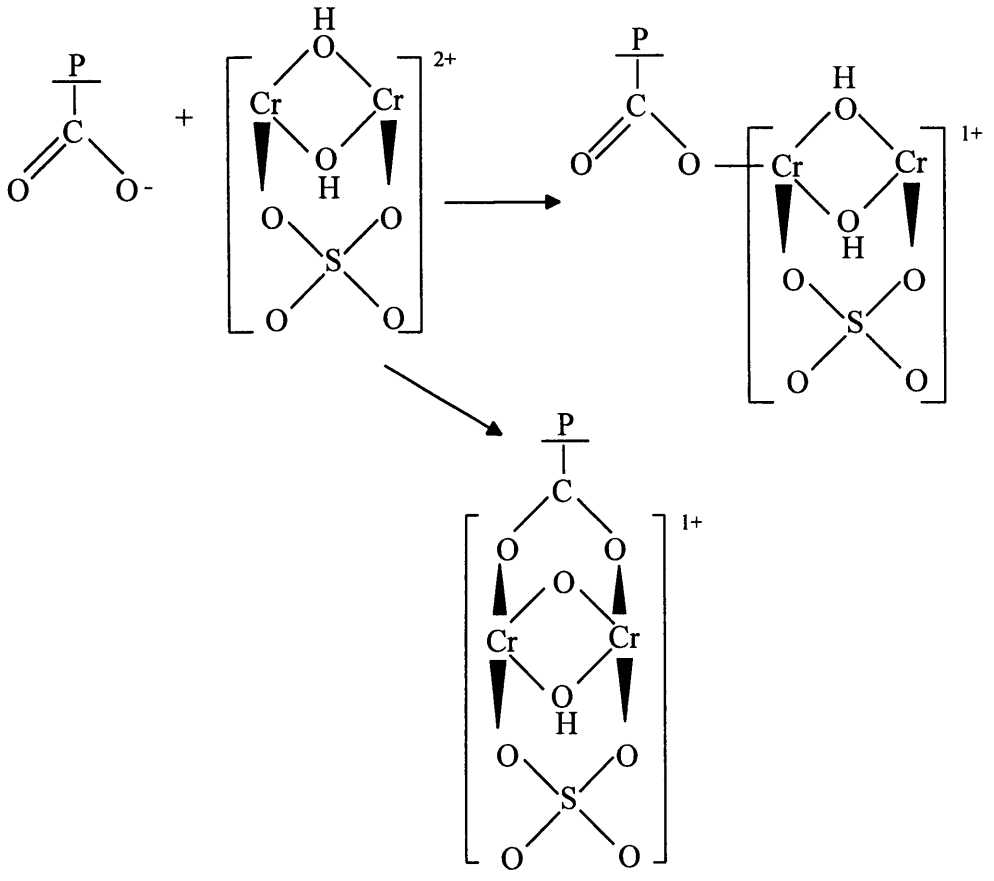
"gentle" fixation combined with a better penetration compared with higher basicity chromium salts.

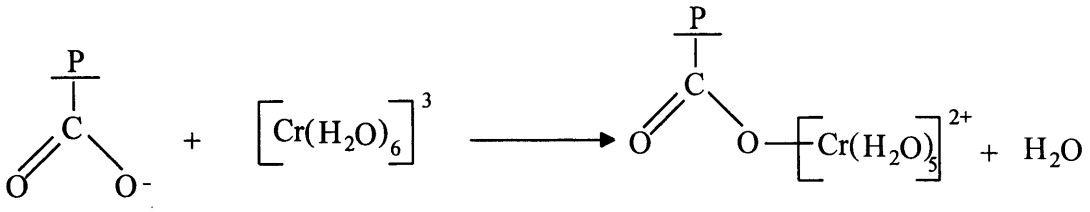


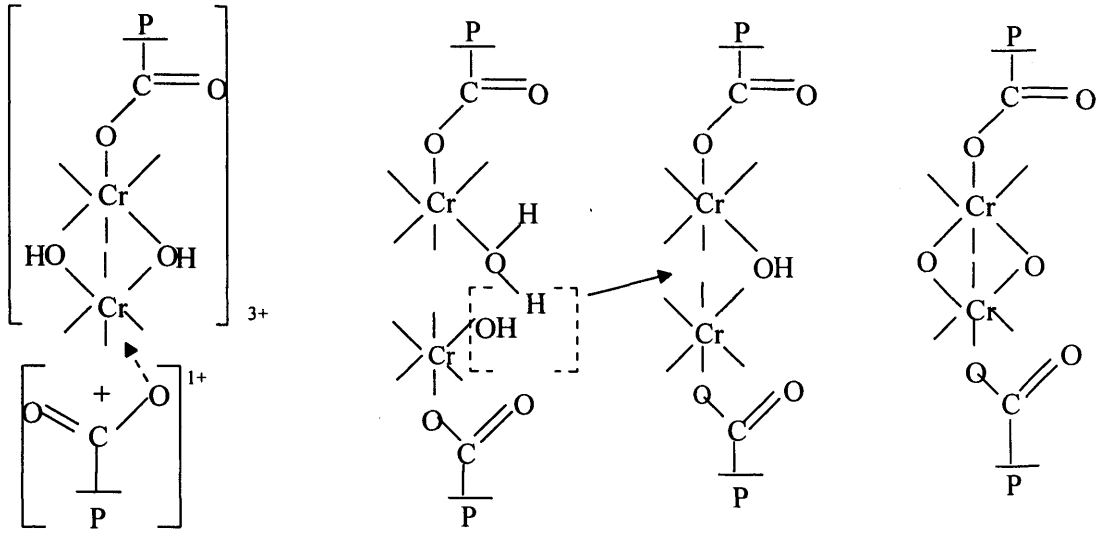
Scheme 5.1

The mechanism of chromium tannage has been studied for 70 years [Gustavson, 1956; Bienkiewicz, 1983; He, 1985]. It is widely accepted that chromium tanning takes place by co-ordination of the carboxyl groups in collagen with the chromium complexes. In other words, the chromium complexes form chemical crosslinks between the ionised carboxyl groups in the collagen molecules. This mechanism was first postulated by Gustavson in 1924. Since then, many

researchers have confirmed Gustavson's theory using different approaches [Bienkiewicz, 1983, Thorstensen, 1958, He, 1981]. A typical reaction between collagen and a chromium complex (from 33% basicity chromium sulphate) is shown in **Scheme 5.2**. During the formation of these chromium complexes, a carboxylate group in the collagen replaces a water molecule and a linkage is formed between bi-nuclear chromium complexes and the collagen molecule.







Scheme 5.2 The reaction between collagen and chromium complexes

P- denotes the collagen [He, 1990]

The chromium based tanning process proceeds in two stages. In the first, usually carried out at low pH (2.5-3), the molecular size of the chromium complexes is relatively small and the reactivity is kept low in order to achieve the best penetration of chromium within the collagen network of hides or skins. In the second stage (fixation), the complexes need to be reactive enough and large enough to form effective crosslinks between the triple helices. This is a critical stage for the tanning and has to be balanced carefully by controlling pH and temperature.

5.1.2 Vegetable tanning

Vegetable tannage used to be the major tannage in leather making, but it was gradually replaced by chromium tannage. Nowadays, due to above mentioned environmental concerns related to chromium pollution, vegetable tanning is once

again drawing the attention of both industry and academia. Many combination tannages based on vegetable tanning materials and non-chromium mineral tannages have been intensively studied and used as an alternative to chromium tannage [Hernandez, 1984; Covington, 1993; Ioannidis, 1989 and Tang, 1993]. From their results, it seems that vegetable tanning will play an increasingly important role in future developments. However, as noted previously vegetable tanning is often a very time-consuming process, in some cases taking up to 6 weeks [He, 1980]. Although new tanning techniques have shortened the tanning time considerably, vegetable tanning is still one of the longest processes in leather making. The reasons for this are due to vegetable tannins' large molecular sizes and colloidal aggregation characteristics, and due to their high affinity to collagen which affects their penetration. In addition, many vegetable tanned leathers have a final tannin content of 25-50%, compared with chromium tanned leather which only has 3-6% Cr_2O_3 content [Heidemann, 1993]. Penetration of such large amounts of high affinity, high molecular mass tanning materials will obviously take a much longer time than other tannages

Vegetable tanning materials are somewhat similar to dye molecules. They both consist of relatively big particles and form aggregates in water. Based on the results of Chapter 3 and 4, it would be a reasonable hypothesis that ultrasound could benefit the vegetable tanning process by reducing the particle size of the tanning material.

Vegetable tannins are naturally occurring materials obtained from the bark, wood, leaves, fruit, root and pods of plants [Haslem, 1966]. Tannins are generally described as water soluble polyphenolic compounds having a molecular mass

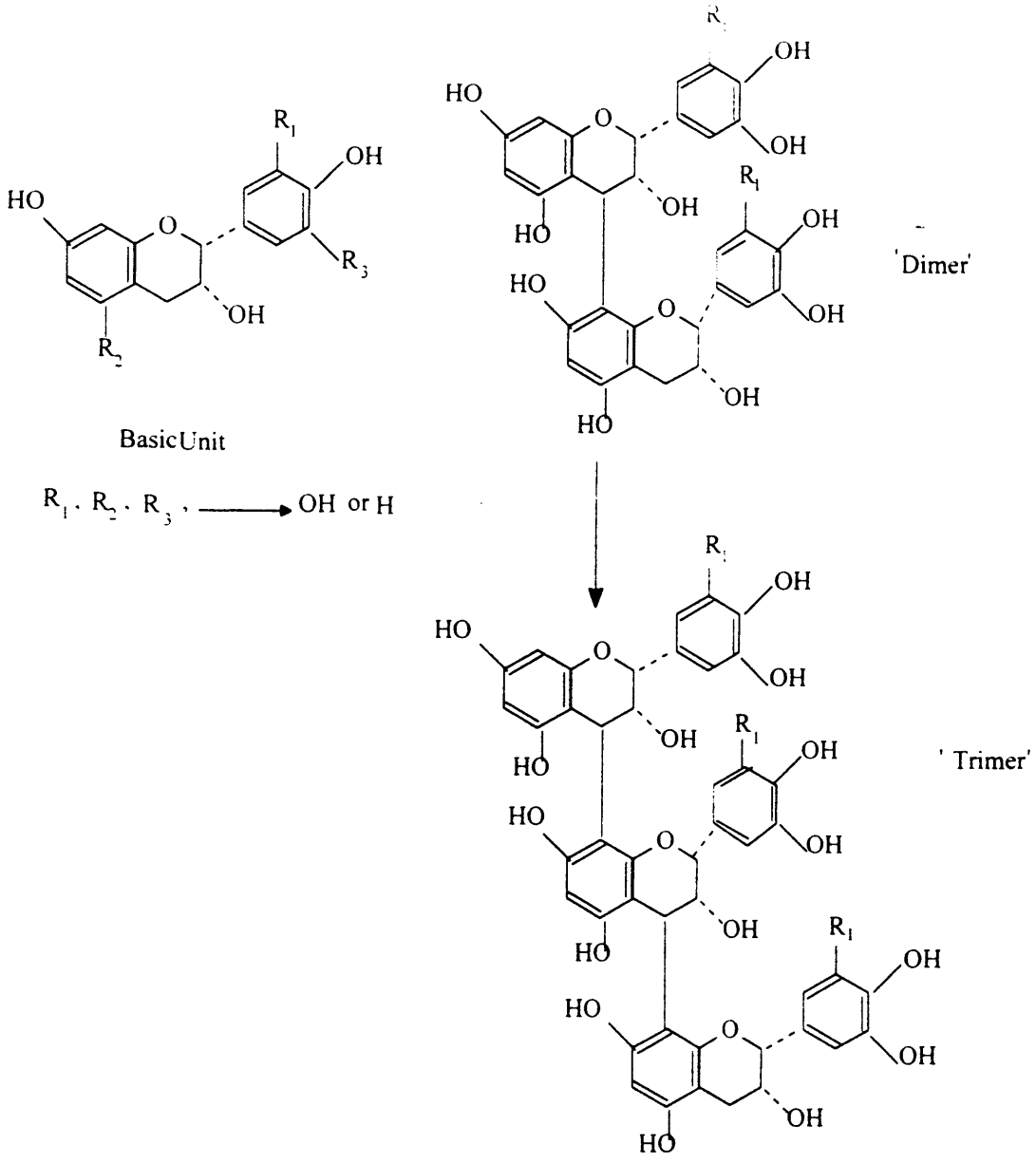
between 500 and 3000 [Zhang, 1985]. Their structures vary from plant to plant. Vegetable tanning materials contain both tannin and non-tannin substances which, due to their similar properties, are very difficult to separate. However, it may be suggested that the non-tannins play a significant part in the tanning process by dispersing the large aggregates of tannin, so that their penetration into the hide or skin is made easier [Zhang, 1985].

Tannins are normally classified into two main groups according to their hydrolysis reaction with acid, i.e.: (1) Pyrogallol, hydrolysable tannins such as chestnut and valonea; (2) Catechol, condensed tannins such as mimosa and quebracho.

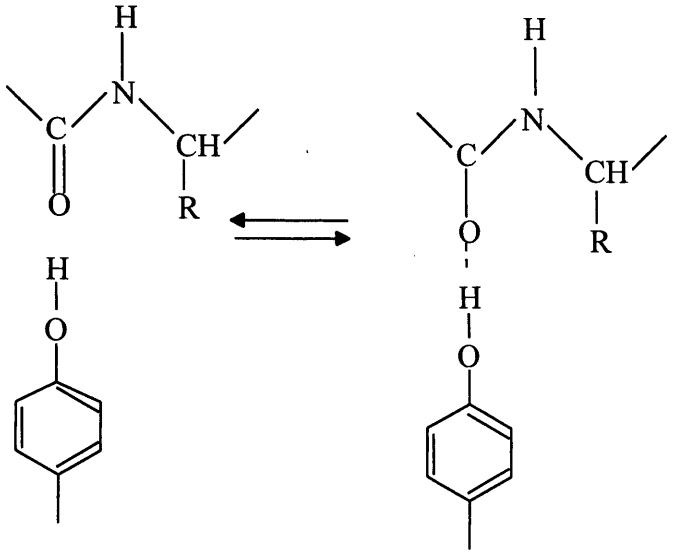
When treated with hot acid, the first group are hydrolysed into sugar and gallic acid or its derivatives such as ellagic acid; the second group are polymerised into even larger molecules or even precipitates, known as phlobaphens. Using condensed tannins may produce better quality leather and give higher shrinkage temperatures than using the hydrolysable tannins [Tang, 1993]. One of the condensed vegetable tannin materials, mimosa, was selected for the present research. Condensed mimosa tannins have been defined as flavone tannins. The basic unit and oligomers of mimosa tannins are shown in **Scheme 5.3** [Heidemann, p 395, 1993]. It has been found that mimosa contains several different substances which are condensed by the basic units into high molecular mass compounds. Such compounds easily form aggregates in an aqueous medium [Zhang, 1985].

It has been suggested that the vegetable tannin combines with collagen via multi-point hydrogen bonding and hydrophobic interactions [Shuttleworth, *et al.* 1968], but the occurrence of some covalent bonding has also been suggested

[Gustavson, 1966]. Although research on vegetable tanning has been carried out for a long time, the mechanism of such tanning is still not fully understood. However, the hydrogen bonding theory is generally accepted and the proposed formation of hydrogen bonds between phenolic groups and the peptide bond is shown in **Scheme 5.4**.



Scheme 5.3 Chemical structure of mimosa

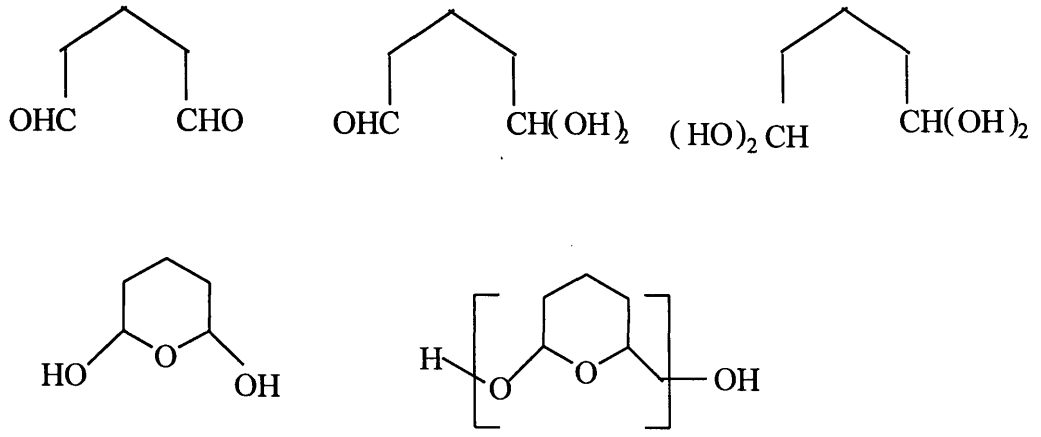


Scheme 5.4 The interaction between vegetable tannin and collagen [Han, 1994]

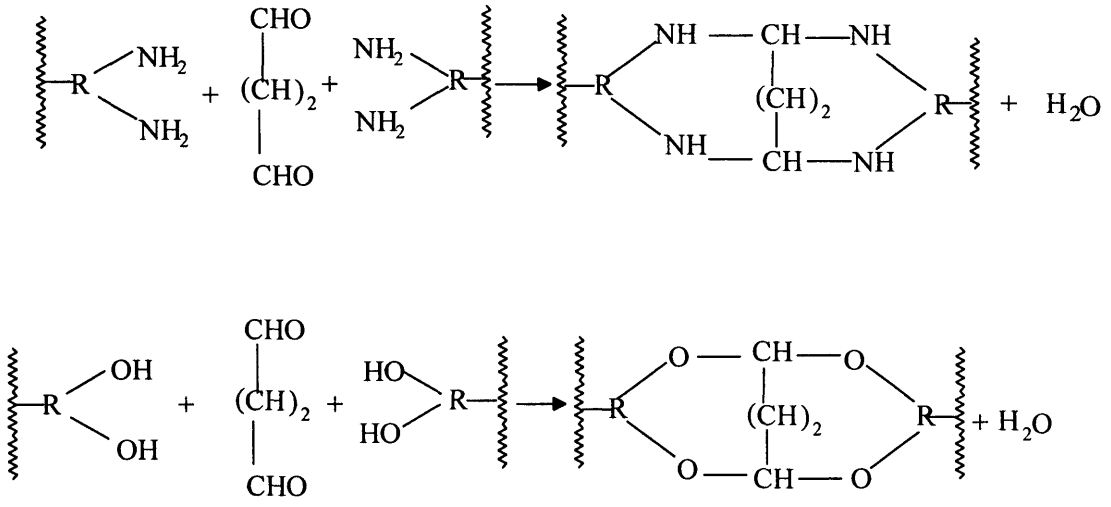
5.1.3 Aldehyde tanning

Formaldehyde and glutaraldehyde (GA) are the main aldehydes used in this type of tanning. GA has better tanning properties and higher effectiveness than formaldehyde. Leather tanned with GA can have a shrinkage temperature as high as 85°C and can also have an unusual stability against washing with solutions of different pH. The reactions between GA and collagen have been extensively studied by many investigators [Fein *et al.*, 1957 and 1959; Blass, 1975], but the real mechanism is still not fully understood.

Commercial solutions of GA are a mixture of monomeric and polymeric species (see **Scheme 5.5**). The proposed tanning mechanism is shown in **Scheme 5.6**.



Scheme 5.5 Monomeric and polymeric species present in an aqueous solution of glutaraldehyde.



Scheme 5.6 The proposed reactions of glutaraldyhyde with collagen [Tang, 1993].

The amount of GA in the exhaust after tannage should be minimised due to its toxicity. It was hypothesised that the application of ultrasound in a pre-tanning process with GA would speed up the process and increase the degree of GA exhaustion (and hence reduce the amount of GA discharge).

5.2. EXPERIMENTAL

5.2.1 Materials

Pickled sheepskins and bovine hides were used for all tanning processes. The bovine hide was re-pickled in the tannery of the British School of Leather Technology (BSLT) in order to increase storage time. The re-pickled hide samples were sealed in plastic bags in order to maintain their moisture content. The tanning materials used in the experiments are shown in Table 5.1. A pre-tanning agent, Neosyn TX (Hodgson Chemicals Ltd) and an efficient degreasing agent, Supralan 80 (Zschimmer & Schwarz), were used in the vegetable and GA tanning processes; their properties are shown in Table 5.2. Other chemicals listed in Table 5.3 were used without further purification.

Table 5.1 The properties of chrome powder and mimosa used in experiments

	Chrome powder	Mimosa
Appearance	Dark green, spray-dried powder	Reddish brown
Solubility in water	Readily and rapidly soluble in either hot or cold water	/
pH of aqueous solution	Approx. 3.0	4.05
Typical analysis	33% basicity, 25% Cr_2O_3, Neutral salts as Na_2SO_4 (25%), chloride (0.15%), iron (0.005%)	Tannin 68%, Non- tannin 24.3%, Insolubles 0.8% Water 6.9%
Supplier	British Chromium & Chemicals Ltd.	Hodgson Chemicals Ltd

Table 5.2 The properties of Neosyn TX and Supralan 80

Neosyn TX (Hodgson Chemicals Ltd)	Active Material	97.0%
	pH of solution	8.0-9.0
	Solubility	Readily miscible with water
	Stability	Stable throughout the pH scale
Supralan 80 (Zschimmer & Schwarz)	Appearance	Liquid, clear, slightly yellowish
	Active matter	Approx. 80%, non-ionic
	pH (10% aqueous solution)	Approx. 6
	Solubility	Miscible with water
	Stability	Stable to a large extent against all usual, regularly concentrated chemicals

Table 5.3 Chemicals used in the tanning processes (purity > 97% unless otherwise stated)

Chemicals	Supplier
Glutaraldehyde (50% solution)	BDH Laboratory Supplies
Iodine	BDH Chemicals Ltd
Potassium iodide	Scientific & Chemical Supplies Ltd
Sodium sulphate	East Anglia Chemicals
Sodium metabisulphite	BDH Chemicals Ltd.
Sodium chloride	Timstar Laboratory Suppliers Ltd
Sodium bicarbonate	
Iron sulphate	
Sodium potassium tartrate	BDH Chemicals Ltd
Ammonium acetate	BDH Chemicals Ltd
Calcium carbonate	East Anglia Chemicals
Chromic potassium sulphate	BDH Chemicals Ltd
Citric acid monohydrate	BEECROFT & PARTNERS
Nitric acid	BDH
Oxalic acid dehydrate	Timstar Lab. Suppliers Ltd
Perchloric acid	BDH
Sodium chloride	Analytical Supplies Ltd
Sodium hydroxide	BDH Chemicals Ltd
Sodium thiosulphate	East Anglia Chemicals
Sulphuric acid	BDH

Table 5. 4 Chromium tanning process

Sample	Tanning conditions (penetration)	Tanning conditions (basfication)	Final pH	Equipment
1	12% chrome powder, 250% water, 35°C for 2 hours	three addition 1% $NaHCO_3$, 35°C for 4 hours	3.2	glass vessel
2	12% chrome powder, 250% water, 20°C for 2 hours	5 additions of 1.7% $NaHCO_3$, 20°C for 4 hours	3.7	glass vessel
3	8% chrome powder, 100% water, 25°C for 2 hours	1.2% $CaCO_3$, 25°C for 1 hour, 35°C for 3 hours	3.6	glass drum
4	12 % chrome powder, 100% water, 25°C for 2 hours	1.8% $CaCO_3$, 25°C for 1 hour, 35°C for 3 hours	3.6	glass drum
5	20% chrome powder, 800% water, 25°C for 2 hours	2% $CaCO_3$, 25°C for 4 hours	3.4	glass vessel
6	25% chrome powder, 600% water, 25°C for 2 hours	2.5% $CaCO_3$, 25°C for 1 hour, 35 °C for 3 hours	3.5	glass vessel
7	8% chrome powder, 1000% water, 25°C for 2 hours (Pickled hide powder)	2% $CaCO_3$, 25°C for 1 hour, 35°C for 3 hours	3.4	glass vessel
8	12% chrome powder, 150% water, 25°C for 3 hours, 35°C for 3 hours	1.8% $CaCO_3$, 25°C for 1 hour, 35°C for 3 hours	3.5	metal drum
9	8% chrome powder, 150% water, 25°C for 2 hours	1.2% $CaCO_3$, 25°C for 4 hours	3.4	metal drum

Note: Each process was conducted either with or without ultrasound; the application of ultrasound was only in the first 3 hours of the tanning process

5.2.2 Tanning procedures

5.2.2.1 Chromium tanning

5.2.2.1.1 Tanning of pickled bovine hide

The re-pickled bovine hide samples were divided into two groups for experiments with and without ultrasound. In the first group, the sample was tanned in the presence of ultrasound for 2 hours, followed by 4 hours "normal" tanning (i.e. without ultrasound). The second group of samples were tanned without ultrasound for 6 hours. The samples were either tanned in the drums (metal or glass) or in the glass vessel. The ultrasound units and other equipment (see Fig. 2.1 and 2.2, Chapter 2) used were the same as those used in previously described processes. All details of tanning procedures are listed in Table 5.4.

As noted before, basification is a very important step in the production of chromium tanned leather. Only a weak alkali, such as sodium bicarbonate, can be used for this treatment. The addition of alkali was made at several points during the basification process in order to control the increase in pH and avoid the production of a chromium hydroxide precipitate on the surface of the leather or in the liquor. In order to improve the basification process, a so called self-basifying agent is often used. Such basification agents normally contain dolomite or magnesium or calcium carbonate. They can slowly neutralise the acid from the chromium tanning and increase the pH gradually to around 4, thus creating suitable conditions for the chromium complexes to react with the carboxyl groups of collagen [He, 1981]. In this present study, a typical self-basification agent, $CaCO_3$, was selected and used. The solubility of $CaCO_3$ depends on the pH of the solution. The higher the pH, the

lower the solubility. When the pH of the solution is over 4, the solubility of $CaCO_3$ becomes very low. As a result, the pH of the tanning liquor is maintained at around 4. The dissolution of $CaCO_3$ in an acid medium can be expressed as follows:

$$CaCO_3 + 2\,H_3O^+ \longrightarrow Ca^{2+} + CO_2 + 3H_2O$$

In addition, the self-basification agent could be added in "one go". This makes process control much simpler than that in the case of using sodium bicarbonate.

The amount of $CaCO_3$ used in the process can be determined using following empirical equation [He, 1983]:

$$C = 0.595 \times S \times p \qquad (5\text{-}1)$$

where C is the amount of $CaCO_3$ based on wet sample weight, and S is the amount of sodium bicarbonate (1g Cr_2O_3 needs about 0.3-0.5g $NaHCO_3$ for adequate basification) [He, p234]. p is the purity of the $CaCO_3$ and the constant 0.595 is the ratio of the equivalent molecular weight of $CaCO_3$ and $NaHCO_3$

A typical tanning process used (Sample 3 from Table 5.4) is summarised as follows. Pickled bovine hide samples (70-100 g) were put into the metal drum which contained 100% water and 6% NaCl (based on wet sample weight) and the drum rotated (50 rpm) for 10 minutes at 25°C. After that, 8 % chromium powder was added into the drum and drum rotation was continued for another 2 hours (penetration stage). After that, the pH of the tanning liquor was tested and 1.2% $CaCO_3$ was added into the drum. The drum was rotated for another 4 hours at 35°C (basification stage). One sample was exposed to ultrasound for one hour in the penetration stage and for another hour in basification stage during a 6 hour tanning process; the control was tanned for 6 hours without ultrasound. The pH was checked regularly during the whole process and was controlled in the range of 3.6-4.0. After

tanning for 6 hours, the tanned samples were washed three times with distilled water (200 ml) and then kept sealed in plastic bags until required for further use.

5.2.2.1.2 Tanning of hide powder

The tanning of air-dried hide powder involved a method used by Atto [1971] in which the hide powder was first pickled and then tanned. The detailed method is as follows (all percentages are based on hide powder weight):

Pickling: 20 g air dried hide powder was added to a jar containing 300 ml distilled water, along with 4 g of NaCl (20% of the hide powder weight). The jar was rotated at 30 rpm for ~20 minutes. After a good dispersion was obtained, 3% concentrated H_2SO_4 was added to the jar which was than rotated for a further 2 hours. The powder was left overnight in the pickling liquor. The final pH of the liquor was found to be 2.4. The powder was then separated from the liquor by pouring into a nylon cloth which was squeezed to remove excess liquor. After that, excess water in the pickled powder was removed by a vacuum pump.

Chromium tanning: 6% NaCl was dissolved in 80 ml of distilled water and the solution was added to the glass vessel. 20 g of pickled wet hide powder was added into the vessel which was then stirred for 30 minutes at 120 rpm. 8% chrome powder (based on Cr_2O_3) was dissolved in 120 ml water and the solution was added to the reaction vessel. The tanning process was carried out at 25°C for 2 hours, then 1.2% $CaCO_3$ was directly added into the reaction vessel and basification was continued for another 4 hours (One sample was exposed to ultrasound for 2 hours). The tanned hide powders were then transferred to another beaker and washed three times in distilled water (100 ml) and the excess water was removed under vacuum. The tanned hide powder was kept in a plastic bag for further use.

5.2.2.2 Mimosa tanning

5.2.2.2.1 Tanning of sheepskin with mimosa

Details of tanning procedures are listed in Table 5.5. A typical example was as follows. Pickled sheepskin samples (50-100 g) were put in the metal drum containing 150% water, 6% NaCl and 10% Na_2SO_4 (percentages of reagents based on the wet weight of the samples). The drum was rotated for 10 minutes at 20°C, and then 5% Supralan 80 and 5% Neosyn TX were added to the drum which was then run for further 2 hours. The pH of the liquor was 4.8 and the shrinkage temperature (T_s) was 65°C. After this pre-tanning process, the tanning liquor was drained and the pelts washed twice for 15 minutes in 200% warm water (~45°C). The pelt was drained, and horsed up overnight. The sample was then sealed in a plastic bag and kept in a refrigerator for further tanning.

Such pretanned sheepskins were then washed in 200% water at 25°C for 15 minutes in the drum and then drained. 20% mimosa and 200% water were added into the drum which was then run for 2 hours at 25°C either with or without ultrasound followed by tanning for another 4 hours at 35°C without ultrasound. The tanned material was then air dried at room temperature.

5.2.2.2.2 Tanning of bovine hide with mimosa

Bovine hide samples were tanned either in the metal drum or in the glass vessel. A typical tanning procedure for each case is as follows.

Tanning in drum

Pickled bovine hide was depickled using 5% sodium chloride, 4% sodium acetate and 100% water at 25°C for 30 minutes after which the pH of the liquor had

reached 4.5. The solution was then drained and 300% water was added into the drum and the hide was washed for 10 minutes to remove the excess salt. The hide samples were dabbed with absorbent tissues and then added into the drum containing 200% water and 30% mimosa extract. The drum was rotated for 2 hours at 25°C either with or without ultrasound followed by another 3 hours drum rotation at 35°C without ultrasound. The tanned samples were then dried in air at room temperature.

Table 5.5 The samples tanned with mimosa under different conditions

Sample	Skin/hide	Tanning conditions	Tanning device
1	pretanned sheepskin	20% Mimosa, 200% water, 25°C for 2 hours, (with or without ULT), 35°C for 3 hours	drum (50 rpm)
2	bovine hide	30% Mimosa, 200% water, 25°C for 2 hours (with or without ULT), 35°C for 3 hours	drum (50 rpm)
3	bovine hide	30% Mimosa, 600% water, 25°C for 3 hours, (with or without ULT) 35°C for 3 hours	glass vessel
4	pretanned bovine hide	30% Mimosa, 600% water 25°C for 3 hours, (with or without ULT) 35°C for 3 hours	glass vessel

Tanning in glass vessel

In this group of experiments, the pickled samples were first depickled following the same procedure as that described for tanning in the drum. They were then tanned in the glass vessel using 30% mimosa extract and 600% water. The bovine hide sample was fully immersed in the tannin liquor for 6 hours; the temperature in the first 3 hours was 25°C and in the last 3 hours it was 35°C. After tanning, the sample was dried in air at room temperature.

In all the above processes, the tannin content in the tanning liquor was measured at various times during the tanning process in order to monitor the exhaustion rate. Details of this procedure are given in section 5.2.3.2.

5.2.2.3 Tanning with glutaraldehyde

Tanning with glutaraldehyde (GA) (as with chromium and mimosa) was carried out either in the drum or in the glass vessel. Details of the tanning conditions used for each of the samples are shown in Table 5.6. The following is an outline of a typical tanning procedure. Pickled sheepskin and bovine hide samples (30-50 g) were put into the drum and then 6% sodium chloride and 10% sodium sulphite (based on wet weight of samples) were added and the drum run for 10 minutes at 35°C. After that, 10% GA (concentration 25% w/w), 4% degreasing agent Supralan 80 (only used for sheepskin) and 500% water were added together into the drum which was then rotated for 40 minutes. The mixture was basified using 5% sodium bicarbonate and 10% sodium sulphite to keep the pH at around 6 during the following hour (one sample was exposed to ultrasound for the first one hour). Then the samples were taken out, washed and kept in a plastic bag until required for further testing.

In order to monitor the progress of the tanning, the tanning liquor was regularly tested to determine the GA content (the testing procedure is detailed in section 5.2.3.3.)

Table 5.6 GA tanning conditions

Sample	skin/hide	Tanning conditions		Process vessel
		Materials/chemicals	Time/Temp.	
1	Bovine hide	10% GA, 250% water 6% NaCl, 10% Na_2SO_4, 50% water, 10% Na_2SO_4, 5% $NaHCO_3$	10 min/ 35°C 120 min/35°C (one sample with ULT for 60 minutes)	metal drum
2	Sheepskin	10% GA, 500% water 10% Na_2SO_4, 6% NaCl 4% Sulpralan 80 (degreasing agent) 50 % water, 10% Na_2SO_4, 5% $NaHCO_3$	20 min/ 35°C 120 min/35°C (one sample with ULT for 60 minutes)	glass vessel
3	Bovine hide	5% GA, 500% water, 10% Na_2SO_4, 6% NaCl 100 % water, 10% Na_2SO_4, 5% $NaHCO_3$	20 min/ 35°C 120 min/35°C (one sample with ULT for 60 minutes)	glass vessel
4	Sheepskin	5% GA, 500% water, 10% Na_2SO_4, 6% NaCl 4% Sulpralan 80 (degreasing agent) 100 % water, 10% Na_2SO_4, 5% $NaHCO_3$	20 min/ 35°C 120 min/35°C (one sample with ULT for 60 minutes)	glass vessel

5.2.3. Measurement and analysis

5.2.3.1 Chromium content and distribution

5.2.3.1.1 Chromium content

The tanned samples were air dried and ground to a powder by a milling machine (APEX Construction Ltd). 1 g of the ground powder was placed in a 500 ml conical flask, and then 5 ml of concentrated nitric acid was added followed by

adding 20 ml of the oxidising mixture (perchloric/sulphuric acid = 2/1 by volume). The mixture was heated in a fume-cupboard and a clear orange coloured solution gradually formed. Then the solution was kept in a fume-cupboard whilst it cooled down.

Approximately 150 ml of cold distilled water and a few anti-bumping granules were added into the above flask and solution. The solution was heated again to boiling point and kept boiling for 10 minutes to remove free chlorine from the solution. The solution was then left to cool down again and diluted with distilled water to 250 ml in a volumetric flask. Then 100 ml of the solutions were transferred into each of the two conical flasks by pipette. Another 10 ml of 10% potassium iodine solution was added into each flask which was then covered and kept away from light for 10 minutes. 1 ml of starch indicator was added to each solution that was then titrated to a pale violet colour with 0.1 M sodium thiosulphate solution. The amount of sodium thiosulphate solution used was recorded. After the whole process, the chromium contents in the leather sample were calculated by following equation [IUC.8]:

$$\text{Amount of } Cr_2O_3\,(\%) = 2.5 \times \frac{T \times M_t \times 152 \times 100}{6W_0} \qquad (5\text{-}1)$$

T: the volume of sodium thiosulphate used (ml).

M_t: the accurate concentration of sodium thiosulphate (0.0994 mol/dm^{-3}).

152: the relative molecular mass of Cr_2O_3.

W_0: the mass of the original sample (g).

5.2.3.1.2 Characterisation of chromium distribution by scanning electron microscopic (SEM) /X-ray backscatter analysis

The content and distribution of chromium in the leather samples was measured using a scanning electron microscope (SEM) with a backscattered X-ray micro-analytical mapping analysis facility. A Hitachi model S-2500 SEM fitted with an X-ray analyser (Link ISIS with a silicon detector, resolution of 133 ev) was used for this work. The cross-section of the sample of interest was prepared by cutting the leather with a sharp blade; specimens were then mounted on metal studs. Colour maps indicating the distribution of elemental chromium from the grain to the flesh sides were obtained by using the ISIS software.

5.2.3.1.3 The amount of chromium in the tanning liquor

In order to monitor the progress of the chromium tanning, the concentration of the chromium ions in the tanning liquor was measured. A colorimetric analysis method was selected, which uses oxalic acid to form a complex with chromium(III). The testing method is summarised as follows:

(1) Determination of the calibration curve

0.96 g of chromium alum, $KCr(SO_4)_2 \cdot 12H_2O$, was dissolved in distilled water and diluted to 100 ml in a volumetric flask. Based on the molecular mass of $KCr(SO_4)_2 \cdot 12H_2O$ and atomic mass of Cr, the chromium content of this solution can be worked out, i.e., 0.001 g/mL.

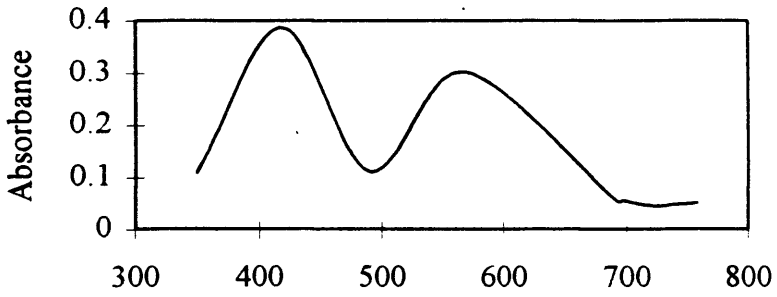
10 mL of this solution was then transferred into a 100 mL beaker, and then approximately 20 mL distilled water together with 2 g of oxalic acid was added into the beaker. The mixture was heated to boil and kept at boiling for three more minutes. A clear violet blue solution was obtained, which indicated that the oxalate

complex of chromium had been formed. After the solution was cooled down, it was transferred to a 50 mL volumetric flask and diluted to the mark with distilled water.

An UV/visible absorption spectrum of this solution is shown in Fig. 5.1(a). It can be seen that the maximum absorbance occur at wavelengths 418 and 570 nm. Since 418 nm is near to the ultraviolet range, the 570 nm band was selected as a characteristic absorption peak for this analysis. The same procedure was repeated using 15, 20 and 25 mL of the chromium alum solution. In this way a relationship between chromium concentration and absorbance was established and shown in Fig. 5.1(b). Using this calibration curve, the concentration of a chromium solution can be easily determined.

(2) Chromium analysis

A certain amount of tanning liquor was taken out from the tanning bath at regular intervals and filtered using filter paper. 5 mL of the filtered liquor was transferred into a 50 mL beaker and then 2 g oxalic acid and 20 mL distilled water were added. The mixture was heated in the same way as described in the preparation for the calibration curve. The solution was cooled down and transferred into a 50 mL volumetric flask and diluted to 50 mL with distilled water. The absorbance of this diluted solution was determined and its concentration was obtained via the calibration curve.



Fig, 5.1(a) UV/visible spectrum of chromium oxalate solution

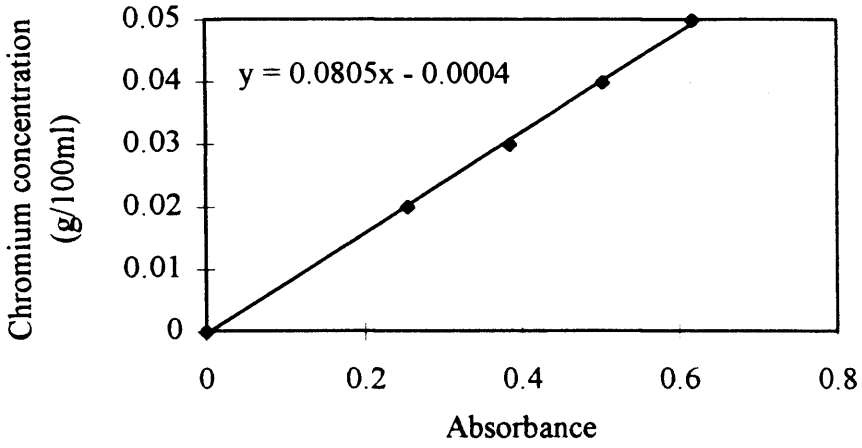


Fig. 5.1(b) The relationship between chromium concentration and absorbance at 570 nm

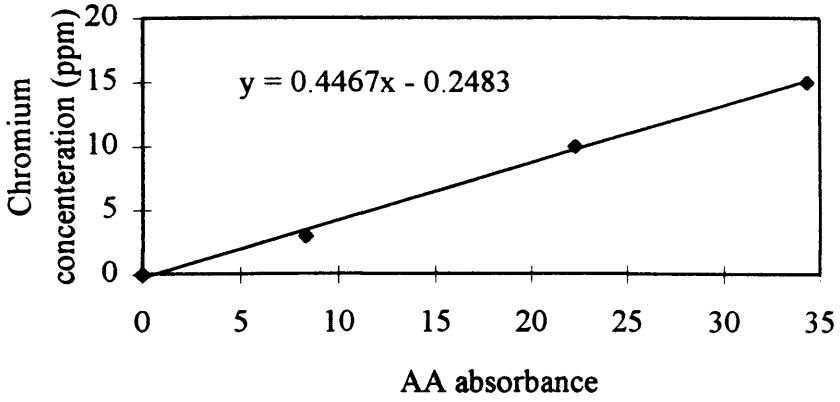


Fig. 5.2 The relationship between chromium concentration and AA absorbance

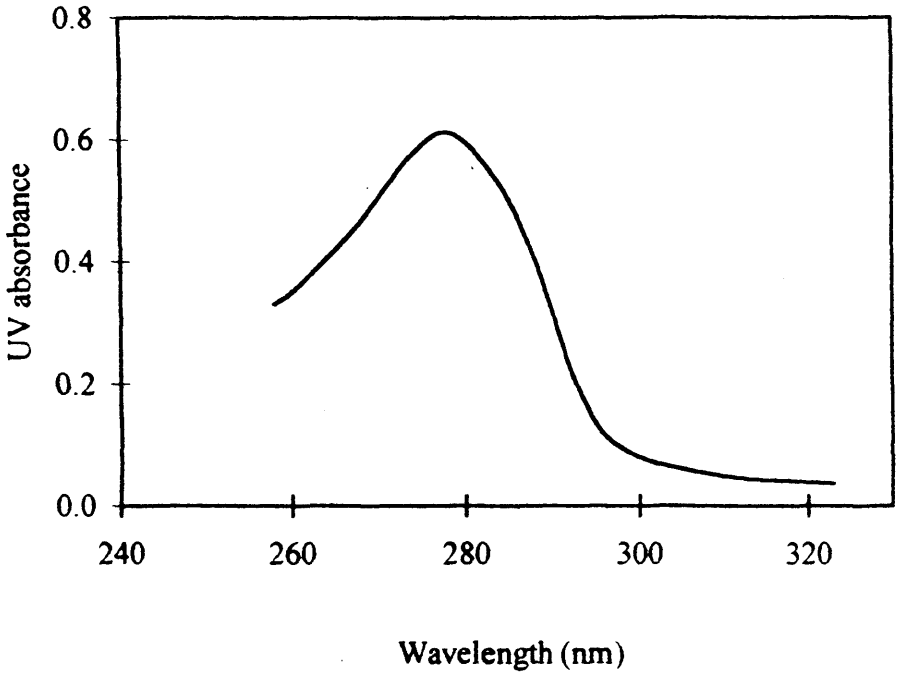


Fig. 5.3 (a) UV spectrum of Mimosa solution

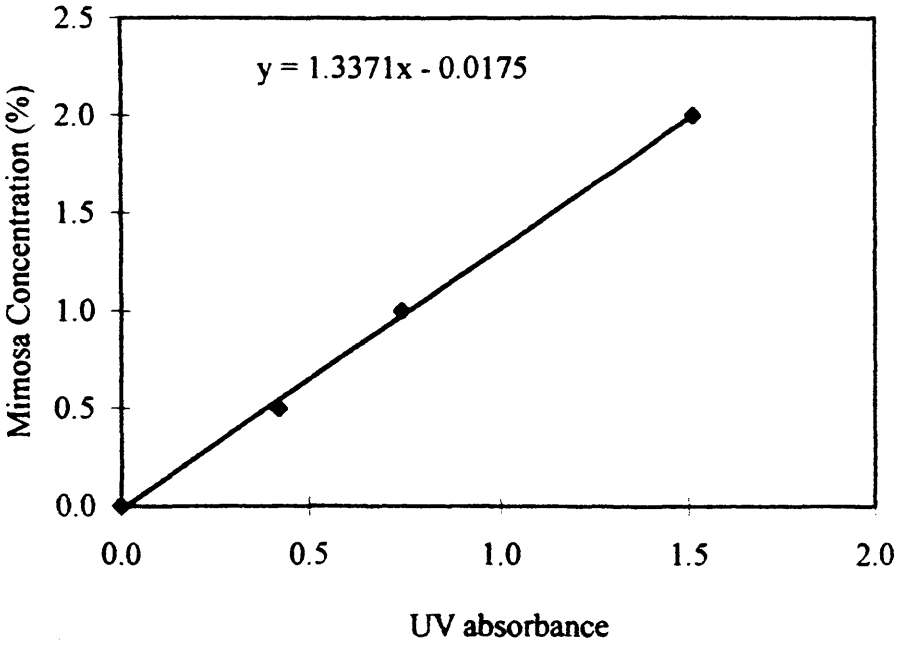


Fig. 5.3 (b) The relationship between Mimosa concentration and UV absorbance

5.2.3.1.4 Leaching chromium in the tanned samples

It has been found that only some of the chromium present in leather is chemically bonded to the collagen molecules to form crosslinks. The crosslinking bonds are responsible for the increase of the shrinkage temperature and other important properties of tanned leather [Santappa, 1982]. In order to assess the tannage it is therefore very important to estimate the amount of the chromium chemically bonded to the collagen. The Toxicity Characteristic Leaching Procedure (TCLP) was used to make such an estimation. This procedure is generally used to measure the amount of leachable chromium (i.e. that is not chemically bonded to the collagen) in wet-blue leather trimmings and shavings. The TCLP extraction solution was prepared by titrating 40 g citric acid in 400 mL distilled water with 1 M sodium hydroxide (NaOH). The final pH was controlled at 5.0 ± 0.1. 5 g of air-dried chromium tanned leather powder was placed in a 500 mL glass jar with 250 mL TCLP extraction solution. The mixture was rotated at room temperature for 48 hours at a speed of 30 rpm. After extraction for 48 hours, the reaction mixture was filtered and a reddish solution was obtained.

The amount of chromium in the extraction solution was determined by both visible spectrophotometry and atomic absorption spectroscopy (AA). The procedure for visible spectrophotometric measurement was the same as that described in section 5.2.3.1.3. The sample prepared for AA was diluted to a very low concentration. 5 mL of the extracted solution was diluted with 250 mL distilled water in a volumetric flask. Chromium concentration was then determined by AA using the calibration curve shown in Fig. 5.2. The calibration curve was established using standard aqueous solutions of chromium nitrate.

5.2.3.2 The analysis of mimosa solutions

In order to understand the effect of ultrasound on mimosa tanning, the solubility, tannin content and viscosity of solutions of mimosa extract were studied before and after ultrasound treatment. Tannin contents in tanning liquors were measured at different time intervals during the tanning process in order to assess the progress of tanning.

5.2.3.2.1. The solubility of mimosa extract

Mimosa extract does not have a constant solubility. Solubility depends not only on temperature but also on the concentration of the solution. Different concentrations of the mimosa liquors were prepared either by ultrasound or by magnetic stirring for 30 minutes at 30°C. The liquors were filtered through a medium filter paper (Whitman 502#) under reduced pressure. The relative amount of residue on the filter paper was calculated using the following equation.

$$\mathrm{Wr} = \frac{W_2 - W_1}{W_0} \qquad (5\text{-}2)$$

Wr - filtration residue (%)

W_1- paper mass

W_2- paper and residue mass

W_0 - initial mimosa mass

5.2.3.2.2 Analysis of tannin in mimosa liquor

For the vegetable tanning process, the concentration of mimosa extract was regularly measured to assess the progress of tanning. Normally, total tannin content

is determined by the hide powder method [SLC2/3]. This method, however, has a somewhat arbitrary dependence on the conditions used and also requires a long time to complete. It is therefore not suitable for rapid accurate measurement of the tannin content during the tanning process. Other methods have been developed by many researchers. For example, Roux [1951] used a UV photometric method to measure the tannin contents in mimosa extract and found this method was very easy to conduct (mimosa extract has two absorption peaks in the ultraviolet range, 203 and 280 nm). Another method, based on colorimetry, was used by Mitchell and Price *et al.* [1924] to determine the mimosa content in tanned leather. It was found that the results obtained using colorimetric method were consistent with those obtained by Roux with UV absorption.

In the present study, the colorimetric method was used to study the tanning kinetics. The ortho-di or tri-hydroxy phenolic species in mimosa can react with ferrous tartrate to form a complex which has blue-violet colour in solution. This can be easily detected by a UV/visible spectrophotometer operating in the visible range. There is a maximum absorption peak at 545 nm for this ferrous-tannin complex. At a given concentration the absorbance of this complex varies with pH, but it keeps more or less constant within the pH range 6.5-8.5. Consequently, an ammonium acetate buffer was used to maintain the pH in this range. The preparation of the reagents used in the testing are summarised as follows.

1 mL of diluted mimosa solution was added to a volumetric flask followed by the addition of 20 mL of distilled water and 5 mL ferrous tartrate reagent; this latter had been prepared by adding 1g ferrous sulphate and 5 g sodium potassium tartrate to 1 litre of distilled water and 5 mL of 10% ammonium acetate. The mixture

was well shaken before the test. The absorbance of the mimosa solution at 545 nm was compared with a blank sample containing the ferrous tartrate reagent, ammonium acetate and water only. Mimosa solutions at concentrations of 0.25%, 0.34% and 0.45% (w/v) were tested to establish a calibration curve to allow calculation of the tannin content of unknown mimosa tannin solutions.

5.2.3.2.3 Particle size of mimosa liquors

Mimosa solutions of 0.5% and 1% (w/v) concentration were sonicated with ultrasound for 30 or 60 minutes at room temperature and then the particle sizes of mimosa were measured using a Coulter Model N4 MD particle size analyser (See Chapter 2).

In order to confirm the above method, a diffusion experiment through a dialysis tube was carried out at room temperature. 200 mL of mimosa liquors with a 4% (w/v) concentration were prepared either by ultrasound or magnetic stirring for 30 minutes and added to the glass vessels where a dialysis tube containing 20 mL distilled water was placed inside (see Fig. 3.3). During the diffusion process, 1 mL of the solution was regularly removed from the dialysis tube and diluted with distilled water to 25 mL, then analysed using a UV spectrophotometer (PYE unicam Sp6-160). The absorbance at a wavelength of 278 nm was monitored during 6 hours diffusion. The one mL of solution removed was replaced with distilled water to maintain the 20 mL volume of liquid in the dialysis tube. The UV spectrum of mimosa solution and and the absorbance-concentration calibration curve are shown in Fig. 5.3 (a, b).

5.2.3.3 Determination of glutaraldehyde content in tanning liquors

The determination of glutaraldehyde (GA) content followed a published method [Pan, 1993]. The GA was reacted with excess sodium bisulphite and a stable bisulphite complex was formed. The excess sodium bisulphite was titrated by a standard iodine solution. The reaction is as follows:

$$CH_2(CH_2\text{-}CHO)_2 + 2\,NaHSO_3 \rightarrow CH_2(CH_2\text{-}CHO\text{-}NaHSO_3)_2$$

$$NaHSO_3 + I_2 + H_2O \rightarrow NaHSO_4 + H_2O$$

According to the amount of iodine used in the sample and blank, the concentration of GA in the liquor can be obtained.

5.2.3.3.1 Preparation of reagents

0.25 M sodium bisulphite was prepared by dissolving 26 g of sodium bisulphite in 1000 mL distilled water. 0.1 M standard iodine solution was prepared. 28 g of iodine and 50 g of potassium iodide were mixed with a small amount of distilled water until the iodine was completely dissolved. The solution was then diluted to 1000 mL in a volumetric flask.

5.2.3.3.2 Testing procedure

3 mL of solution was taken from the tanning bath and transferred into a conical flask. 10 mL of 0.25 M sodium bisulphite solution was added and left for 5-10 minutes to allow the reaction to complete. The reaction solution was titrated by the standard iodine solution using starch solution as an end-point indicator. A blank test was carried out using 3 mL of distilled water instead of tanning solution. The volumes of standard iodine solution used in both sample and blank testing were

recorded. The glutaraldehyde content in the tanning bath was determined by the equation (5-3).

$$GA(g/l) = \frac{0.1\,M(V_2 - V_1)}{2V}1000$$

$$= \frac{100\,M(V_2 - V_1)}{2V} \quad (g/L) \qquad (5\text{-}3)$$

Where V - sample volume (mL)

M - molarity of iodine

V_1 - volume of iodine to titrate sample (mL)

V_2 - volume of iodine to titrate blank (mL)

5.2.4 Hydrothermal stability of tanned leather

5.2.4.1 T_s measurement by conventional method

Shrinkage temperature (T_s) was measured in a liquid medium (water or paraffin). This is a conventional method used in all tanneries. A specimen with a size of 4×1 cm was fixed onto the test apparatus by clipping both ends of sample and the apparatus immersed into a beaker containing the liquid. The beaker was heated by a Bunsen burner with a very low heating rate. When the sample shrinks it turns the indicating needle. The temperature at this point was recorded as the shrinkage temperature.

5.2.4.2 T_s measurement using differential scanning calorimetry (DSC)

The DSC method has been widely used for shrinkage temperature evaluation by many researchers [Naghski, 1966, Kronick, 1986, Takenouchi, 1995]. In the present study, a computer controlled DSC (Mettler TC 10A, located at BLC The

Leather Technology Centre) was used. A wet-blue leather sample (5~10 mg) was placed into the sample pan and sealed with the lid, the sample pan was then placed in the heating chamber and heated from 20 to 130°C at a heating rate of 5°C per minute. The onset temperature and the peak temperature of a thermal event can be obtained from a DSC trace. After DSC testing, all the samples were dried and weighed to allow the value of enthalpy change per unit gram of sample to be determined.

5.2.4.3 Area shrinkage

Apart from the longitudinal shrinkage, the samples also shrank crosswise during heating. The loss of area at shrinkage can be used to characterise the hydrothermal stability of tanned leather. Circular leather samples with a diameter of 44 mm were immersed into a boiling water bath for 10 minutes. The changes in the diameter of the wet samples were measured for comparative studies of the extent of area loss [Covington, 1989].

5.2.5 The degree of tannage (vegetable tannage)

5.2.5.1 Estimation of the absorbed tannin in tanned leather

In order to estimate the amount of absorbed tannin in tanned leather, the following experiment was designed. Two samples from the same hide with the same size were weighed before tanning. Sample 1 was used to measure the water content. The wet weight (G_{w1}) of the sample was measured and then it was put into an oven set at 100°C and left to dry for 3 hours. The weight after drying was G_{d1}. The water content in the samples was obtained using the following equation:

$$a\,(\%) = \frac{G_{w1} - G_{d1}}{G_{d1}} \qquad (5\text{-}4)$$

where a (%) is the water content in the sample before tanning

It was assumed that the water contents in all samples before tanning were the same. Given the water content in sample 1, the dry weight of sample 2 before tanning can be obtained as G_{d2}. After tanning, sample 2 was dried in the oven (100°C) for three hours and weighed again to obtain its dry weight (G_{t2}). The tannin substance absorbed by sample 2 after tanning was calculated by the following equation:

$$T(\%) = \frac{G_{t2} - G_{d2}}{G_{d2}} \qquad (5\text{-}5)$$

where T (%) is the percentage of tannin substance absorbed based on the sample dry weight.

5.2.5.2 The degree of tannage measured by the standard method

Another method which can be used to determine the degree of tannage is the standard official method IUC3-7 and 10. The amount of bonded tannin can be obtained by mass balance after measuring the moisture content, hide substance, grease content, water solubles and ash. The degree of tannage can then be estimated by the following equation:

Bonded tannin (%) = 100% - (moisture %+ hide substance % + grease content % + water solubles % + ash of insolubles %) (5-6)

Degree of tannage = bonded tannin (%) / hide substance (%) (5-7)

5.3 RESULTS AND DISCUSSION

5.3.1 The effect of ultrasound on the kinetics of tanning and the properties of tanned leather

5.3.1.1 Chromium tanning

5.3.1.1.1 Tanning kinetics

Many factors affect the chromium uptake and fixation in skins or hides. Such factors include the surface charge of the pickled skin or hide, the concentration of chromium in the tanning liquor, the tanning temperature, pH and masking agents. The kinetics of the tanning process were studied in order to evaluate the effect of ultrasound and its modulation by the factors noted above. The tanning process was followed by measuring the concentration of the cationic chromium ions (Cr^{3+}) in the tanning liquor at a series of time intervals over the whole process.

Chromium ions (Cr^{3+}) in aqueous solutions occur as hydrated hexaquochromium ions, $Cr(H_2O)_6^{3+}$. The most important property of this ion, from the point of view of tanning chemistry, is that the water held can be exchanged by other ions, e.g. carboxylic acids or hydroxyls. The following order has been established based on their water displacing abilities in this respect [He, p 191, 1981].

$$H_2O < ClO_4^- < NO_3^- < Cl^- < SO_4^{2-} < CN^- < HCOO^-$$

$$< SO_3^- < COO^- \text{ in collagen} < CH_3COO^- < {}^-OOC\text{-}COO^- < OH^-.$$

Clearly from this order the H_2O molecules in the hydrated hexaquochromium complex can be easily replaced by $^-OOC\text{-}COO^-$ ion and a more stable chromium complex will be formed. The reaction product shows a violet blue colour, so the concentration of the solution can be easily detected in the visible range using a visible spectrophotometer.

Figs. 5.4-5.6 show the tanning kinetics of pickled bovine hide tanned under different conditions. The detailed tanning procedures and conditions are summarised in Table 5.4. The results show that the rate of depletion of chromium is slightly greater when ultrasound is used. This indicates that ultrasound slightly increased the reaction rate of the chromium tannage. However, the degree of increase is not large, which is consistent with previous researchers' work [Ernst, 1950; Herfeld, 1978].

Chromium tanning is based on cross-linking of the chromium complex to carboxyl groups on collagen molecules. Due to these linkages between polypeptide chains, the melting point of the crystalline collagen fibrils is increased. This is manifest in an increase in the shrinkage temperature. Previous researchers have found that the space between collagen molecular chains is about 1.5-1.7 nm , much larger than the dimension of either the chromium ion or its complex. In the early stages of the tanning process, due to the low pH (2.5~2.8), most chromium complexes are binuclear species with a diameter of ~0.7 nm [Heidemann and Keller, 1970]. Thus, there should be no difficulty for such chromium complexes to penetrate into the spaces between these molecular chains. This may be why only a small effect of ultrasound is observed. In the case of sample 6, for instance, the chromium contents in the tanning liquor after 180 minutes were 61 mg/100mL (with ultrasound) and 64.5 mg/100mL (without ultrasound). This result is very different from that obtained in dyeing and fat-liquoring processes (cf. Figs. 3.5-8). This would seem to be due to differences in the properties of the different liquors. In dyeing and fat-liquoring, the liquors are of a colloidal or emulsion type (i.e. they are not true solutions). Consequently, compared with chromium ions in solution, their penetration into the collagen fibrils is more difficult. So for dyeing and fatliquoring

the cavitation effect of ultrasound reduces the colloid/emulsion particle size markedly and so increases penetration. Such an effect can not be expected for the chromium tanning liquor.

Previous research has shown that most of the time in chromium tanning process is taken up by the polymerisation of the chromium complexes [Santappa, 1982, Sharphouse, 1980, He, 1980]. From the tanning kinetics curves (Figs. 5.4-6), it seems that ultrasound could not speed up this process. This was also found by Ernst in the early 1950s [Ernst, 1950]. However, some improvement in shrinkage temperature was observed and this will be discussed in section 5.3.2.1.

5.3.1.1.2 Chromium contents in the leather sample

Table 5.7 shows the chromium content (represented by Cr_2O_3) in the leather samples tanned under different tanning conditions. The results show that there was a slight increase in the chromium content in the sample which had been tanned in the presence of ultrasound for two hours during the six hour tanning process. The increases in Cr_2O_3 contents, when ultrasound was used, were less than 8%. Another feature which can be noticed from Table 5.7 is the influence of various tanning conditions on chromium content. For samples 1 and 2, the chromium offer was the same but different basification processes were used (see Table 5.4). With or without ultrasound, the chromium content is nearly 1.5 times higher for sample 2 than for sample 1. This must be due to the difference in the final pH. The pH profiles during the tanning process for these two samples are shown in Fig. 5.7. Clearly, the higher the final pH in the liquor, the higher the chromium content was in the leather.

Table 5.7 Chromium (III) oxide content in tanned leather

Sample	1	2	3	4	5	6	7
with ULT (%)	2.68	3.98	2.60	3.27	2.84	3.63	1.89
without ULT (%)	2.53	4.01	2.39	3.13	2.79	3.38	1.84
improvement (%)	5.93	-0.01	8.78	4.42	1.79	7.39	2.72
Final pH	3.16	3.88	3.6	3.6	3.5	3.4	3.4

Note: The details of the tanning procedures used are shown in Table 5.4

Another factor affecting the chromium content in the final product (Tables 5.4 and 5.7) is the concentration of chromium in tanning liquor. When the tanning process was conducted in a long float (1000% water based on the wet weight of leather, e.g., in the tanning of sample 7), the chromium content in the tanned sample is lower than that found after tannage in a short float (100% water, sample 3). This is in spite of the fact that sample 7 was pickled hide powder which had a larger surface area and thus should be able to absorb more chromium.

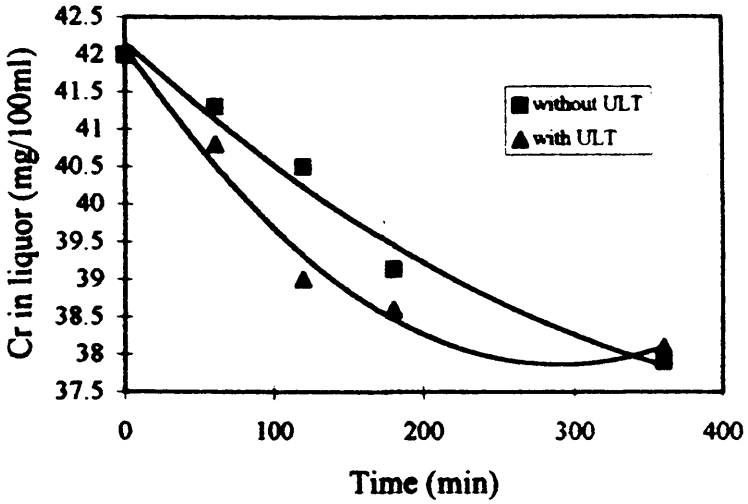


Fig. 5.4 Chromium concentration in float vs time during tannage (sample 5)

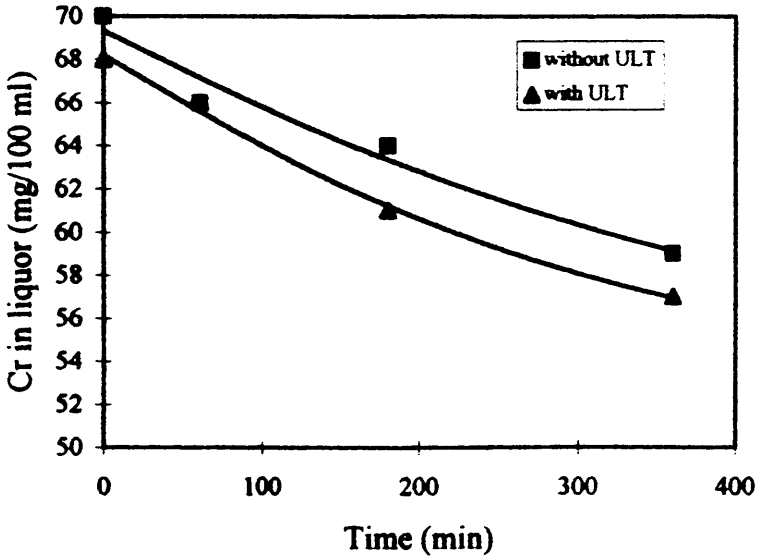


Fig. 5.5 Chromium concentration in float vs time during tannage (sample 6)

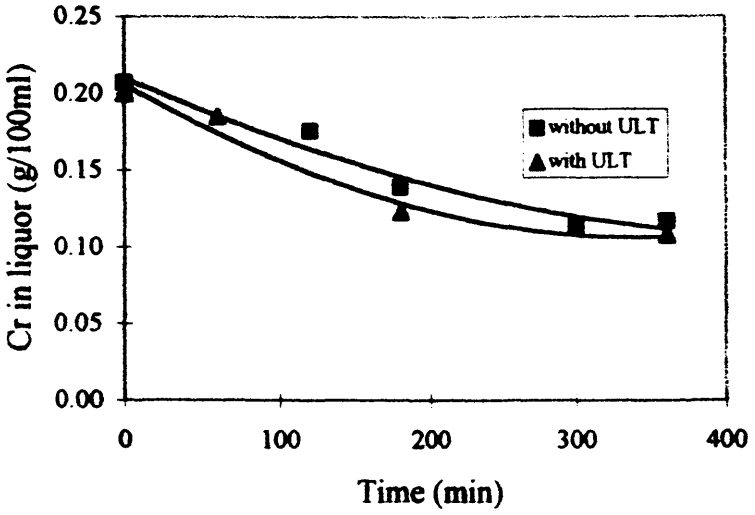


Fig. 5.6 Chromium concentration in float vs time during tannage (sample 8)

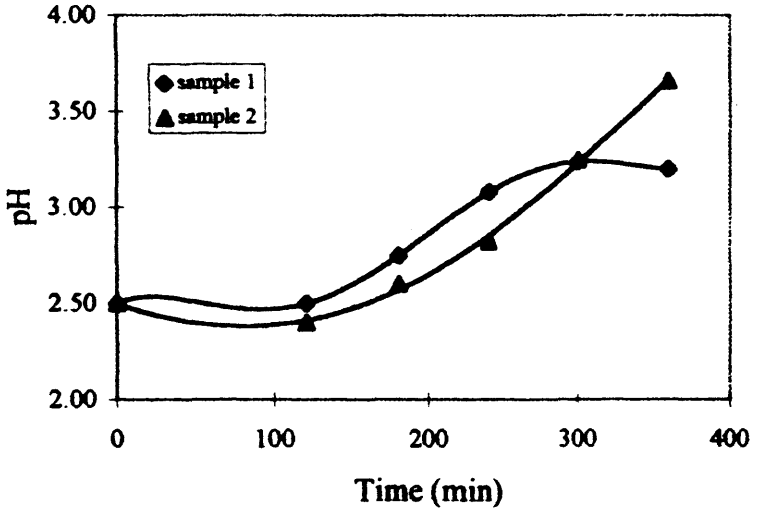


Fig. 5. 7 pH vs time during tannage (sample 1 and sample 2 with ultrasound)

Table 5.8 Leachable chromium in tanned leather samples

Sample	3		4		5		6	
Ultrasound	with	without	with	without	with	without	with	without
Cr_2O_3 in leather (%) (I)	2.68	2.39	3.28	3.02	2.84	2.72	3.64	3.38
Cr in leather (%) (II)	1.83	1.64	2.24	2.07	1.94	1.86	2.49	2.32
Amount of Leachable Cr in leather (mg/g) (UV method) (III)	7.15	7.57	9.55	8.46	7.10	7.74	10.32	9.74
Amount of Leachable Cr in leather (mg/g) (AA method) (IV)	9.24	9.54	11.03	11.03	9.10	9.21	12.7	11.7
Cr leached % (UV) (III/II)	0.38	0.46	0.425	0.41	0.37	0.42	0.53	0.42
Cr. leached % (AA) (IV/II)	0.504	0.58	0.49	0.53	0.47	0.49	0.55	0.51

The above discussions are concerned with the overall chromium contents of the tanned leather. However, as noted in the previous sections, not all of the absorbed chromium is chemically bonded to the collagen chains. The chemical bonding between chromium complexes and the carboxyl groups of the collagen molecules is believed to occur in different ways. It has been found [Gustavson, 1953] that only 10% fixed chromium (3.5% as Cr_2O_3 based on the leather weight) participates in multi-point binding with collagen, i.e. the attachment of the chromium complex to at least two reactive carboxyl groups. It is believed that only such multi-point crosslinking will generate a higher shrinkage temperature for leather [Gustavson, 1953 and Santappa, 1982]. However, most of the chromium ions only bind with one reactive carboxyl group of collagen in chromium tanned leather, so called uni-point binding. In addition, there is still a certain amount of chromium which is not chemically bonded at all but is only filling the spaces within the collagen fibrils. Such chromium may easily be removed from the collagen by the application of tri or bicarboxylic acid with which it reacts to form a stable complex [He p191, 1985].

In the present work, the chromium held physically within the fibres was extracted by the procedures used to determine the amount of free chromium which may be leached out from leather to the environment when it is disposed of. The testing procedure has been described in section 5.2.3.1.4. Table 5.8 shows the results obtained from UV and AA analysis.

From these results, it can be seen that in general the amounts of leachable chromium in the samples tanned with ultrasonic treatment are lower than those for samples tanned without ultrasound in all cases except for sample 6. It was believed

that the chemically bonded chromium will not be easily leached out [Heidemann, p 297, 1993]. This result suggests that a higher hydrothermal stability for the tanned leather might be obtained by using ultrasound tanning process.

Figs. 5.8-10 show the chromium distribution over the cross sections of the tanned leather samples. The maps were obtained from the SEM/backscattered X-ray analyser. In the micrographs, the brighter the area the higher is the chromium density. It can be seen that the sample tanned with ultrasound shows a more even chromium distribution than that tanned without ultrasound. This is particularly apparent in the case of using the glass vessel without drumming action (Fig. 5.10). Thus the use of ultrasound can improve the evenness of chromium distribution.

5.3.1.2 Mimosa tannage

5.3.1.2.1 Tanning kinetics study

Besides chromium tanning, the vegetable tanning process was also investigated. Pickled bovine hide and sheep skin were tanned with mimosa under various conditions (see Table 5.5). Tannin contents in the tanned liquor were measured periodically during the tanning process in order to study the kinetics of tanning. The results are shown in Figs. 5.11-14.

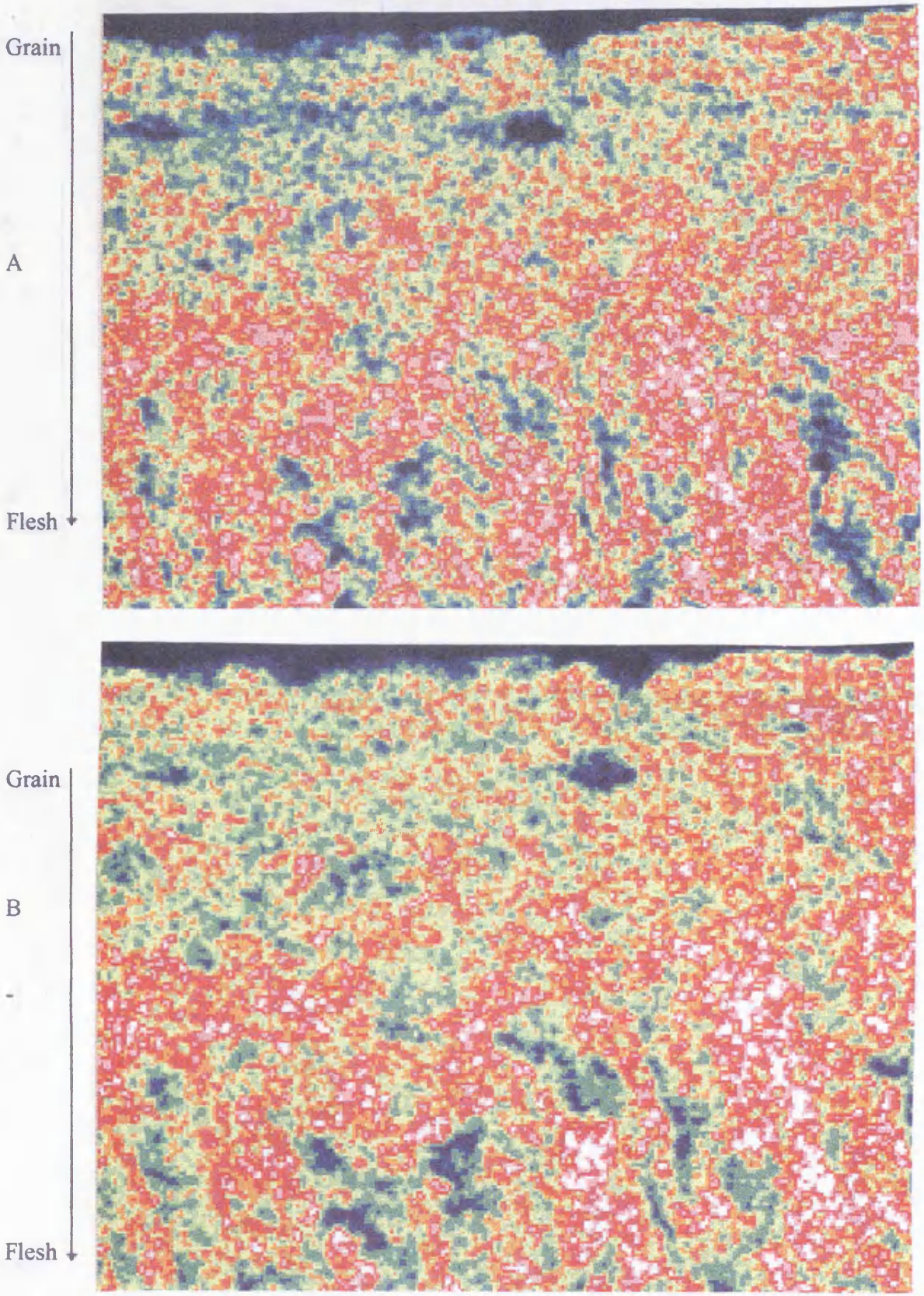


Fig. 5.8 SEM/ X-ray map of Chromium distribution in Sample 3

A- with ultrasound B- without ultrasound

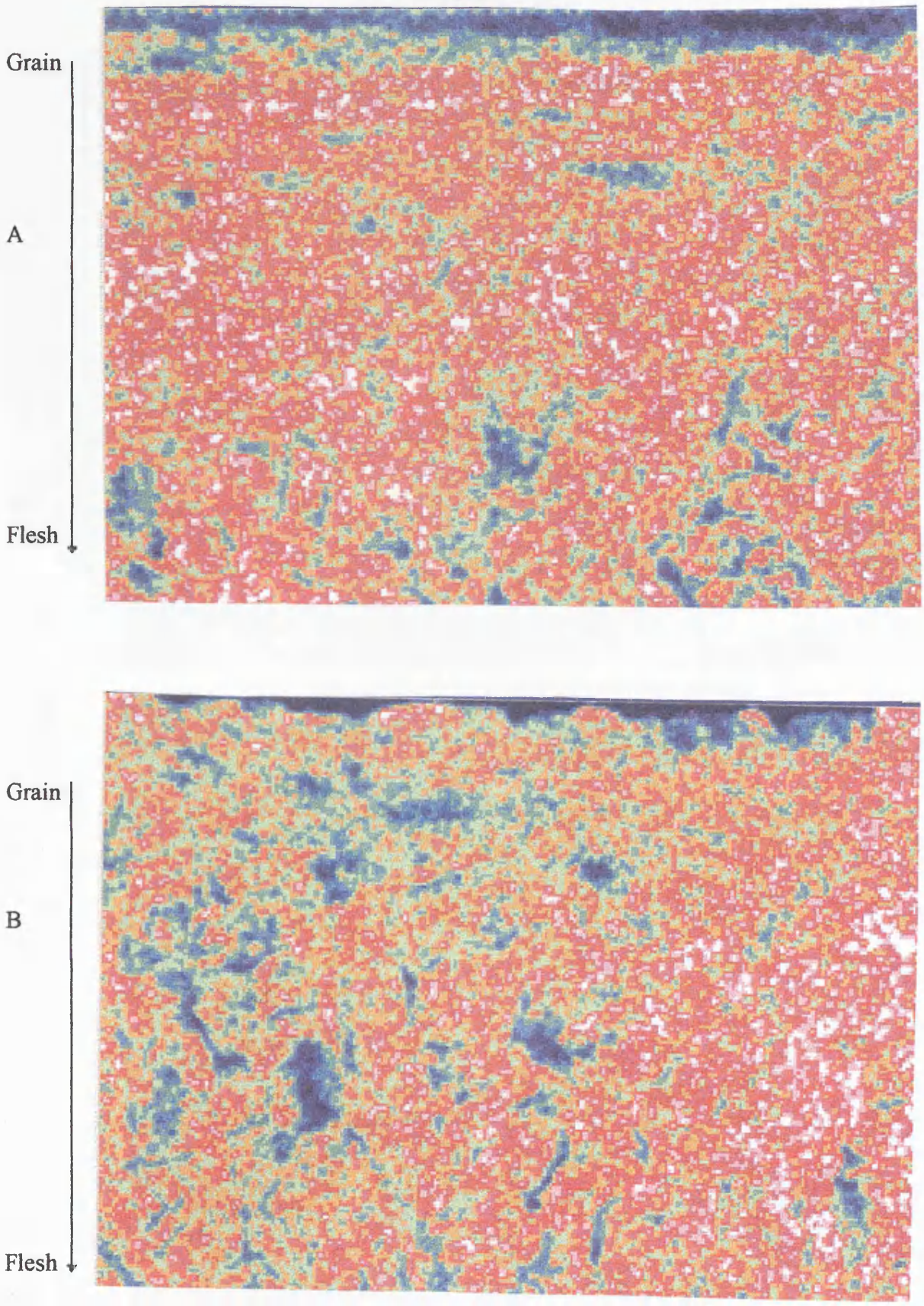


Fig. 5.9 SEM/ X-ray map of Chromium distribution in Sample 4

A- with ultrasound B- without ultrasound

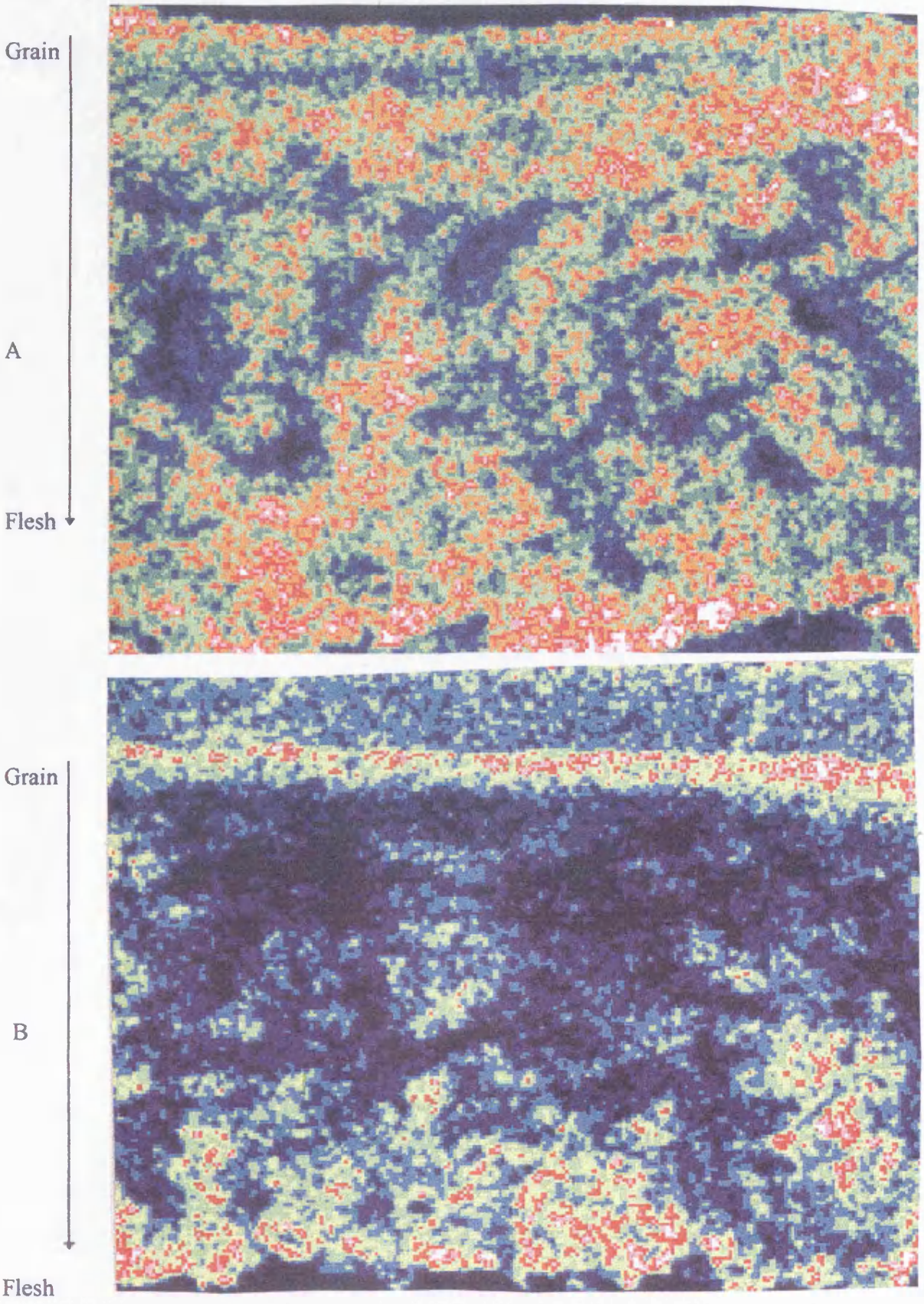


Fig. 5.10 SEM/ X-ray map of Chromium distribution in Sample 5

A- with ultrasound B- without ultrasound

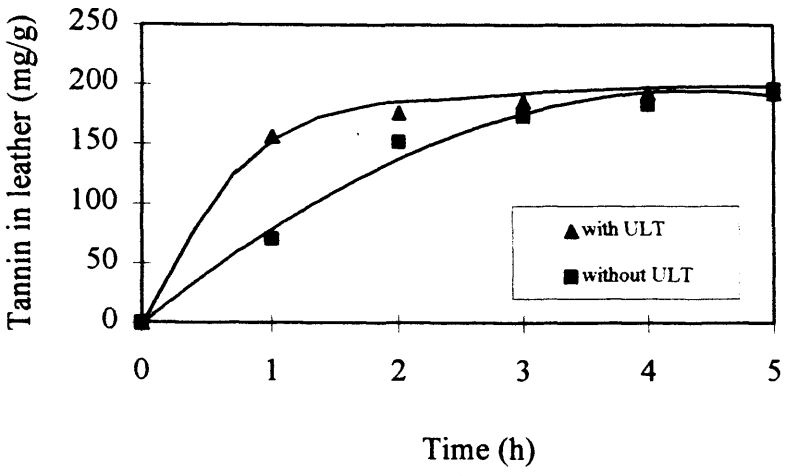


Fig. 5.11 Tannin content in the leather vs tanning time (Sample 1 sheepskin tanned in a metal drum)

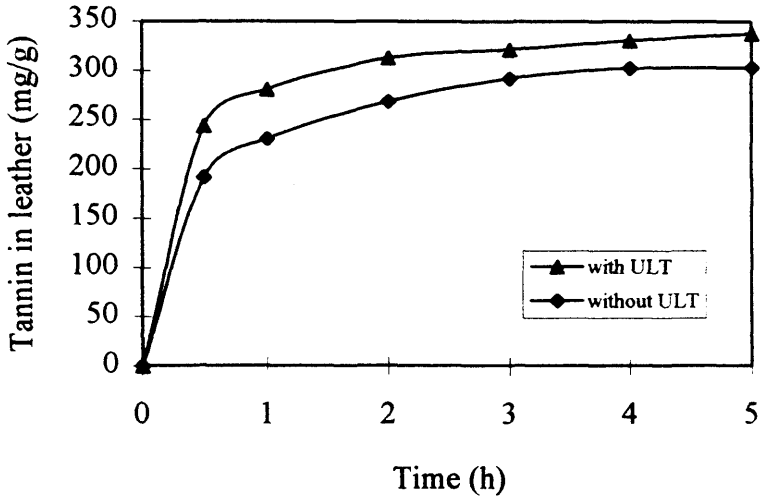


Fig.5.12 Tannin content in the leather vs tanning time (Sample 2, bovine hide in a metal drum)

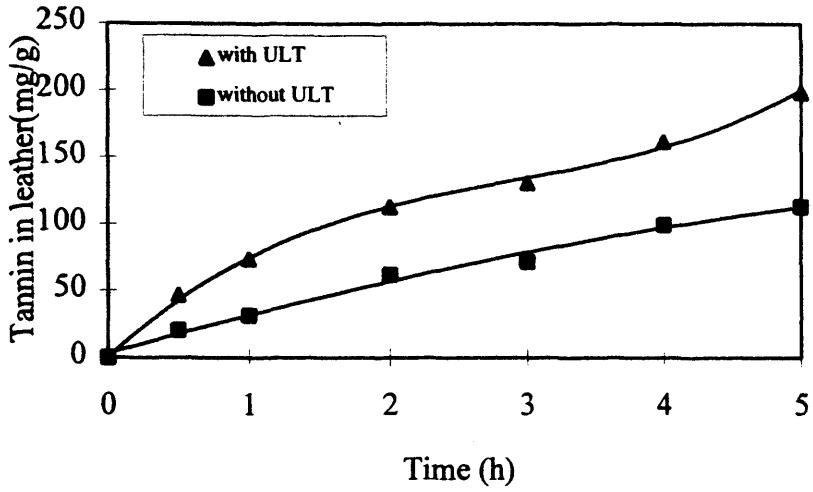


Fig. 5.13 Tannin content in leather vs tanning time (Sample 3 , bovine hide tanned in glass vessel)

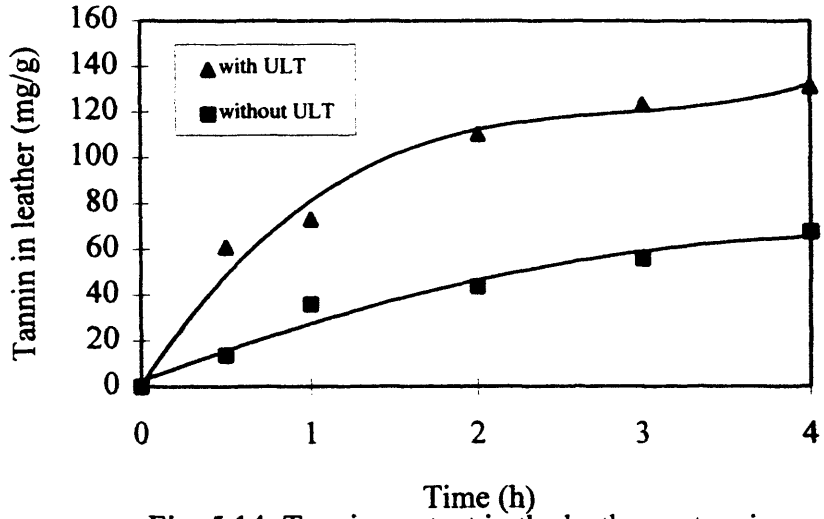


Fig. 5.14 Tannin content in the leather vs tanning time (Sample 4 pretanned bovine, in glass vessel)

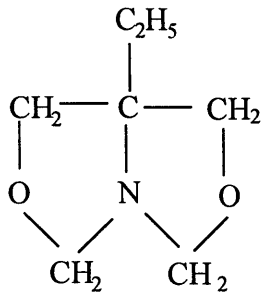
Clearly in each case, the vegetable tanning process is considerably accelerated by using ultrasound. In addition, the results obtained in the glass vessel (Figs. 5.13-14) are more pronounced than those obtained in the metal drum (Figs. 5.11-12). The reason for this is similar to that described in Chapter 3 for dyestuffs (cf. section 3.4.1.5). From Fig. 5.13 (sample 3), it can be seen that the tannin content (110 mg/g) after only 2 hours in the ultrasonic process is higher than that obtained after 5 hours with the non-ultrasonic process (99 mg/g). The rate of tanning has been accelerated more than two times. Ernst found some similar results when he used ultrasound in vegetable tanning [Ernst, 1950].

Most vegetable tannins, e.g. mimosa, consist of highly polymerised and bulky molecular structures (**Scheme 5.3**), which form large clusters in aqueous solution [Bienkiewicz, 1983]. Hydrogen bonding and the hydrophobic effect appear to be responsible for such molecular aggregation. The presence of such large aggregates clearly inhibits the penetration process. It will be seen later (section 5.3.4) that the vigorous cavitation produced by ultrasound breaks down the aggregation of the polyphenol molecules in mimosa. Apart from this reduction in the particle size of the mimosa solution, the use of ultrasound itself will increase the diffusion coefficient due to its powerful mechanical agitation effects. In addition, ultrasound can be expected to increase the solubility of mimosa. This latter aspect will be discussed in a later section (section 5.3.3.1). All these factors facilitate an increase in the rate of penetration of the tannin into the hide.

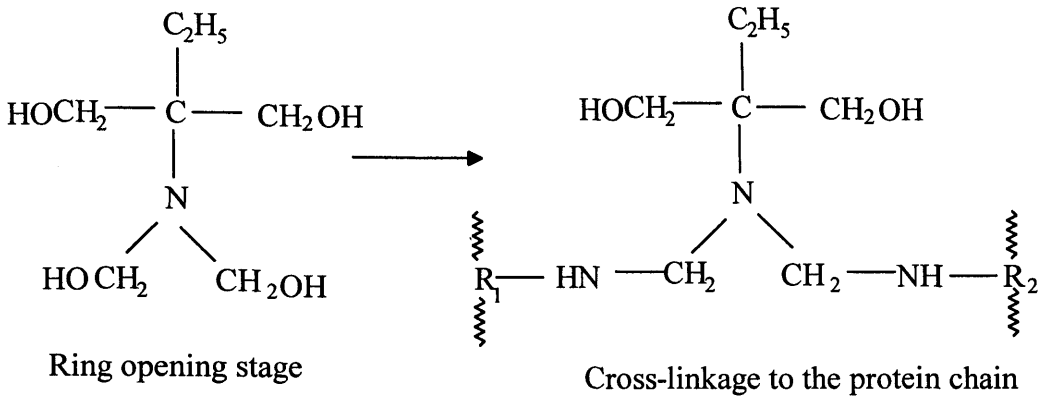
Another interesting feature of these results is the difference between sample 3 (Fig. 5.13) and sample 4 (Fig. 5.14). Sample 4, which was a bovine hide pre-tanned using the proprietary product "Neosyn TX" (see below), had a lower tannin

content after a given time than that of sample 3 which was also a bovine hide but without the pretannage (Table 5.5). For example, the tannin contents at 4 hours were 162 mg/g (with ULT) or 99 mg/g (without ULT) for sample 3 and 131 mg/g (with ULT) or 67 mg/g (without ULT) for sample 4 respectively. These differences may be explained as follows.

"Neosyn TX"® is produced by the reaction of aminohydroxy compounds with aldehyde. The bifunctional nature of this product means that it can easily react with collagen to form a crosslink [Dasgupta, 1977]. **Scheme 5.7** shows the structure of "Neosyn TX", and the proposed reaction between it and the collagen molecule is shown in **Scheme 5.8** [Dasgupta, 1977, Gill, 1985].



Scheme 5.7 The structure of Neosyn TX [Dasgupta, 1977]



Scheme 5.8 The reaction between collagen and Neosyn TX [Gill, 1985]

It may be assumed that when sample 4 was pre-tanned, some of the amino groups in the collagen became bonded to the hydroxyl groups of the Neosyn TX, and the number of unreacted amino groups in the collagen was reduced. Thus, fewer amino groups were available for reaction with phenolic hydroxyls in the mimosa. Meanwhile, the isoelectric point of collagen should also be lowered. Therefore, the affinity of mimosa to collagen would be reduced. This suggests that a reverse process might be better, that is, vegetable tanning first and followed by Neosyn TX tanning. This is because in such an order, Neosyn TX can react with both collagen and vegetable tannin, therefore the vegetable tannin can be strongly bonded to the collagen and not easily removed. However, it should be pointed out here that reduced affinity of tannins to collagen may help the penetration process. Thus a proper balance between the needs for affinity and for penetration is important.

5.3.1.2.2 The degree of tannage

In vegetable tanning, the interaction between tannins and collagen is based on the functional groups on the collagen molecular chains, e.g., -NH-CO-, -OH, -

NH_2, -COOH, *etc.*, and the phenolic groups in the tannins. Hydrogen bonds between these groups, plus hydrophobic interaction, results in a relatively strong linkage between collagen and tannin. However, unlike chromium tanned leather, vegetable tanned leather contains much more tanning materials (25-50%) than chrome tanned leathers (3-6%). Such a large amount of tanning material cannot be all bonded to collagen. Much of the material is physically incorporated in the structure as a filler. Some of this material can be washed out by water, and some can be removed by alkalis and polar solvents [Bienkiewicz, p393, 1983]. Tannin materials which cannot be washed out by water are termed bonded tannin. In order to determine the degree of tannage (the mass ratio of bonded tannin to protein), the amount of bonded tannin has to be determined. However, the amount of bonded tannin material in leather cannot be easily determined directly. The normal procedure is to measure hide substance, and the amount of washable tannin, water, salts and other insoluble materials and then by mass balance to find out the bonded tannins. Obviously, the error of this method is dependent on the accumulated error of individual tests for the substances listed above. However, until now there has been no better way to measure the amount of bonded tannin. In the present study, besides this official method, another method was used to estimate the progress of tanning. This method measured the mass change before and after tanning (section 5.2.5.1). Although this method cannot give the amount of bonded tannin, it does give a quick and clear indication of the magnitude of the effect of ultrasound on the progress of tanning. Table 5.9 shows typical results from this procedure.

Table 5.9 Tannin absorbed by sample 4 (pretanned bovine hide)

	with ULT	without ULT
water content before tanning (%)	103	103.2
wet weight of sample before tanning (g)	10.35	10.40
dry weight of sample before tanning (g)	5.09	5.12
dry weight after tanning (g)	5.73	5.42
tannin in leather %	**12.57 %**	**5.86 %**

The results in the table clearly show that the amount of tannin absorbed by the leather after tanning with ultrasound was twice as much as that obtained without ultrasound for the same period of time. This is consistent with the results shown in Fig. 5.14. Improvement in tanning rate by ultrasound is also confirmed by the results from tannin penetration testing, as will be discussed in the next section.

Table 5.10 shows the results obtained by the official method. Clearly the degree of tannage for the samples tanned in the presence of ultrasound is higher than that obtained without ultrasound. The increase in the degree of tannage is, however, smaller than the increase in total tannin content after using ultrasound.

Table 5.10 The degree of tannage

sample	Sample 1 pre-tanned sheepskin		Sample 2 pickled bovine hide	
condition*	200% water, 20% Mimosa		200% water, 30% Mimosa	
Ultrasound	with	without	with	without
sample mass (g)	4.4187	4.7628	7.4609	7.3541
moisture %	12.08	12.17	13.11	13.52
grease %	1.99	1.69	1.85	1.79
hide substance %	51.45	52.85	57.96	58.89
water solubles %	13.42	14.69	9.26	10.28
ash of insolubles	0.283	0.378	0.378	0.523
bonded tannin %	20.77	18.22	17.44	15.47
degree of tannage %	40.38	34.46	30.09	26.27

* for more detail see Table 5.5

5.3.1.2.3 Tannin penetration

As noted before, diffusion or penetration is a very slow process in vegetable tanning due to their large particle size and high affinity to collagen. In this section, the results of studies of tannin penetration into the hides and skins are presented and discussed. After a five hours tanning process, the tanned leather samples were cut into thin slices to examine the cross section by an optical microscope. The degree of penetration was determined under the microscope and the results are listed in Table 5.11.

Table 5.11 The degree of tannin penetration (%) within the cross section of the sample

Sample	With ULT	Without ULT
1	100	100
2	100	100
3	86	62
4	66	57

From Table 5.11, it is apparent that the degrees of tannin penetration are higher for the samples tanned with ultrasound than for those tanned without ultrasound. The degree of tannin penetration is lower in sample 4 than in sample 3, apparently because the former has been pretanned with Neosyn TX. Neosyn TX pretannage has increased neither tannin uptake nor the degree of penetration. For the samples (1 and 2), tanned in the metal drum, the tannin penetrated evenly throughout the cross-section. The reason for this is the same as that described in Chapter 3. Since even without ultrasound 100% penetration was observed over the time scale examined, it is not possible to judge the effect of ultrasound in this case. However, for tanning within the glass vessel where a longer float length (i.e. low concentration) and less mechanical agitation were used, an increase of tannin penetration was observed after using ultrasound. In Fig. 5.15 optical micrographs of the cross-section of the leather show the tannin penetration in sample 3 after 5 hours tannage. It can be seen that the centre of the samples remains untanned. However, this untanned part is much less in the ultrasound treated sample than that without ultrasonic treatment.

with ULT

without ULT

Fig. 5.15 Optical micrographs showing tannin penetration in sample 3 (magnification, ×30)

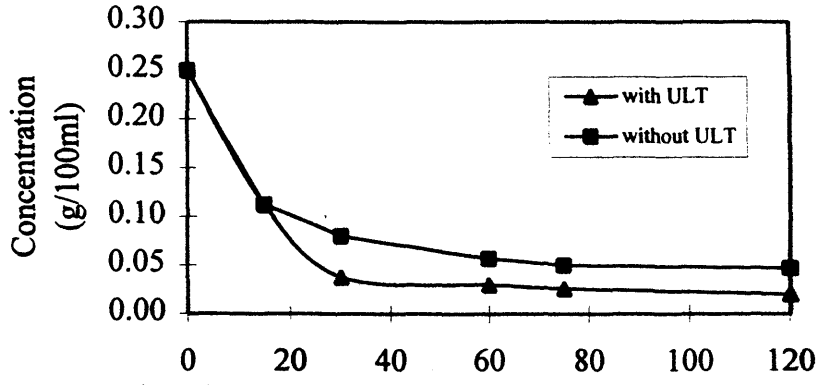


Fig. 5.16 GLutaraldehyde concentration in the float vs tanning time (Sample 1)

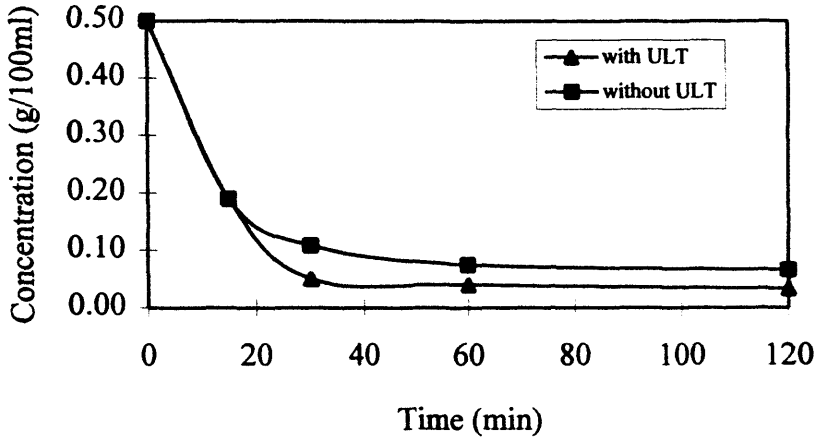


Fig. 5.17 Glutaradehyde concentration in the float vs tanning time (Sample 2)

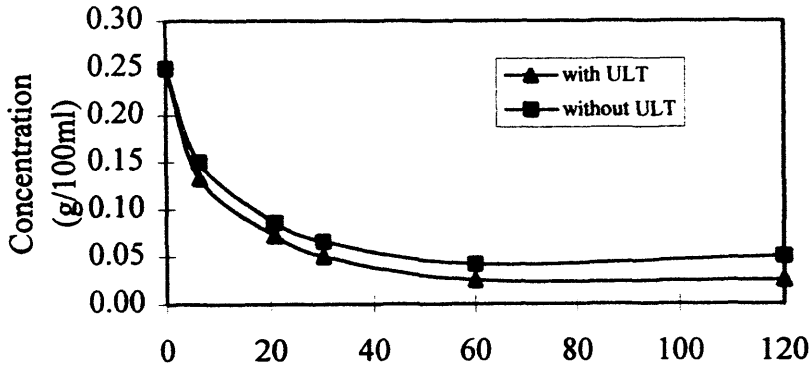


Fig. 5.18 Glutaraldehyde concentration in the float vs tanning time (Sample 4)

5.3.1.3 Glutaraldehyde tanning process

Glutaraldehyde (GA) is widely used in the tannery as a pre- or re-tanning agent. GA can increase the shrinkage temperature in a very short time. Due to its small molecular size and excellent miscibility with water, almost 85% of GA can be absorbed by leather in the first hour of tanning [Fein, 1959]. In the present study, the GA tanning process was investigated both with and without ultrasound. Sheepskin and bovine hide were tanned under different tanning conditions (details of the procedures are shown in Table 5.6).

The concentrations of GA in the tanning liquor are plotted against time in Figs. 5.16~18. From these results, it is apparent that, similar to chromium tanning, ultrasound has only a small influence on the GA tanning. It can be seen that, over the first 30 minutes, there is no much difference in GA exhaustion between ultrasound and non-ultrasound processes. However, with increasing time, the difference becomes gradually more noticeable, and at the end of the tanning process, this difference reaches ~0.03g/100mL. Although ultrasound hardly benefits the penetration process, it does help to raise the shrinkage temperature of the leather (see section 5.3.2.3)

5.3.2 Effect of ultrasound on the hydrothermal stability of tanned leather

Shrinkage temperature (T_s) of tanned leather is an effective indicator which can be used to assess the progress of tanning and the degree of crosslinking [Bienkiewicz, p243, 1983]. During the tanning, a small piece was cut from the sample every hour and subjected to T_s measurement. The change in T_s with the tanning time was obtained.

Another method used to determine T_s was differential scanning calorimetry (DSC) method. Since the water content in leather affects T_s significantly [Komanowasky, 1991], all the samples were immersed in distilled water for one hour and the excess water was removed by laboratory tissue prior to DSC testing. Before testing, samples were weighed on a torsion balance. After DSC testing, the samples were dried in an oven at 100°C for 24 hours and weighed again to obtain the dry weight of samples. The onset temperature of the DSC thermogram is believed to correspond to the shrinkage temperature of collagen quite well [Naghski, 1966]. However, as well as the onset temperature (T_s), the extrapolated onset temperature (T_e), peak temperature (T_p), and total enthalpy change during denaturation (ΔH_{ENDO}) were also recorded.

5.3.2.1 Chromium tanned leather

(a) Results from boiling test (IUP 12)

Figs. 5.19-22 show dependence of T_s on tanning time for processing with and without ultrasound under different tanning conditions. It can be seen that in the first two hours, the T_s increase was greater when ultrasound was used, but after that the rate of increase of T_s for the samples tanned both with and without ultrasound was nearly the same. The increases of shrinkage temperatures for all the samples at different times during the tanning process are listed in Table 5.12. From this table, it is clear that the values of T_s increase for the samples tanned with and without ultrasound are not so different after one hour basification process (i.e. after 180 minutes of the tanning process). As stated before, for the slow basification process, ultrasound cannot give much improvement.

Table 5.12 Increase (°C) of T_s compared to the initial T_s before tanning, during the course of tanning process.

Sample	3		4		8		9	
Time (min)	A	B	A	B	A	B	A	B
120	11	6	10	6	11	7	15	10
180	22	20	27	25	29	26	23	20
240	28	25	32	29	36	30	25	22
360	35	32	39	37	41	37	32	27

Note A- with ultrasound applied for 2 hours during tanning

B- without ultrasound

From the results, it can be seen that the shrinkage temperatures of the ultrasound treated samples are 3~5°C higher than those which were not subjected to ultrasound. This is because the amount of fixed chromium in the leather was increased after ultrasonic treatment (see section 5.3.2). As described in previous chapters, the strong shear force caused by cavitation can break some of the weaker chemical linkages [Mark, 1945] and so may disrupt some of the hydrogen bonding between the collagen fibres and expose more reactive sites for the chromium [Gutmann, 1955]. Therefore more crosslinking bonds may be formed in the sample tanned with ultrasound.

(b) Results from DSC

Figs. 5.23-27 show DSC thermograms of samples tanned with and without ultrasound and the onset temperature (T_s), extrapolated onset temperature (T_e) and peak temperature (T_p), the enthalpy change (ΔH_{ENDO}) are recorded in Table 5.13.

Table 5.13 Data from DSC thermograms of chromium tanned leather samples

Sample	Temperature (°C)			ΔH_{ENDO} (J/g)
	T_s	T_e	T_p	
3 (with ULT)	104	109	113	34.5
3 (without ULT)	102	104.4	105	48.8
4 (with ULT)	108	110	113	27.6
4 (without ULT)	104	107	112	30.4
5 (with ULT)	100	102	105	/
5 (without ULT)	97	98	102	/
7 (with ULT)	89	93	98	34.5
7 (without ULT)	89	91	97	35.7

with ULT: 2 hours sonication during a 6 hours tanning process

It can be seen that the onset and peak temperatures of leather samples 3, 4 and 5 (Table 5.4) were shifted upwards by about 3~5°C when ultrasound was used during tanning. However the DSC curves for sample 7 (hide powder) tanned with and without ultrasound are very similar. Another point is that the enthalpy changes (ΔH_{ENDO}) of the leather samples tanned in the presence of ultrasound show a lower

value than that of samples tanned without ultrasound. Thus, the increase of T_s after using ultrasound is due to an decreased entropy change.

Table 5.14 Area loss of samples during shrinkage in boiling water for 10 minutes

Sample	3		4		5		6	
Ultrasound	B	A	B	A	B	A	B	A
D_0 (mm)*	42	42	42	42	42	42	42	42
D_1 (mm)*	31	37	41	41.5	30	31	35	35
Area loss (%)	43.5	22.4	9.29	4.7	48.9	45.4	30.5	30.5

* D_0 and D_1 represent the diameter of samples before and after shrinkage respectively.

A - with ULT B - without ULT

The improvement of hydrothermal stability were also confirmed by the data from measurements of area loss during shrinkage in boiling water for 10 minutes (see section 5.2.4.3). Table 5.14 shows the area loss of the samples tanned either in the presence or absence of ultrasound. The results show that the reductions in the area of the samples tanned in the presence of ultrasound were less than the sample tanned without ultrasound. For sample 3, the reduction of the area was 22.4% when ultrasound was used, but was 43.5% without ultrasound. For samples 5 and 6, a smaller effect of ultrasound is apparent, because these samples have lower chromium contents and lower shrinkage temperatures. These results of area loss give further support to the above suggestion that the use of ultrasound increases chromium fixation in the leather.

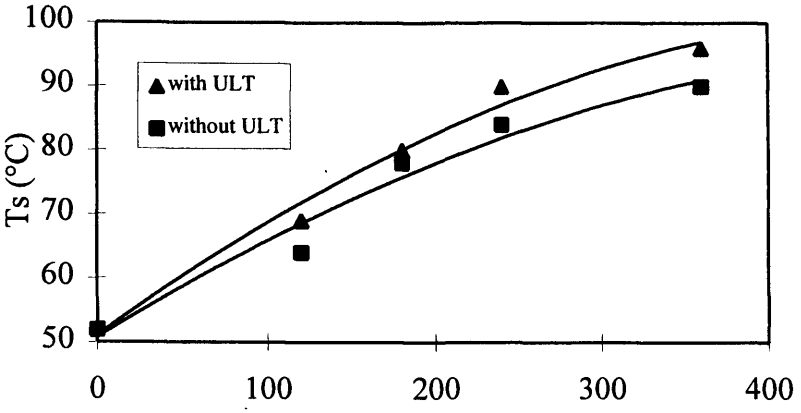


Fig. 5. 19 Shrinkage temperature, Ts,g against tanning time (sample 3)

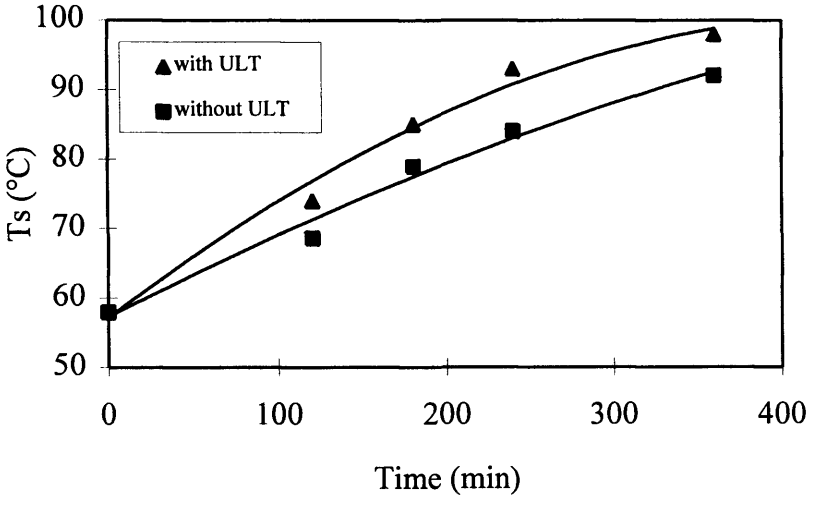


Fig. 5.20 Shrinkage temperature, Ts, against tanning time (sample 4)

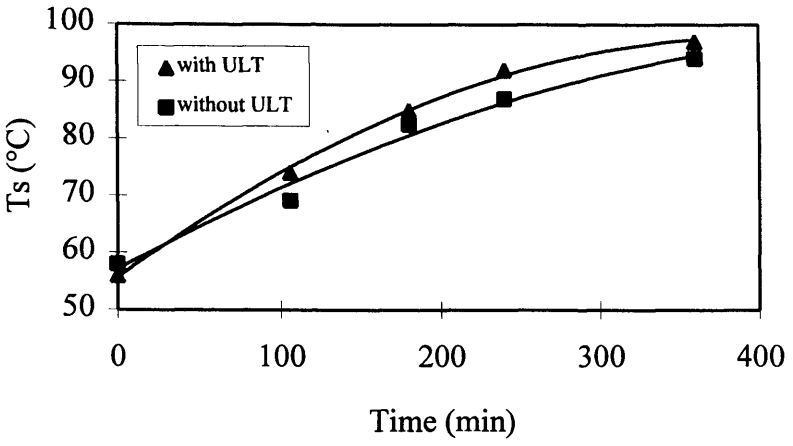


Fig. 5. 21 Shrinkage temperature, Ts, against tanning time (sample 8)

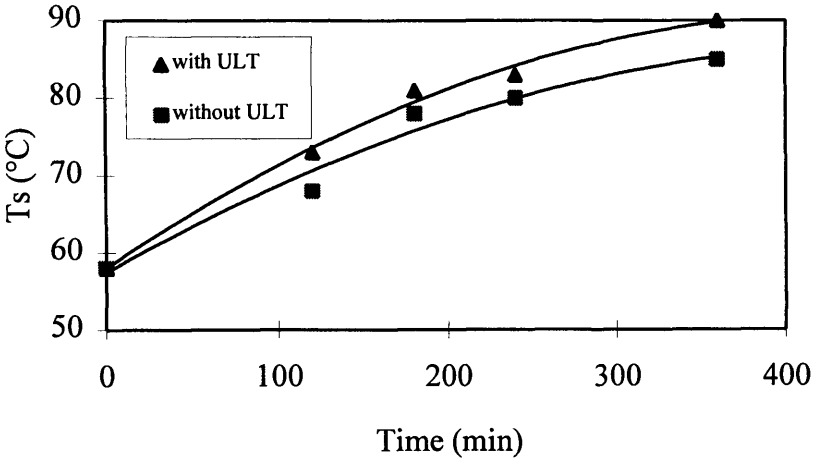


Fig. 5. 22 Shrinkage temperature, Ts, aganist tanning time (sample 9)

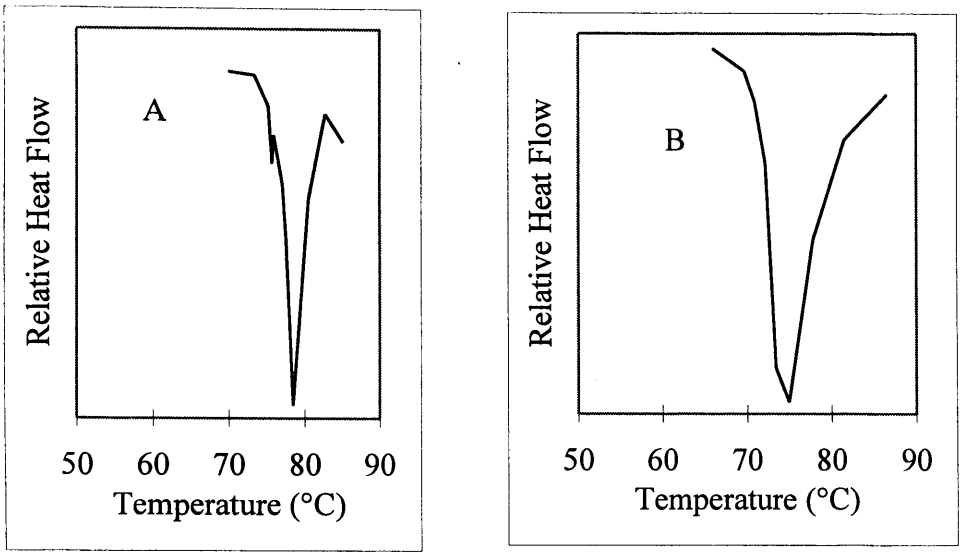


Fig. 5.23 DSC thermograms of retanned pickled sheepskin and untabnned bovine hide

A- sheepskin B- bovine hide

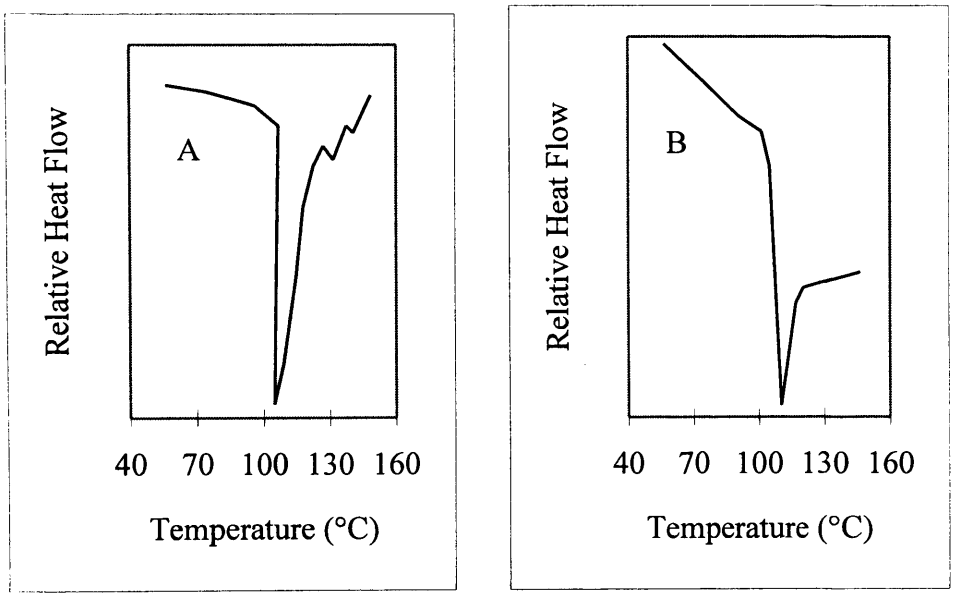


Fig. 5.24 DSC thermograms of Sample 3 (Chrome tanned)

A- without ULT B- with ULT

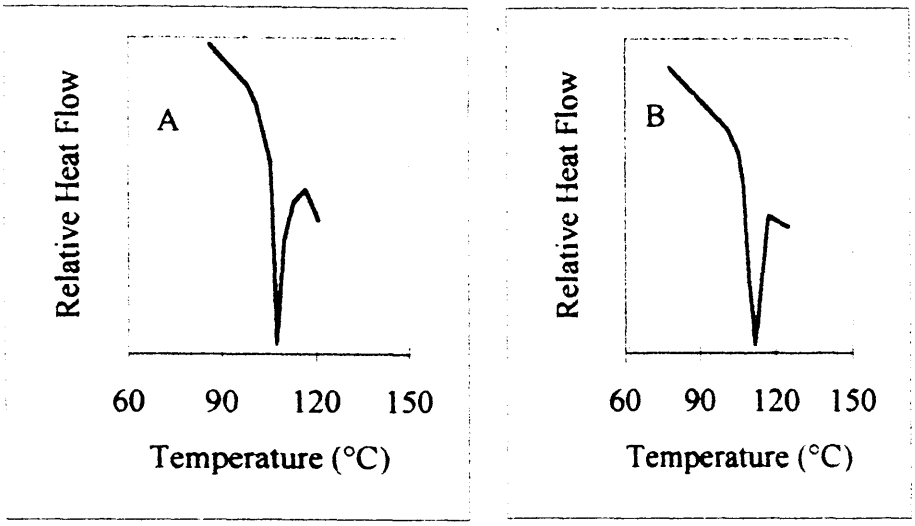


Fig. 5.25 DSC thermograms of Sample 4 (Chrome tanned)
A- without ULT B- with ULT

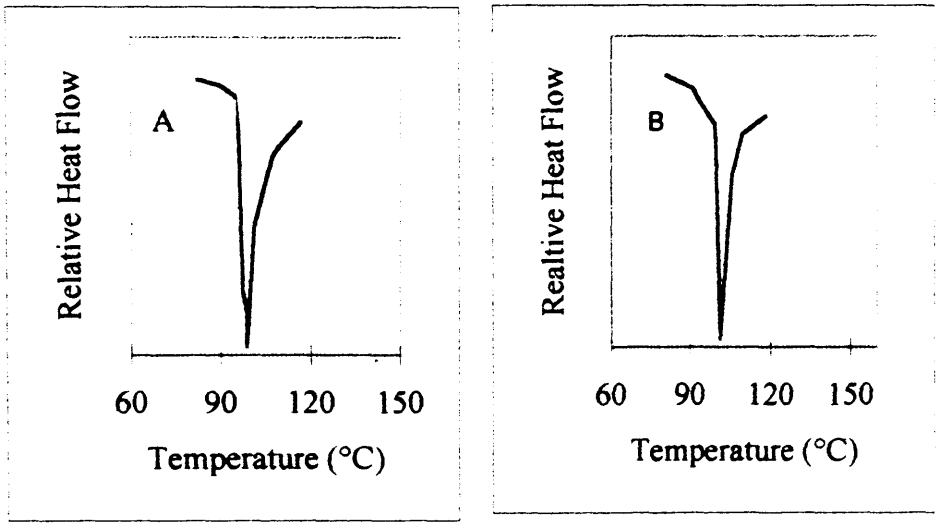


Fig. 5.26 DSC thermograms of Sample 5 (Chrome tanned)
A- without ULT B- with ULT

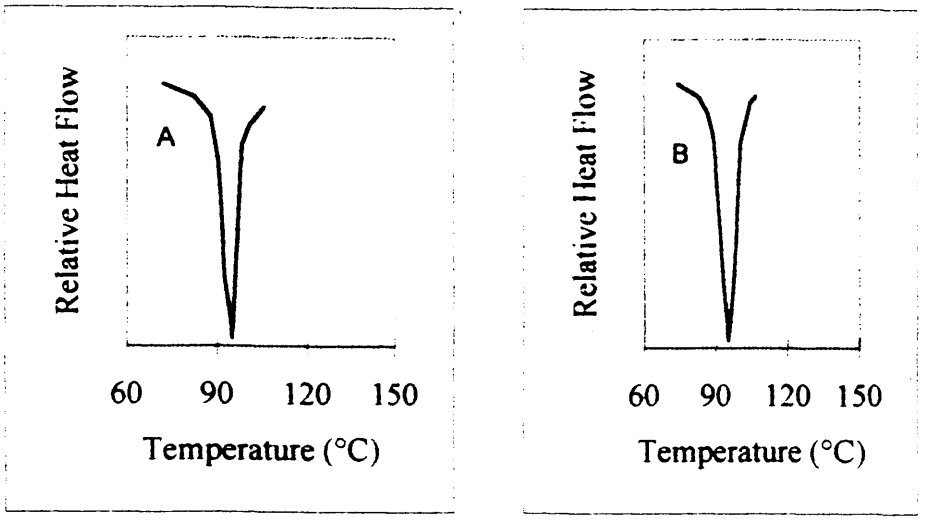


Fig. 5.27 DSC thermograms of Sample 7 (chrome tanned hide powder)
A- without ULT B- with ULT

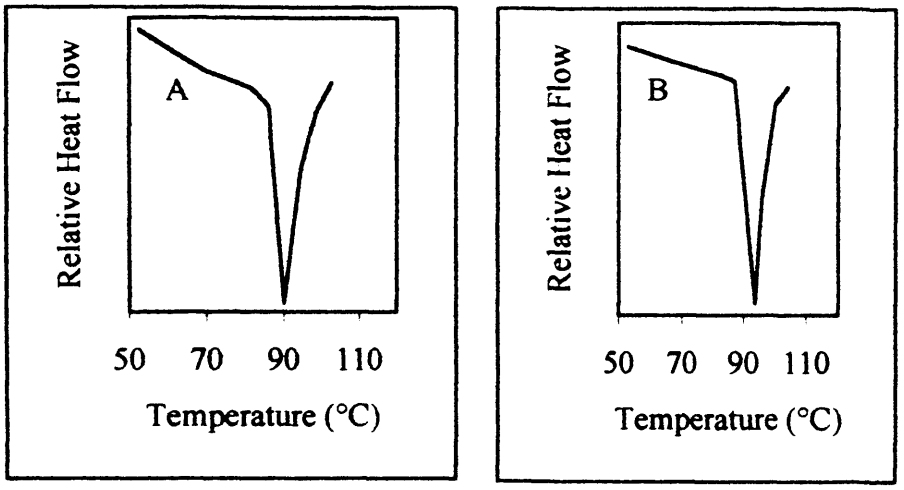


Fig. 5.28 DSC thermograms of Sample 1 (Mimosa tanned)
A- without ULT B- with ULT

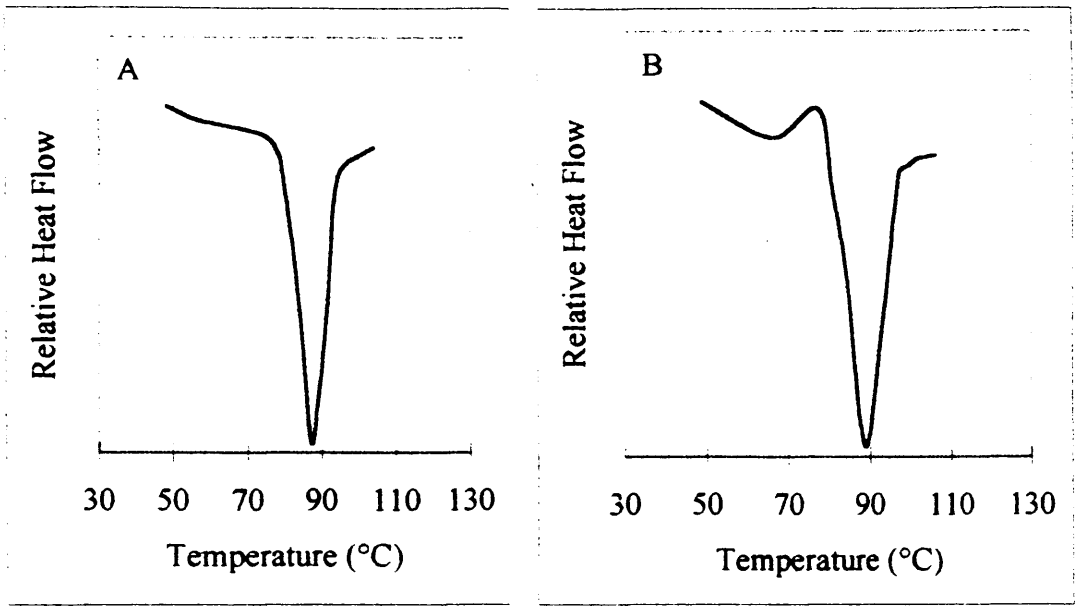


Fig.5.29 DSC thermograms of Sample2 (Mimosa Tanned)
A- without ULT B- with ULT

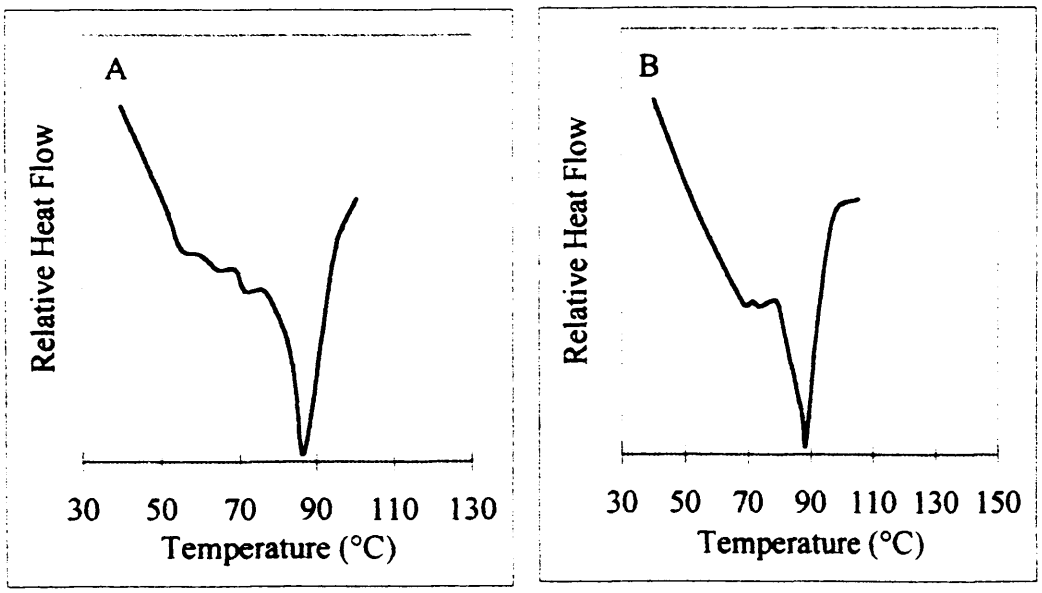


Fig. 5.30 DSC thermograms of Sample 4 (Mimosa Tanned)
A- without ULT B- with ULT

5.3.2.2 Mimosa tanned leather

Figs 5.28-30 show the DSC curves obtained for mimosa tanned leather. The onset temperatures and peak temperatures for all samples are listed in Table 5.15. It can be seen that in general, shrinkage temperatures are higher for the samples tanned in the presence of ultrasound. When sample 4 was tanned for five hours in the glass vessel, the inner layer still remained untanned. This can be seen very clearly from its DSC traces (Fig. 5.30) which have two endothermal peaks at ~74 and 87°C respectively. The peak at the lower temperature may be associated with the shrinkage of the untanned fraction of the hide, because this peak occurs at about the same temperature as that for untanned samples (Fig. 5.23). Such a multi-peak characteristic of DSC thermograms has also been observed by other researchers for different tanning processes [Tang, 1993; Covington, 1991]. However, for samples 1 and 2, only one sharp peak can be observed in their DSC thermograms (Figs. 5.27 and 5.28). This is because they are uniformly tanned, which is supported by the results of tannin penetration (section 5.3.1.2.3)

Although the tannin contents in the samples tanned with ultrasound were clearly higher than those tanned without ultrasound (Fig. 5.13 and 5.14), the shrinkage temperatures was not significantly altered by ultrasound (Table 5.15). During the tanning process, T_s values for the tanned samples were regularly measured by the official method (IUP/2). T_s is plotted against the tanning time in Fig. 5.31. It can be seen that T_s had already reached 83°C after 2 or 3 hours tanning although the middle layer of the hide or skin remained untanned. Thereafter, T_s only increases by 1-2°C in the final 3 hours of the tanning period.

Table 5.15 T_s (°C) of mimosa tanned samples measured by DSC.

Sample	1		2		4	
	Onset	Peak	Onset	Peak	Onset	Peak
with ultrasound	88.8	93	78.5	87.3	85.1	88.2
without ultrasound	85.5	88.9	78.9	87	82.4	87

5.3.2.3 Glutaraldehyde tanning

Figs. 5.32-34 show the DSC curves for leather tanned by glutaraldehyde (GA) under different conditions; data are listed in Table 5.16. Results show that a slightly higher shrinkage temperatures was obtained when ultrasound was used in the process.

Table 5.16 T_s of glutaraldehyde tanned sample measured by DSC.

Sample	a	b	1		2		3	
Ultrasound	/	/	A	B	A	B	A	B
T_s (°C)	74.0	69.6	85.0	84.6	81.9	79.2	82.3	79.7
T_e (°C)	75.8	70.0	86.5	86.8	83.7	80.8	86.0	85.0
T_p (°C)	78.1	74.5	87.6	87.0	84.3	82.4	86.7	85.3
ΔH_{ENDO} (J/g)	28.0	54.8	17.7	31.9	19.3	7.2	25.24	21.8

Note: A - Ultrasound was applied in the first hour; B - without ultrasound.
a - pickled sheepskin; b - pickled bovine hide

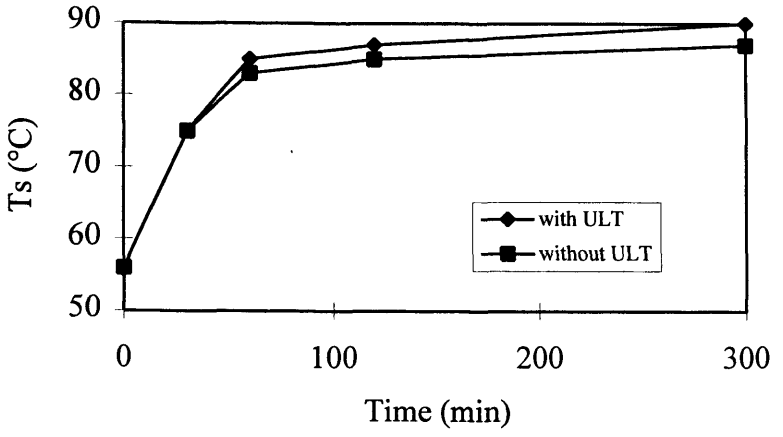


Fig. 5. 31 Shrinkage temperature by boiling test vs tanning time (Sample 4 mimosa tanned)

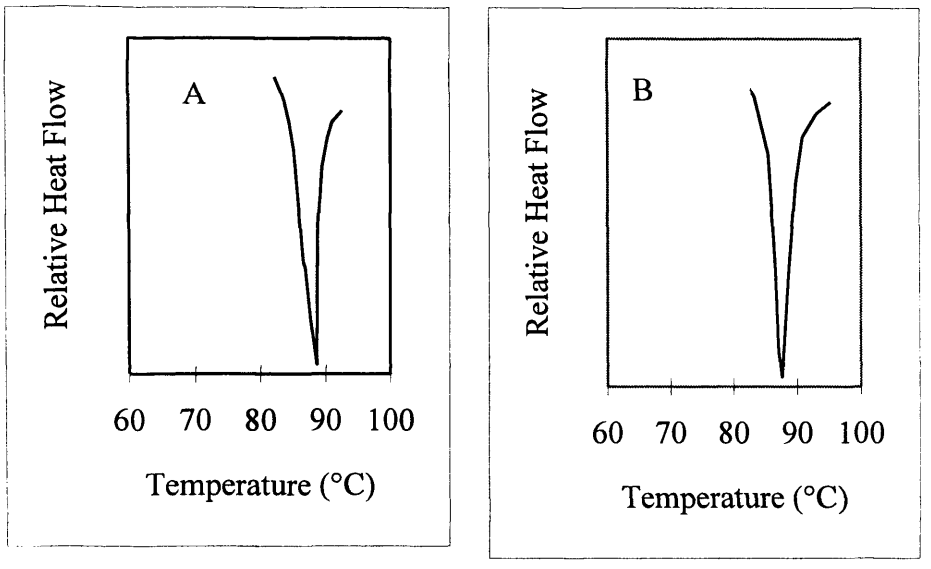


Fig. 5. 32 DSC thermograms of Sample 1 (Glutaraldehyde tanned)

A- without ULT B- with ULT

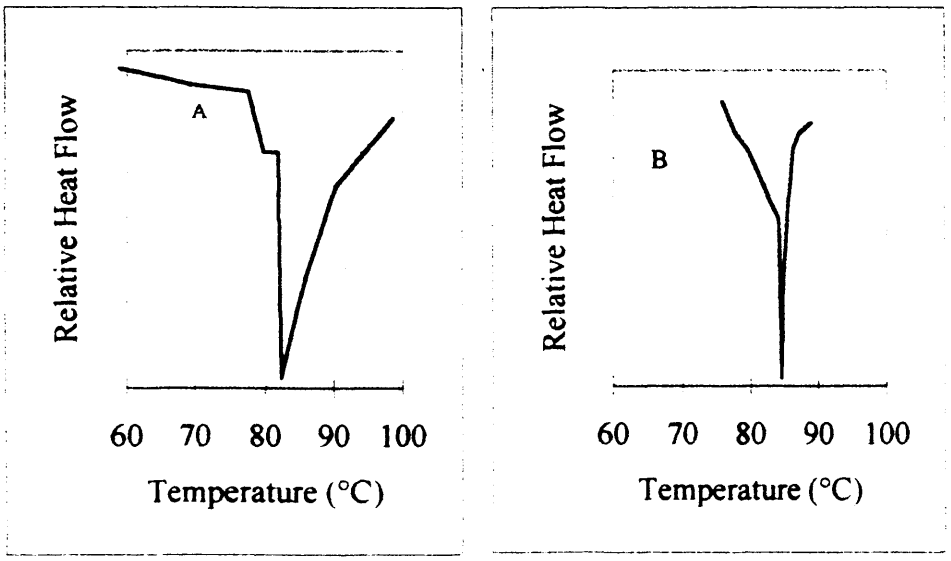


Fig. 5.33 DSC thermograms of Sample 2 (Glutaraldehyde tanned)
A- without ULT B- with ULT

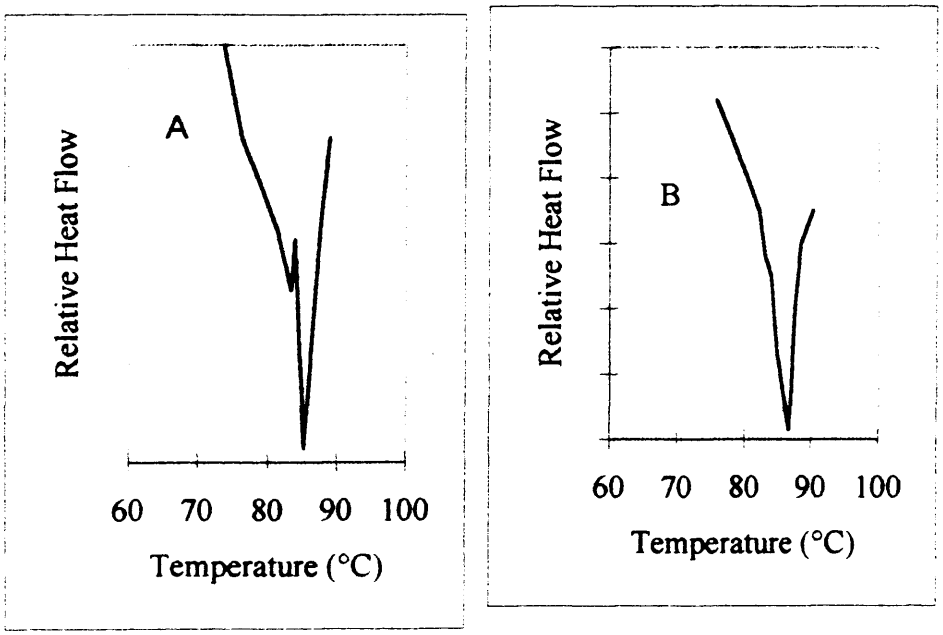


Fig. 5.34 DSC thermograms of Sample 3
(Glutaraldehyde tanned)
A- without ULT B- with ULT

5.3.3 Effect of ultrasound on the properties of mimosa

From the results obtained in mimosa tanning, it has been found that the tanning process is greatly speeded up by using ultrasound. In order to find the reason for this, the properties of mimosa liquor treated with and without ultrasound were studied. The results from this part of the work are discussed below.

5.3.3.1. The solubility of mimosa

When the concentration of mimosa in water is above 5%, a precipitate will form. However, as more tannin material is added, more is precipitated as well as dissolved until there is a phase transition to a gel phase [Zhang, 1993]. This implies that mimosa does not have a constant solubility at a given temperature. In the present study, the solubility of mimosa was investigated by measuring the amount of residue left after filtration at different concentrations. A series of aqueous mixture with concentrations of 5, 10, 15 and 20% (w/v) was prepared either by ultrasound or by magnetic stirring, and then filtered through a medium filter paper. The amount of residue in each case is listed in Table 5.17.

The results in Table 5.17 show that the amount of residue from the sample prepared by ultrasound is much less than that prepared by magnetic stirring, especially when the concentration is in the range of 10-15%. The reduction in the amount of the residue obtained by using ultrasound was in the range of 24-51%. These results indicate that ultrasound can improve the dispersion of mimosa.

Table 5.17 The amounts of residues after filtration of mimosa liquors at room temperature

Mimosa conc. (%, w/v)	5		10		15		20	
Preparation method	A	B	A	B	A	B	A	B
Residue (mg)	14.5	15.1	20.4	25.2	62.2	92.6	159	170
Residue (%)	0.29	0.31	0.41	0.51	0.41	0.62	0.78	0.85
Residue reduction (%)	6.9		24.4		51.2		8.3	

A - Mimosa liquor prepared by sonication for 30 minutes

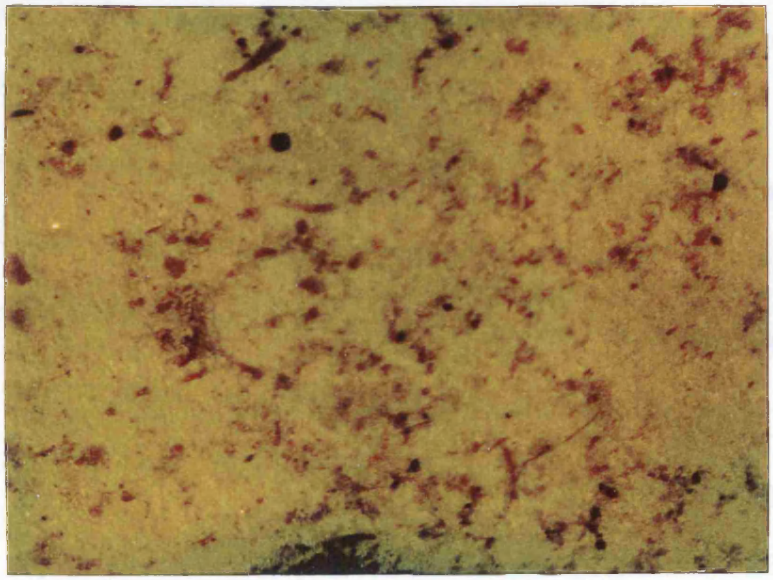
B - Mimosa liquor prepared by magnetic stirring for 30 minutes

Another observation which should be mentioned was that there was a difference in appearance between mimosa liquors prepared by ultrasound and magnetic stirring. The one prepared by ultrasound had a clear layer on the top and cloudy suspension at the bottom of the beaker, whilst the one prepared by magnetic stirring was entirely in a cloudy state. After centrifugation for 10 minutes, this difference became even more evident. Mimosa is a colloidal system containing a mixture of various sizes of phenolic compounds. These compounds have different degrees of polymerisation [Bienkiewicz, 1983]. The behaviour of vegetable tannins in water is somewhat similar to that of the dyestuffs discussed earlier (Chapter 3). It is reasonable to conclude that the strong shear force and jet effect generated by cavitation act to break down the aggregates and fragment large particles into smaller ones. As implied by equation (4-2) in Chapter 4, the solubility of mimosa should thereby be improved. The reduction of particle size of mimosa liquor is evidently supported by particle size measurement as well as a diffusion experiment using a dialysis tube (see section 5.3.3.4).

Fig 5.35 shows optical micrographs of the residues after filtration of the mimosa liquors (concentration 10% (w/v), magnification ×40). The micrographs show clearly that the amount of residues of mimosa liquor prepared with ultrasound treatment are much less than those liquor prepared without ultrasonic treatment; and the particle size also appears to be smaller.

Another interesting feature observed in this experiment is that the ultrasound treated mimosa seems more mould-resistant. Two groups of mimosa solutions (5%, w/v) were prepared, the first by magnetic stirring and the second by ultrasound irradiation (both for 30 minutes). The samples were then kept at room temperature in the laboratory for three weeks. Surprisingly it was found that the sample prepared by magnetic stirring became mildewed on the surface of the liquor, but the one prepared by ultrasound remained unchanged. Clearly this means that ultrasound can have the same effect as a biocide. This type of effect was also observed for leathers tanned using these two liquors. When kept in a plastic bag, the one tanned with liquor prepared with ultrasound showed no mould whereas the other did. It has been reported that power ultrasound can disrupt biological cell walls and so thereby can destroy bacteria [Mason, 1993]; in this case, the power ultrasound is disrupting fungal spores. Thus the use of ultrasound in leather making can result in a reduction in the amount of biocide products required in leather production. Also in tropical countries, using ultrasound should allow mimosa tanning liquors to be kept for a longer period without showing microbial degradation.

A



B

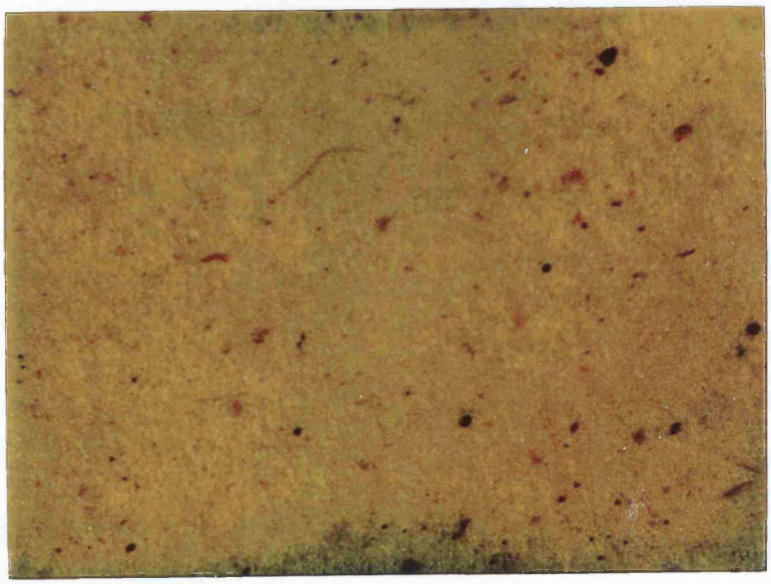


Fig. 5.35 Mimosa residues after filtration (magnification ×40)

A- without ULT B - with ULT

5.3.3.2 Tannin content in Mimosa

Another interesting result obtained was the greater tannin content of the mimosa liquor treated by ultrasound. Tannin content was measured by means of visible spectrophotometry (section 5.2.3.2) and the results are shown in Table 5.18. The results show clearly that the tannin contents in the solution are increased by up to 7% after ultrasound treatment. This is probably due to break down of aggregates so that more polyphenolic groups are exposed. However, when the treatment time was prolonged, the results appear to show a reverse tendency with the tannin contents reducing by 1-2%. This may be the result of oxidation of polyphenols, as free radicals can be generated by applying ultrasound. Karpman [1962] obtained similar results.

Table 5.18 Absorbance of mimosa tannin at a wavelength of 545 nm.

Concentration (%)	No ULT	15 min ULT	30 min ULT	60 min ULT
0.25	0.283	0.292	0.287	0.291
0.34	0.374	0.381	0.399	0.375
0.45	0.394	0.418	0.419	0.411

5.3.3.4 Particle size of Mimosa liquor

Vegetable tannin is dispersed in water in two different forms: firstly the soluble form which is constituted of individual molecules; secondly the colloidal form which comprises two or more molecules associating together [Zhang, 1985]. The molecular mass of tannin molecules varies with their source and can be as high

as 10,000. The molecule may be hydrated, containing 200-600% water, and may have a diameter of 20-40 Å [Reich and Legutke 1960]. Reich and Legutke also found that micelle size increases with concentration of tannins and salts but decreases with pH. Besides the above colloidal particles, there are some even larger particles of 6-13 μm [Bienkiewicz, p398, 1983]. This dimension is much greater than that of the channels between adjacent polypeptide chains. This might be one of the main reasons why vegetable tanning takes such long time to complete. It was hypothesised that the reason why ultrasound improves the rate of tanning is that it reduces particle size. Thus the change in particle size of mimosa liquor before and after ultrasound treatment was investigated. Table 5.19 lists the mean particle sizes in the liquor before and after ultrasound treatment.

Table 5.19 The mean particle size (nm) of Mimosa liquors at 25°C prepared with or without ultrasound

Concentration (w/v)	0.5%		1%	
Test method	SDP	Unimodel	SDP	Unimodel
with ULT	375 ± 129	292 ± 106	461 ± 280	326 ± 120
without ULT	520 ± 230	343 ± 120	865 ± 430	390 ± 140

The results are the average of ten measurements.

SDP/Unimodel are the different analysis system

The above results clearly indicate (a) that the mean particle size of the mimosa liquor was reduced after using ultrasound and (b) that the particle size depended on the concentration. It is believed that vegetable tannins are hygroscopic colloids, and easily form polydisperse solutions in water with labile aggregates. It

can be seen from Table 5.19 that, when the concentration changed from 0.5% to 1%, the particle size was increased by about 60% for the sample prepared by magnetic stirring and 22% for the sample prepared with ultrasound.

The reduction of particle size of mimosa liquor is further supported by a diffusion experiment using a dialysis tube (see section 5.2.3.2.3). The results are shown in Fig. 5.36 as a plot of UV absorbance of mimosa (at a wavelength of 280 nm) against the diffusion time. Clearly the diffusion of liquor prepared by ultrasound was faster than that prepared by magnetic stirring, indicating a reduction of diffusion coefficient. This means the particle size is reduced.

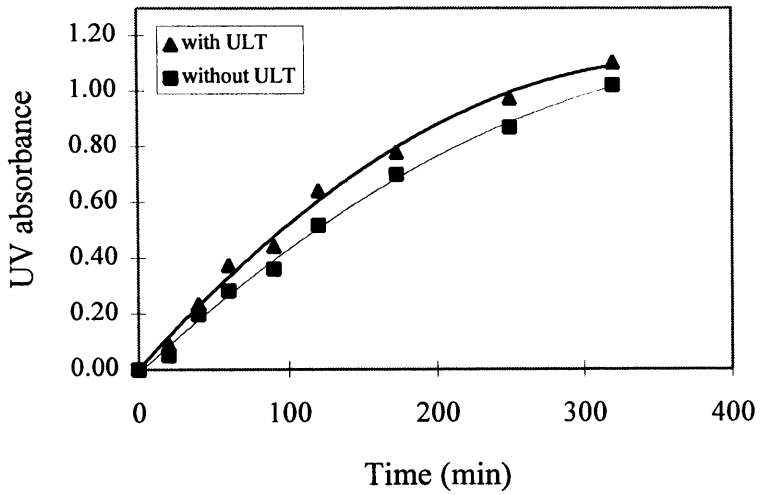


Fig. 5.36 UV absorbance of Mimosa against diffusion time (at 280 nm)

It appears that the strong shear force arising from cavitation may be responsible for breaking down the mimosa aggregates and reducing their mean particle size. Fig. 5.37 contrasts the distribution of particle sizes of mimosa liquors prepared by ultrasound and by magnetic stirring. For the liquor prepared by

ultrasound, a narrower distribution and much smaller particle size was obtained. These results support the conclusion that the reduction of the particle size of mimosa liquor is one of the main reasons why ultrasound can speed up the mimosa tanning process.

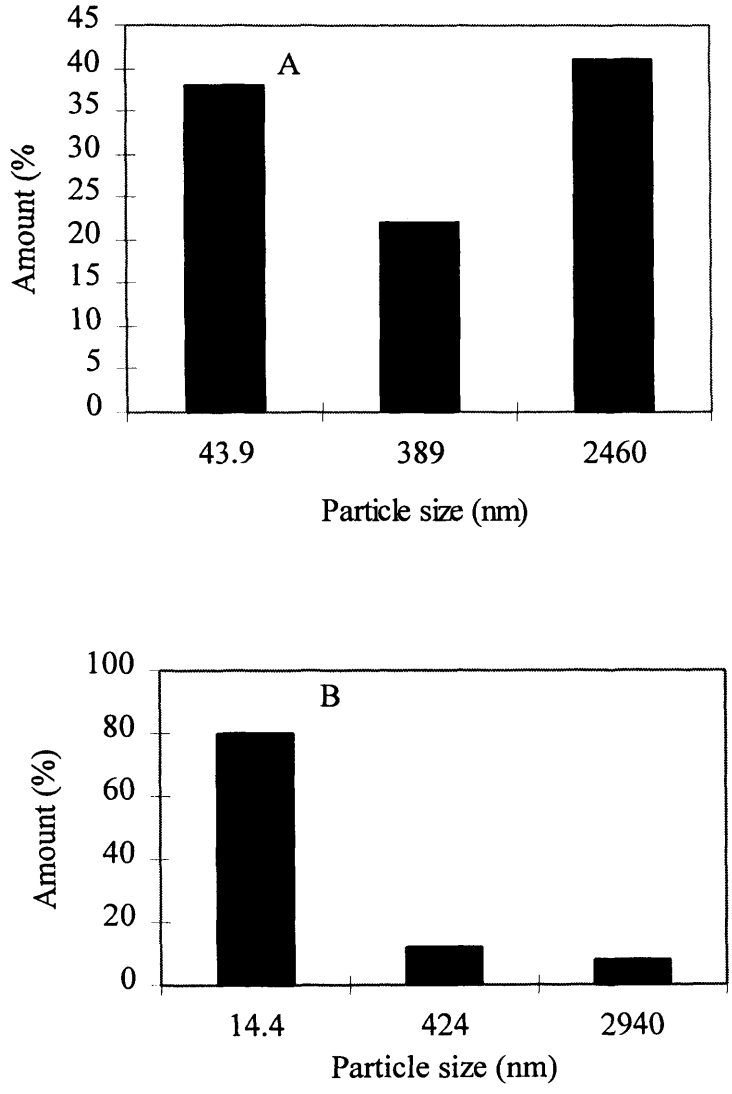


Fig. 5.37 The distribution of mimosa particle size

A - without ULT B - with ULT

5.4 CONCLUSION

From the results presented in this chapter, it can be concluded that the use of ultrasound in chromium, aldehyde and vegetable tanning can enhance these processes with various degree of success. For chromium and aldehyde tanning in a metal drum or glass vessel, ultrasound only has a relatively small influence on the efficiency of the processes, whereas for vegetable tanning the process is greatly speeded up with tanning time being shortened by 50%. Nevertheless for *all* tannage types examined tanning in the presence of ultrasound gives some improvements. Firstly shrinkage temperature is increased by about 3-5°C. Secondly, for chrome tanning the chromium content in leather is increased by 4-8% and the amount of fixed chromium is also increased. Thirdly the penetration or evenness of distribution of all types of tanning material is improved. Finally in the case of mimosa, ultrasound treatment of the liquor leads to a much improved dispersion with increased solubility and a reduction by 30% in particle size.

CHAPTER 6

CONCLUDING REMARKS

6.1 CONCLUSIONS

The effects of power ultrasound on tanning, dyeing and fatliquoring processes of leather making have been investigated. The results indicate that ultrasound can be a useful tool for improving these leather making processes but it is more effective for dyeing, fatliquoring and vegetable tanning than chrome and aldehyde tanning. From the results of the present study, the following conclusions can be drawn.

The dyeing process

By using ultrasound, the rate of dyeing for all types of leather samples can be increased. The dyeing process can either be shortened by 40-70% or be carried out at a lower temperature (by ~20°C). Whether or not samples are dyed with mechanical agitation, higher dye uptakes are obtained in material treated with ultrasound. Ultrasound is more effective in accelerating the dyeing process when it is used at the initial stage rather than at the late stage; the application of ultrasound throughout the whole process appears unnecessary. The effect of ultrasound on the dyeing process also depends on the properties of dyestuffs and leather samples used: in general, ultrasound is more effective in accelerating the dyeing process which has greater difficulty in achieving good penetration or high dye uptake. Ultrasound influences the dyeing process mainly by increasing the dye diffusion coefficient, thus

increasing the penetration and dye uptake. This is mainly due to the cavitation effect of ultrasound which results in a reduction of dye aggregation and an increase of dye diffusion.

The fatliquoring process

Higher oil contents in the leather can be achieved when samples are fatliquored in the presence of both ultrasonic irradiation and mechanical agitation. Using ultrasound can shorten the fatliquoring time by ~30%. Alternatively, it is possible to have a lower temperature fatliquoring process using ultrasound (e.g. the same oil content can be obtained at 20°C with ultrasound as at 40°C without ultrasound). It is more effective to apply ultrasound in the late stage than in the early stage of the fatliquoring process.

When ultrasound is used for preparing fatliquor emulsion, a high quality oil-in-water emulsion is obtained with a finer particle size (20-30% reduction compared to. that prepared by mechanical stirring). By using this fatliquor pre-treated with ultrasound, the oil content of leather may be significantly increased. A particular advantage of using ultrasound is that a marked increase (up to 87%) of the oil content in the middle layer of leather is obtained. The main reason for this improved oil penetration and distribution is due to the reduction of fatliquor emulsion particle size.

The tanning process

The effects of ultrasound on chromium, aldehyde and vegetable tanning are quite different. For chromium and aldehyde tanning, ultrasound only has a slight

influence on the rate of tanning, whereas the vegetable tanning process is greatly speeded up and the tanning time can be shortened by 50%. Nevertheless ultrasound gives some improvements for all tannages. Firstly the shrinkage temperature is increased by about 3-5°C. Secondly, chromium or aldehyde contents in leather tanned in the presence of ultrasound are 4-10% higher than those in the samples tanned without ultrasound. Thirdly, the amount of leachable chromium in the leather is also reduced by using ultrasound.

The properties of mimosa liquor are also improved by treatment with ultrasound: the solubility of mimosa is increased and the precipitate in the liquor is reduced by up to 50%; and the particle size is reduced by up to 50%. A significant reduction in the tendency of mimosa liquor and tanned leather to become mouldy is achieved by using ultrasound.

6.2 FUTURE WORK

Beyond the present study, there are still theoretical and practical areas that can be explored as follows.

- Further investigation and understanding of the effects of ultrasound on the physical and chemical properties of dyeing/tanning solutions and fatliquors emulsions, especially the colloidal behaviour of dyeing solutions and fatliquors. The results obtained in the present study strongly suggest that the characteristics of colloidal and emulsion particles are very sensitive to irradiation by ultrasound. Further study of the colloidal behaviour of various dyeing solutions and fatliquor emulsions would be helpful.

- Based on the results described in the previous sections, one prediction that can be made is that ultrasound will improve the fur leather making processes to a great extent. Normally fur leather is tanned in a paddle vessel and the process is very time-consuming due to the long float length used.
- In order to evaluate the commercial potential of the present study, the process should be scaled-up to pilot production process experiments. However, the technical challenge is how to locate and operate ultrasound transducers in a rotating drum, which may be 4 meters in diameter and 2 meters in width and loaded with more than 50 hides. This needs more fundamental studies in the engineering aspects of ultrasonics.
- The use of ultrasound in some other processes of leather making, such as unhairing, degreasing, retanning and finishing, needs to be investigated. The processes mentioned are likely to benefit from the cavitation effect of ultrasound.

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APPENDIX I SHEEPSKIN TANNING PROCEDURE (BSLT)

Sheepskin, 4 kg

Operation	Chemical/other substance	Temperature/Time	Note
Pretanning	5% Na_2SO_4 2% HCOONa 4% SANDOZIN AD 3% formaldehyde 50% water	35°C/20 minutes	
Neutralising	0.5% soda ash 12.5% water	35°C/15 minutes three times	T_s = 78-82°C
washing	200% water 200% water 200% water	45°C/30-45 minutes 50°C/20minutes, twice 25°C/20 minutes	pH 4 pH 5.3 pH 6.5, T_s = 71°C
chrome tanning Basification	1% H_2SO_4 100% water 6% Cr_2O_3 (33% basicity) 1.2% $NaHCO_3$	20°C/10 minutes 25°C/7 hours 30-35°C, four additions	pH 3.2 T_s = 98°C
Washing	200% water	35°C/10 minutes twice	
Neutralising	0.5% HCOONa 1.25% NH_4HCO_3	35°C/10 minutes 35°C/40 minutes	
Vegetable tanning	3% Mimosa 3% Neosyn AC3 200% water	45°C/30 minutes	

APPENDIX II DIFFUSION COEFFICIENT

Fick's fist law of diffusion can be expressed as follows.

$$\frac{ds}{dt} = -DA\frac{dc}{dx} \qquad \text{(I-1)}$$

where D is the diffusion coefficient. ds/dt is the rate of diffusion of dye across an area A at any point in the diffusion membrane and dc/dx is the concentration gradient of dye at that point. Due to the very thin thickness of the membrane, dc/dx could be expressed as $\sim\Delta c/l$, so equation (I-1) is converted into (I-2).

$$\frac{ds}{dt} = -DA\frac{\Delta c}{l} \qquad \text{(I-2)}$$

where $\Delta c = C_2\text{-}C_1 = -(C_1\text{-}C_2)$; C_1 and C_2 are, respectively, the dye concentrations in the dyeing bath and in the dialysis tube.

$$\frac{ds}{dt} = DA\frac{C_1 - C_2}{l} \qquad \text{(I-3)}$$

Assuming before dialysis, the amount of dye in the dyeing bath is g_0 and at time t, the amount of dye which has diffused into dialysis tube is g. The volumes of the dye solution in dyeing bath and the dialysis tube are V_1 and V_2 respectively. Therefore (I-3) can be changed into (I-4).

$$dg = DA\frac{dt}{l}[(g_0 - g)/V_1 - g/V_2] \qquad \text{(I-4)}$$

Assuming $\lambda = V_2/V_1$ and integrating (I-4),

$$\int_0^g \frac{dg}{\lambda g_0 - g(1+\lambda)} = \int_0^t \frac{DA}{lV_2}dt \qquad \text{(I-5)}$$

Assuming that the diameter of dialysis tube is d, A/V_2 will be 4/d and (I-5) will become

$$\frac{1}{1+\lambda}\ln\frac{\lambda g_0}{\lambda g_0 - g(1+\lambda)} = \frac{4D}{\mathrm{d}\,l}t \qquad \text{(I-6)}$$

and

$$D = \frac{1}{(1+\lambda)}\frac{\mathrm{d}l}{4t}\ln\frac{C_0}{C_0 - C(1+\lambda)} \qquad \text{(1-7)}$$

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APPENDIX I SHEEPSKIN TANNING PROCEDURE (BSLT)

Sheepskin, 4 kg

Operation	Chemical/other substance	Temperature/Time	Note
Pretanning	5% Na_2SO_4 2% HCOONa 4% SANDOZIN AD 3% formaldehyde 50% water	35°C/20 minutes	
Neutralising	0.5% soda ash 12.5% water	35°C/15 minutes three times	T_s = 78-82°C
washing	200% water 200% water 200% water	45°C/30-45 minutes 50°C/20minutes, twice 25°C/20 minutes	pH 4 pH 5.3 pH 6.5, T_s = 71°C
chrome tanning Basification	1% H_2SO_4 100% water 6% Cr_2O_3 (33% basicity) 1.2% $NaHCO_3$	20°C/10 minutes 25°C/7 hours 30-35°C, four additions	pH 3.2 T_s = 98°C
Washing	200% water	35°C/10 minutes twice	
Neutralising	0.5% HCOONa 1.25% NH_4HCO_3	35°C/10 minutes 35°C/40 minutes	
Vegetable tanning	3% Mimosa 3% Neosyn AC3 200% water	45°C/30 minutes	

APPENDIX II DIFFUSION COEFFICIENT

Fick's fist law of diffusion can be expressed as follows.

$$\frac{ds}{dt} = -DA\frac{dc}{dx} \qquad \text{(I-1)}$$

where D is the diffusion coefficient. ds/dt is the rate of diffusion of dye across an area A at any point in the diffusion membrane and dc/dx is the concentration gradient of dye at that point. Due to the very thin thickness of the membrane, dc/dx could be expressed as $\sim\Delta c/l$, so equation (I-1) is converted into (I-2).

$$\frac{ds}{dt} = -DA\frac{\Delta c}{l} \qquad \text{(I-2)}$$

where $\Delta c = C_2\text{-}C_1 = -(C_1\text{-}C_2)$; C_1 and C_2 are, respectively, the dye concentrations in the dyeing bath and in the dialysis tube.

$$\frac{ds}{dt} = DA\frac{C_1 - C_2}{l} \qquad \text{(I-3)}$$

Assuming before dialysis, the amount of dye in the dyeing bath is g_0 and at time t, the amount of dye which has diffused into dialysis tube is g. The volumes of the dye solution in dyeing bath and the dialysis tube are V_1 and V_2 respectively. Therefore (I-3) can be changed into (I-4).

$$dg = DA\frac{dt}{l}[(g_0 - g)/V_1 - g/V_2] \qquad \text{(I-4)}$$

Assuming $\lambda = V_2/V_1$ and integrating (I-4),

$$\int_0^g \frac{dg}{\lambda g_0 - g(1+\lambda)} = \int_0^t \frac{DA}{lV_2}dt \qquad \text{(I-5)}$$

Assuming that the diameter of dialysis tube is d, A/V_2 will be 4/d and (I-5) will become

$$\frac{1}{1+\lambda}\ln\frac{\lambda g_0}{\lambda g_0 - g(1+\lambda)} = \frac{4D}{\mathrm{d}\,l}t \qquad \text{(I-6)}$$

and

$$D = \frac{1}{(1+\lambda)}\frac{\mathrm{d}l}{4t}\ln\frac{C_0}{C_0 - C(1+\lambda)} \qquad \text{(1-7)}$$